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OBTENCIÓN DE MONÓMEROS DE BIOPOLÍMEROS A PARTIR DE BIOMASA RESIDUAL

TESIS DOCTORAL POR

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RESUMEN

El desarrollo industrial del último siglo ha dependido en gran medida de materias primas de origen fósil, especialmente para la producción de energía y la obtención de productos químicos. Los plásticos constituyen una de las familias más relevantes de derivados del petróleo con amplia implantación en nuestra sociedad. Así, entre el 5-10% de la nafta procesada se destina a la producción de plásticos. Su producción y la posterior gestión como residuos al final de su vida útil, genera importantes consecuencias ambientales. A las emisiones de gases de efecto invernadero inherentes a su proceso productivo, debe añadirse el hecho de que los plásticos son, en su inmensa mayoría, no biodegradables. Por lo tanto, se acumulan en los ecosistemas, particularmente en los océanos, donde se descomponen en microplásticos. Estos microplásticos son ingeridos por los organismos marinos, alterando la cadena alimentaria y la biodiversidad.

La reducción de estos problemas ambientales pasa por el desarrollo de plásticos sostenibles, es decir, utilizar biomasa como materia prima para obtener polímeros de propiedades similares a los de origen fósil. Esta Tesis Doctoral se centra en el estudio y optimización de las diferentes etapas que componen el proceso productivo del ácido 2,5-furandicarboxílico (FDCA, por sus siglas en inglés), compuesto clave en la producción del furanoato de polietileno (PEF). El PEF es el polímero sostenible que puede reemplazar al tereftalato de polietileno (PET), uno de los plásticos de mayor producción mundial. Ambos compuestos poseen propiedades mecánicas similares, principalmente en términos de resistencia y durabilidad.

El proceso de producción de FDCA a partir de biomasa lignocelulósica implica diferentes etapas. Inicialmente, la fracción hemicelulósica debe someterse a hidrólisis ácida para obtener azúcares reductores y, posteriormente, mediante deshidratación, los aldehídos cíclicos que constituyen las moléculas plataforma de este proceso. Concretamente, furfural a partir de las pentosas, y 5-hidroximetilfurfural (HMF) a partir de las hexosas. Para garantizar una buena eficacia en la hidrólisis, la biomasa lignocelulósica residual debe ser pretratada, eliminando la lignina y dañando la estructura recalcitrante de la celulosa. La etapa clave en la formación del FDCA es la oxidación de estos aldehídos. En el caso del HMF, la oxidación produce directamente el FDCA. Por el contrario, la ruta a partir de furfural produce ácido furoico (FCA), siendo necesaria una etapa adicional de carboxilación para obtener el FDCA.

Respecto a la primera etapa (hidrólisis-deshidratación), inicialmente se aborda una optimización paramétrica (temperatura, catalizador) y estudio cinético de la reacción para maximizar la obtención de furfural y HMF a partir de celulosa microcristalina, considerando un sistema que combina catálisis homogénea (HCl) y heterogénea (zeolita β). Estos resultados fueron extrapolados a un sistema real, utilizando serrín de pino como materia prima. En este caso, la presencia de lignina requirió del estudio comparativo de diferentes pretratamientos para favorecer el acceso del catalizador a los polímeros de interés (celulosa y hemicelulosa), eliminando las interferencias de la lignina. Se consideraron pretratamientos oxidativos y reductores, evaluando el efecto de la dosis de los agentes y las condiciones del proceso (tiempo y temperatura).

La etapa de oxidación compone la parte más significativa de este trabajo. Inicialmente, se estudia de forma separada para el furfural y el HMF. La obtención de FCA a partir de furfural se aborda considerando dos agentes oxidantes: el peróxido de hidrógeno y el oxígeno. Estos dos enfoques permiten la comparación entre dos mecanismos de reacción, evaluando si es posible trabajar con un oxidante en fase líquida, lo que implicaría un mejor control teórico de la reacción por encontrarse ambos reactivos en la misma fase. Los resultados experimentales, evaluando diferentes catalizadores y condiciones de operación, permiten concluir que la alta reactividad del peróxido de hidrógeno da lugar a un proceso complejo, difícilmente controlable, con multitud de compuestos laterales (ácido maleico, ácido fórmico, CO_2 , etc.), siendo difícil maximizar la producción del FCA, ya que éste se produce mediante la oxidación parcial del furfural. En contraste, el oxígeno proporciona un proceso más estable, alcanzando selectividades a FCA sensiblemente superiores.

En base a los resultados de oxidación de furfural, se aborda también la oxidación del HMF, en este caso considerando únicamente el catalizador Au/TiO_2 . Estos estudios abarcan, además de la optimización de temperatura y presión de oxígeno (único oxidante considerado, teniendo en cuenta lo observado con furfural), el análisis de la influencia del ratio NaOH/HMF ya que, en este caso, la formación de FDCA compite con la oligomerización de HMF y la consiguiente formación de huminas (sólidos que desactivan el catalizador por bloqueo de los centros activos).

Finalmente, teniendo en cuenta que a partir de biomasa lignocelulósica la formación de furfural y HMF ocurriría simultáneamente, se ha explorado la posibilidad de realizar la

oxidación de la mezcla de ambos aldehídos, simulando la relación de concentraciones esperable tras un proceso de hidrólisis. Estos estudios, si bien requieren una optimización buscando el equilibrio entre las condiciones óptimas identificadas de forma individual, permiten considerar la etapa de oxidación sin necesidad de extraer selectivamente los aldehídos. Consecuentemente, supone un ahorro considerable en los costes de operación del proceso. Además de la optimización paramétrica, se realiza un estudio cinético para evaluar si las conclusiones extraídas en los estudios individuales son aplicables a la situación de mezcla.

La última etapa del proceso se refiere a la carboxilación del ácido furoico obtenido por oxidación del furfural (la oxidación del HMF ya produce el FDCA deseado). La práctica inexistente bibliografía referente a la carboxilación del ácido furoico indica que es una reacción sólido fluido condicionada técnicamente por la dificultad para alcanzar un buen contacto entre el CO_2 y el sólido, y económicamente por el elevado coste del cesio, elemento requerido para generar una sal fundente (furoato de cesio), que facilite la interacción sólido-gas. En la literatura, estos experimentos se llevan a cabo a elevada presión de CO_2 , lo que aleja el proceso de las condiciones esperables para una reacción de valorización de CO_2 atmosférico capturado. Se ha evaluado la viabilidad de realizarlos a menor presión, obteniendo una producción de FDCA no despreciable. Para orientar las modificaciones del proceso y aumentar su sostenibilidad, se ha llevado a cabo un exhaustivo análisis bibliográfico que abarca otras reacciones de carboxilación. A partir de este estudio, se han extraído ideas prometedoras para futuras optimizaciones en fase líquida, como la utilización de complejos de cobre como ligandos, o el uso de sistemas binarios considerando disolventes orgánicos polares apróticos.

ABSTRACT

The industrial development of the last century has heavily relied on fossil-based raw materials, particularly for energy production and the manufacture of chemicals. Plastics are one of the most significant families of petroleum-derived products, widely integrated into our society. Between 5-10% of processed naphtha is used in the production of plastics. The manufacturing of plastics and their subsequent management as waste at the end of their life cycle have considerable environmental consequences. In addition to the greenhouse gas emissions inherent in their production process, most plastics are non-biodegradable. As a result, they accumulate in ecosystems, particularly in the oceans, where they decompose into microplastics. These microplastics are ingested by marine organisms, disrupting the food chain and biodiversity.

Reducing these environmental problems requires the development of sustainable plastics, meaning using biomass as a raw material to produce polymers with properties similar to those derived from fossil sources. This PhD Thesis focuses on the study and optimization of the various stages involved in the production process of 2,5-furandicarboxylic acid (FDCA), a key compound in the production of polyethylene furanoate (PEF). PEF is a sustainable and biodegradable polymer that can replace polyethylene terephthalate (PET), one of the most widely produced plastics globally. Both compounds have similar mechanical properties, particularly in terms of strength and durability.

The production process of FDCA from lignocellulosic biomass involves several stages. Initially, the hemicellulosic fraction must undergo acid hydrolysis to obtain reducing sugars, which are then dehydrated to form cyclic aldehydes, the platform molecules for this process. Specifically, furfural is obtained from pentoses, and 5-hydroxymethylfurfural (HMF) from hexoses. To ensure effective hydrolysis, the residual lignocellulosic biomass must be pretreated, removing lignin and disrupting the recalcitrant structure of cellulose. The key step in FDCA formation is the oxidation of these aldehydes. In the case of HMF, oxidation directly produces FDCA. In contrast, the route starting from furfural yields furoic acid (FCA), requiring an additional carboxylation step to obtain FDCA.

Regarding the first stage (hydrolysis-dehydration), a parametric optimization (temperature, catalyst) and kinetic study of the reaction were initially conducted to maximize the production of furfural and 5-HMF from microcrystalline cellulose, considering a system

combining homogeneous (HCl) and heterogeneous (β zeolite) catalysis. These results were extrapolated to a real system using pine sawdust as raw material. In this case, the presence of lignin necessitated a comparative study of different pretreatment methods to facilitate the catalyst's access to the target polymers (cellulose and hemicellulose) by removing lignin interference. Oxidative and reductive pretreatments were considered, evaluating the effects of the agents' dosage and process conditions (time and temperature).

The oxidation stage represents the most significant part of this work. Initially, it was studied separately for furfural and HMF. The production of FCA from furfural was approached using two oxidizing agents: hydrogen peroxide and oxygen. These two approaches allowed a comparison between two reaction mechanisms, evaluating the feasibility of working with a liquid-phase oxidant, which would theoretically provide better control of the reaction since both reactants are in the same phase. The experimental results, evaluating different catalysts and operating conditions, led to the conclusion that the high reactivity of hydrogen peroxide results in a complex process that is difficult to control, with the formation of numerous by-products (maleic acid, formic acid, CO_2 , etc.), making it challenging to maximize FCA production, as it is formed through the partial oxidation of furfural. In contrast, oxygen provides a more stable process, achieving significantly higher selectivities for FCA.

Based on the furfural oxidation results, the oxidation of HMF was also addressed, in this case considering only the Au/TiO_2 catalyst. These studies included not only the optimization of temperature and oxygen pressure (the only oxidant considered, given the observations with furfural) but also the analysis of the influence of the NaOH/HMF ratio, as FDCA formation competes with the oligomerization of HMF and the consequent formation of humins (solids that deactivate the catalyst by blocking active sites).

Finally, considering that the formation of furfural and HMF would occur simultaneously from lignocellulosic biomass, the possibility of oxidizing a mixture of both aldehydes was explored, simulating the expected concentration ratio after a hydrolysis process. Although these studies require optimization to balance the individually identified optimal conditions, they allow for the consideration of the oxidation step without the need for selective extraction of the aldehydes. Consequently, this represents a significant reduction in process operating costs. In addition to parametric optimization, a kinetic study

was performed to assess whether the conclusions drawn from the individual studies are applicable to the mixed scenario.

The final stage of the process concerns the carboxylation of furoic acid obtained from furfural oxidation (since the oxidation of 5-HMF already produces the desired FDCA). The practically non-existent literature on furoic acid carboxylation indicates that it is a solid-fluid reaction, technically constrained by the difficulty of achieving good contact between CO₂ and the solid, and economically by the high cost of cesium, an element required to generate a molten salt (cesium furoate) that facilitates solid-gas interaction. In the literature, these experiments are conducted under high CO₂ pressure, which distances the process from conditions expected for atmospheric CO₂ valorization reactions. The feasibility of conducting them at lower pressure was evaluated, yielding a non-negligible FDCA production. To guide process modifications towards greater sustainability, an extensive literature review on other carboxylations was conducted, from which ideas for future liquid-phase optimizations were derived, such as using copper complexes as ligands or considering binary systems with polar aprotic organic solvents.

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DIFUSIÓN DE LA TESIS DOCTORAL

Dissemination of the PhD Thesis

ARTÍCULOS CIENTÍFICOS

Las publicaciones derivadas de la realización de la presente Tesis Doctoral se enumeran a continuación, siguiendo el orden de discusión en el apartado de resultados:

1. "Zeolite-assisted acid hydrolysis of cellulose: Optimization of reaction conditions and chemical pretreatments for enhancing HMF yields", Paula Rapado, Diego Garcés, Laura Faba, Salvador Ordóñez. *Industrial Crops and Products* 212 (2024) 118309. **Capítulo 4.1.** <https://doi.org/10.1016/j.indcrop.2024.118309>
2. "Influence of delignification and reaction conditions in the aqueous phase transformation of lignocellulosic biomass to platform molecules", Paula Rapado, Laura Faba, Salvador Ordóñez. *Bioresource Technology* 321 (2021) 124500. **Capítulo 4.2.** <https://doi.org/10.1016/j.biortech.2020.124500>
3. "Role of the different catalytic sites in the H₂O₂-mediated aqueous-phase furfural partial oxidation", Paula Rapado, Laura Faba, Salvador Ordóñez. *Journal of Environmental Chemical Engineering* 11 (2023) 111466. **Capítulo 4.3.** <https://doi.org/10.1016/j.jece.2023.111466>
4. "Selective and stable production of furoic acid by furfural aerobic oxidation at controlled mild-pH conditions", Paula Rapado, Laura Faba, Salvador Ordóñez. *Applied Catalysis A: General* 670 (2023) 119536. **Capítulo 4.4.** <https://doi.org/10.1016/j.apcata.2023.119536>
5. "Biomass to plastics: from HMF to fructose for the synthesis of 2,5-furandicarboxylic acid over Au/TiO₂", Paula Rapado, Cristina Lois, Marina Cano, Laura Faba, Salvador Ordóñez. *Catalysis Today* 445 (2024) 115036. **Capítulo 4.5.** <https://doi.org/10.1016/j.cattod.2024.115036>
6. "Carboxylation reaction for integrating CO₂ capture with the production of renewable monomers", Laura Faba, Paula Rapado, Salvador Ordóñez. *Greenhouse Gases: Science and Technology* 13 (2022) 227-244. **Capítulo 4.6.** <https://doi.org/10.1002/ghg.2175>

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Paula Rapado, Laura Faba, Salvador Ordóñez

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2. *Comparison of oxygen and hydrogen peroxide as oxidants for obtaining furoic acid from furfural over supported gold catalysts*

Paula Rapado, Laura Faba, Salvador Ordóñez

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3. *Oxidation of furfural/5-hydroxymethylfurfural mixtures to furanic acids over Au/TiO₂: kinetics and inhibition effects*

Paula Rapado, Laura Faba, Salvador Ordóñez

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*Nothing in life is to be feared, it is only to be understood. Now is the time to understand more,
so that we may fear less.*

Marie Curie (1867-1934)



1. INTRODUCCIÓN



1.1. ANTECEDENTES: DEPENDENCIA DE MATERIAS PRIMAS FÓSILES

El desarrollo industrial del último siglo ha estado intrínsecamente ligado al uso intensivo de materias primas fósiles, no solo para la producción de energía, sino también para la fabricación de productos químicos. La industria petroquímica ha sido el motor del crecimiento global, proporcionando los componentes fundamentales para una amplia gama de productos que van desde plásticos, disolventes y fertilizantes, hasta materiales utilizados en la construcción, la medicina y la tecnología. Sin embargo, este crecimiento también ha sido una de las principales causas de la crisis medioambiental que enfrentamos hoy.

Si nos centramos en la huella de carbono, es decir, en la cantidad total de emisiones de gases de efecto invernadero, especialmente CO₂, que se generan directa o indirectamente durante la fabricación de productos químicos a partir de hidrocarburos fósiles, observamos que esta actividad contribuye significativamente a incrementar dicha huella. La extracción, refinado y transformación de petróleo y gas natural liberan cantidades significativas de gases de efecto invernadero (GEI), sobre todo CO₂, contribuyendo al cambio climático (**Figura 1.1**). Además, los procesos de conversión de estos recursos fósiles en productos químicos producen grandes cantidades de residuos, lo que agrava aún más los problemas ambientales.

Un aspecto clave en esta crisis es la producción masiva de plásticos, que ha generado una sobreacumulación de estos residuos en el medio ambiente (**Figura 1.2**). Entre el 5 y el 10% de la nafta procesada en refinerías se destina a la fabricación de diversos tipos de plásticos. Estos materiales no son biodegradables y su resistencia al deterioro, junto con una

deficiente gestión como residuos, ha llevado a que grandes cantidades terminen en los océanos y en ecosistemas terrestres, causando daños a la biodiversidad y afectando a las cadenas alimentarias. La combinación de estos factores ha llevado a un punto de inflexión donde es necesario replantear tanto los métodos de producción como los tipos de productos químicos que utilizamos.

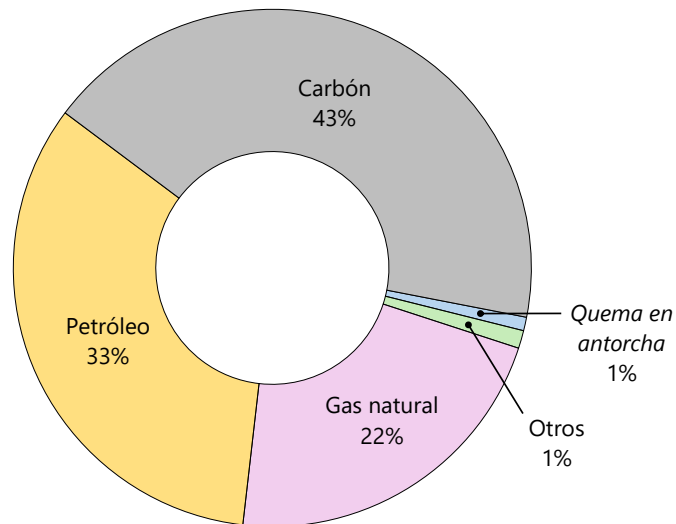


Figura 1.1. Emisiones de CO₂ debidas a la extracción, refino y transformación de materias primas no renovables. [1]

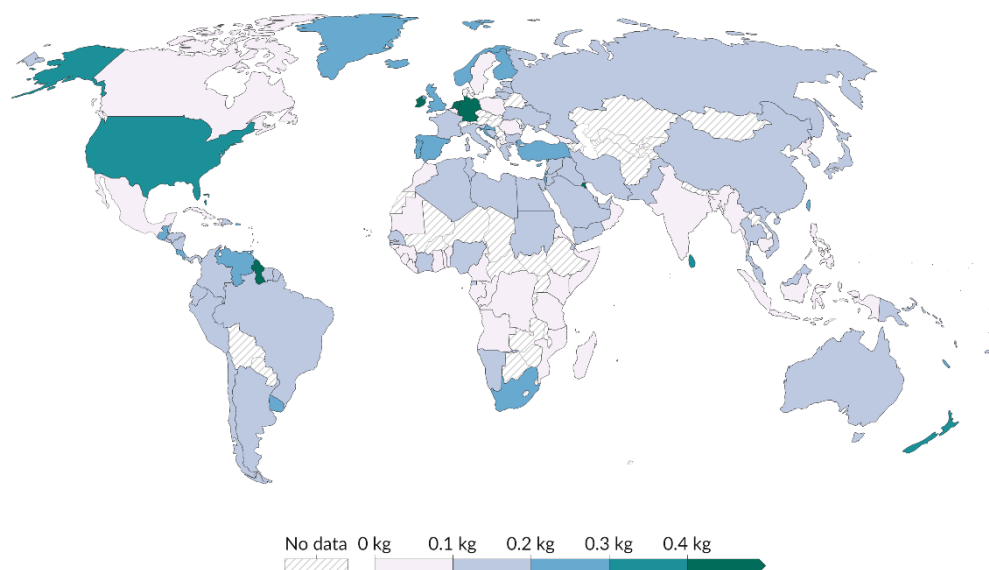


Figura 1.2. Generación de residuos plásticos expresada en kilogramos por persona y día [2]

En respuesta a esta crisis, la industria química se enfrenta a la necesidad de adoptar enfoques más sostenibles. Las regulaciones ambientales cada vez más estrictas y la demanda de productos más ecológicos han motivado la búsqueda de soluciones innovadoras. Esto incluye la química verde, un enfoque que promueve el diseño de productos y procesos que reduzcan o eliminen el uso y generación de sustancias peligrosas. Además, políticas internacionales como los Acuerdos de París y los Objetivos de Desarrollo Sostenible (ODS) de la ONU (**Figura 1.3**) exigen que las industrias reduzcan su impacto ambiental mediante el desarrollo de tecnologías limpias y la transición hacia fuentes de materias primas más sostenibles.



Figura 1.3. Objetivos de Desarrollo Sostenible para alcanzar una huella neutral de carbono [3]

La Conferencia de las Partes (COP), como foro internacional clave en la lucha contra el cambio climático, juega un papel crucial en la formulación de estrategias para mitigar los impactos ambientales. Desde su establecimiento en 1995 bajo la Convención Marco de las Naciones Unidas sobre el Cambio Climático (CMNUCC), las COP han sido fundamentales para coordinar esfuerzos globales. La COP 21 en 2015, por ejemplo, resultó en el Acuerdo de París, para limitar el calentamiento global a menos de 1.5 °C por encima de los niveles preindustriales [4]. La última COP 28, celebrada en Dubái a finales de 2023, realiza un balance sobre el Acuerdo de París concluyendo de que aún estamos muy lejos de limitar el aumento de la temperatura en el valor establecido. Se firmó el Acuerdo de Dubái, que reconoce la necesidad de reducir las emisiones de gases efecto invernadero. A este respecto, este acuerdo sugiere impulsar la búsqueda de materias primas renovables para la producción de

plásticos, destacando que solamente el 8.3% de los plásticos empleados corresponden a plásticos reciclados post-consumo y tan solo el 1.5% de los plásticos producidos en 2021 son de origen renovable [5]. Por lo tanto, el desarrollo de un proceso sostenible para la síntesis de plásticos va a jugar un papel clave para alcanzar las emisiones netas de dióxido de carbono cero para 2050 [6].

1.1.1. Cambio climático

El efecto invernadero es un proceso natural que permite que la Tierra mantenga una temperatura adecuada para la vida. Este fenómeno ocurre porque ciertos gases en la atmósfera, como el dióxido de carbono (CO_2), el metano (CH_4) y el vapor de agua (H_2O), entre otros, tienen capacidad de atrapar radiación electromagnética dispensándola en forma de calor. La radiación solar (en la zona del visible-ultravioleta) atraviesa la atmósfera y calienta la superficie terrestre. Por su parte, la Tierra emite esta energía en forma de radiación infrarroja, que es parcialmente absorbida y reemitida por los gases de efecto invernadero (GEI), evitando que todo el calor escape al espacio (**Figura 1.4**). Este proceso mantiene la temperatura promedio de la Tierra en unos $15\text{ }^{\circ}\text{C}$ [7].

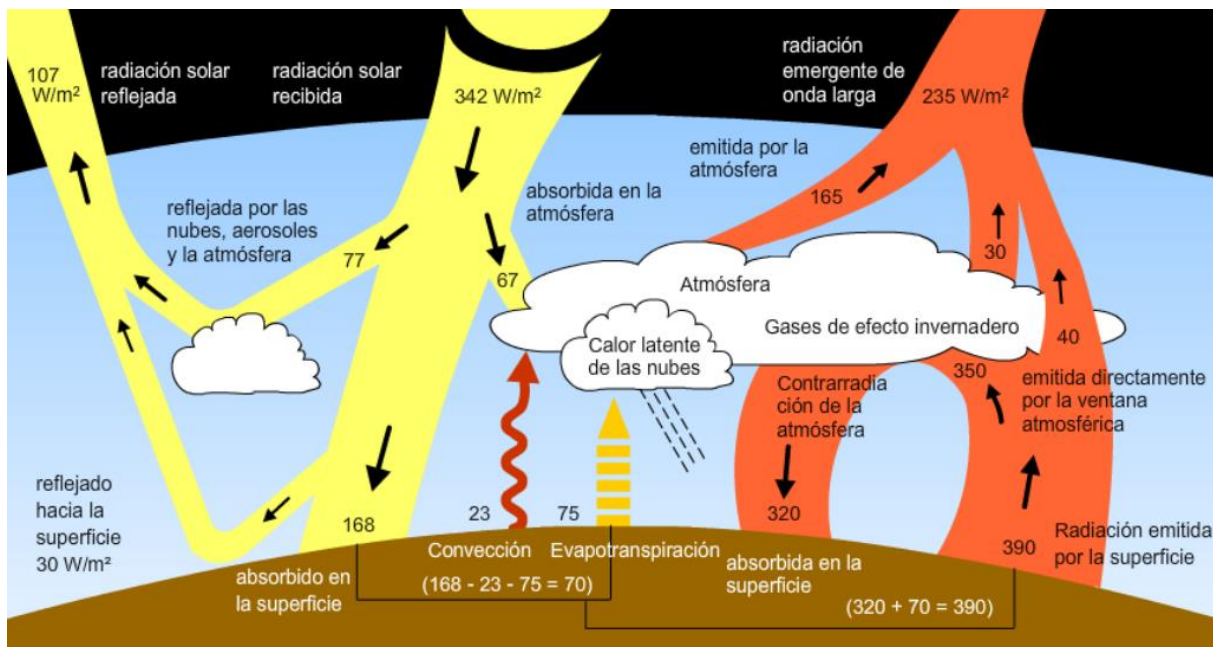


Figura 1.4. Esquema del mecanismo del efecto invernadero [8]

Sin la capacidad de los gases de efecto invernadero para retener el calor, la temperatura promedio del planeta sería alrededor de $-18\text{ }^{\circ}\text{C}$ [9]. Esta diferencia de

aproximadamente 33 °C destaca la importancia crítica del efecto invernadero para la vida tal como la conocemos. Sin embargo, el calentamiento global se refiere al aumento gradual de la temperatura promedio de la superficie de la Tierra, especialmente en las últimas décadas del siglo XX y principios del siglo XXI, atribuido principalmente a la actividad humana, especialmente debido al aumento de la concentración de GEI en la atmósfera (**Figura 1.5**).

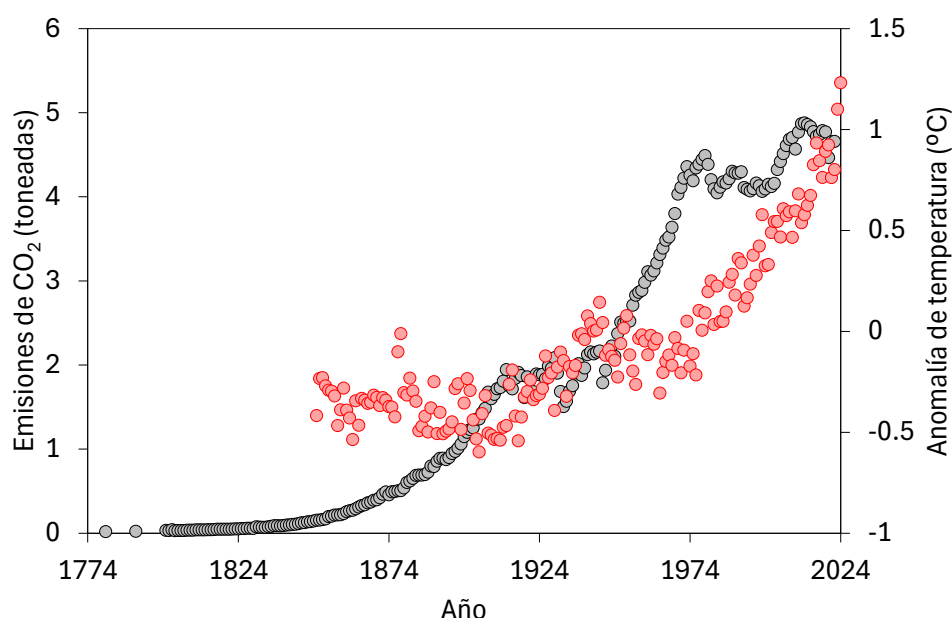


Figura 1.5. Emisiones de CO₂ de origen antropogénico (gris) y variaciones de temperatura (rojo) en relación con la temperatura promedio del período 1961-1990 [10]

Las evidencias del cambio climático son múltiples y variadas, desde cambios en la temperatura atmosférica y oceánica, el deshielo de los casquetes polares y glaciares, el aumento del nivel del mar, la acidificación de los océanos, y cambios en los patrones climáticos, como el aumento de fenómenos meteorológicos extremos. El calentamiento global es un fenómeno complejo y multifacético que representa uno de los mayores desafíos ambientales de nuestro tiempo. Su comprensión y mitigación requieren una colaboración global, políticas efectivas y acciones concertadas a todos los niveles de la sociedad siendo la disminución de GEI y el empleo de material primas renovables las formas más efectivas de disminuir la contribución de origen antropogénico ya que la quema y procesamiento de combustibles fósiles genera emisiones masivas de gases de efecto invernadero. En los últimos años, la producción de productos químicos basada en fuentes fósiles ha sido responsable de una parte significativa de las emisiones globales de CO₂. Procesos como el craqueo de hidrocarburos para producir etileno y propileno, que son los precursores de

muchos polímeros plásticos, son altamente intensivos en energía. Esto subraya la necesidad urgente de reducir la dependencia de estas materias primas para disminuir la huella de carbono de la industria.

1.1.2. Inestabilidad derivada del uso de materias primas fósiles

La concentración de materias primas fósiles en ciertas regiones geográficas plantea un desafío significativo para la industria química (**Figura 1.6**). Durante décadas, el petróleo, el gas natural y el carbón han sido las principales fuentes de compuestos químicos base, como hidrocarburos aromáticos, olefinas y alcanos, que se utilizan para sintetizar una amplia variedad de productos. La disponibilidad abundante de estos recursos y su bajo coste relativo permitieron el desarrollo de procesos químicos eficientes que sustentan la producción de plásticos, detergentes, medicamentos, fertilizantes y otros productos esenciales para la vida moderna.

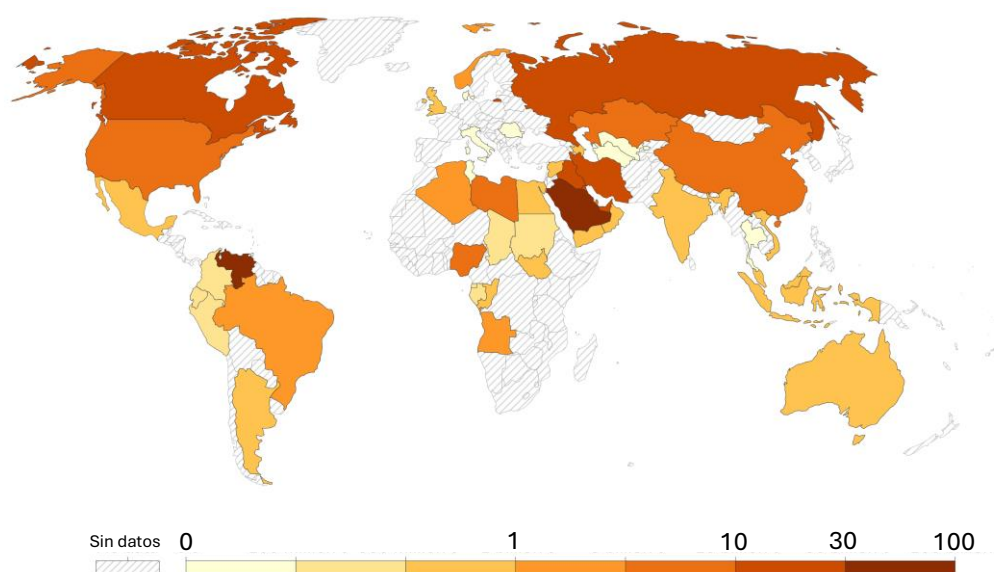


Figura 1.6. Reservas de petróleo en 2022 expresadas en billones de toneladas [11]

No obstante, a medida que se explotan los yacimientos más accesibles, el coste de extracción de estas materias primas aumenta, haciendo que los precios de los productos químicos derivados sean más elevados. La disminución de las reservas de petróleo y gas natural, junto con las fluctuaciones geopolíticas, también incrementa la incertidumbre en torno a la seguridad del suministro. Esto no solo afecta la estabilidad económica de las

industrias que dependen de estos insumos, sino que también pone en riesgo la continuidad de la producción de productos químicos esenciales.

Para evitar estos problemas, la industria química está explorando activamente nuevas rutas de síntesis que no dependan de materias primas fósiles. El uso de residuos industriales y el desarrollo de procesos de reciclaje químico avanzado permiten recuperar materiales y reintroducirlos en la cadena de valor, disminuyendo así la necesidad de introducir recursos fósiles nuevos. Asimismo, la captura y reutilización de gases como el CO₂ abre la posibilidad de generar productos químicos con menor impacto ambiental, al transformar un desecho en un recurso fomentando así un modelo económico de economía circular, en el que el reciclaje y la reutilización son los pilares para minimizar los residuos y el impacto ambiental.

La inestabilidad generada por el uso de materias primas fósiles no solo está vinculada a su disponibilidad, sino que también representa un obstáculo significativo para la sostenibilidad de la producción global de productos químicos. Innovar en nuevas fuentes de materias primas y procesos es esencial para asegurar que la industria pueda continuar satisfaciendo la demanda sin comprometer el medio ambiente.

1.1.3. Consumo de plásticos y su impacto ambiental

La producción de plásticos, en particular, ha sido uno de los principales responsables de esta dependencia de las materias primas fósiles. Los polímeros sintéticos, que se derivan principalmente del petróleo y gas natural, han revolucionado la industria debido a su versatilidad, durabilidad y bajo coste. Sin embargo, su masiva producción y el largo tiempo que tardan en degradarse están causando una crisis ambiental sin precedentes (**Figura 1.7**). Si bien los plásticos son esenciales en muchas aplicaciones (empaquetado, automoción, medicina), es evidente que el enfoque actual debe cambiar.

La gestión de los residuos plásticos también es un problema principalmente debido al uso masivo de plásticos de un solo uso. En la **Figura 1.8** se muestran las cantidades de residuos plásticos generados en función de cada polímero. A pesar de los esfuerzos por mejorar las tasas de reciclaje, solo una fracción de los plásticos se recicla efectivamente. De los aproximadamente 400 millones de toneladas de plásticos producidos anualmente, menos del 10% se recicla de manera efectiva, mientras que el resto se destina a vertederos o se libera en el medio ambiente. Esta baja tasa de reciclaje se debe a varios factores, incluyendo la

complejidad de los materiales plásticos, la falta de infraestructura adecuada y la degradación de los plásticos durante el reciclaje.

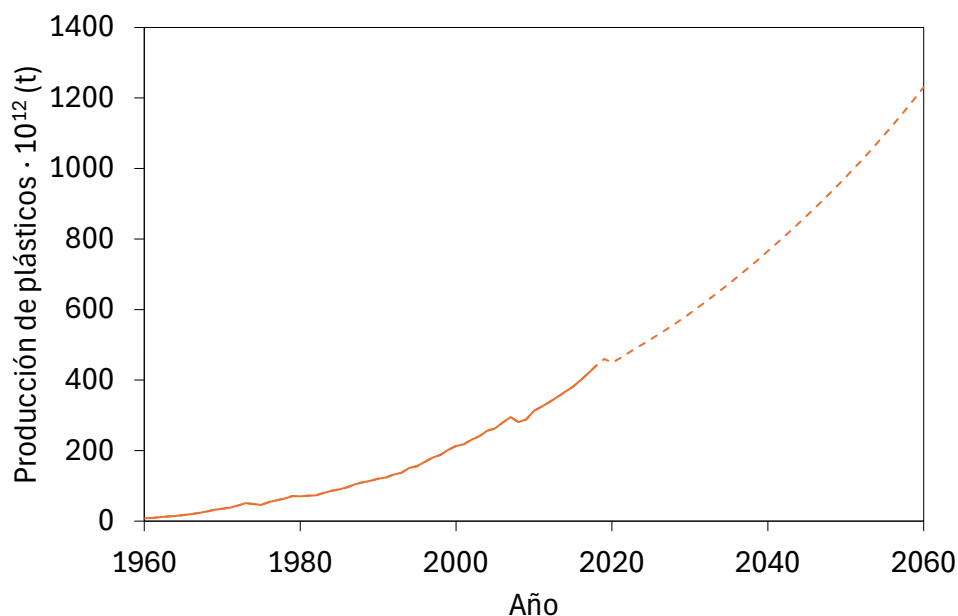


Figura 1.7. Producción de plásticos mundial con previsión hasta 2060 [12]

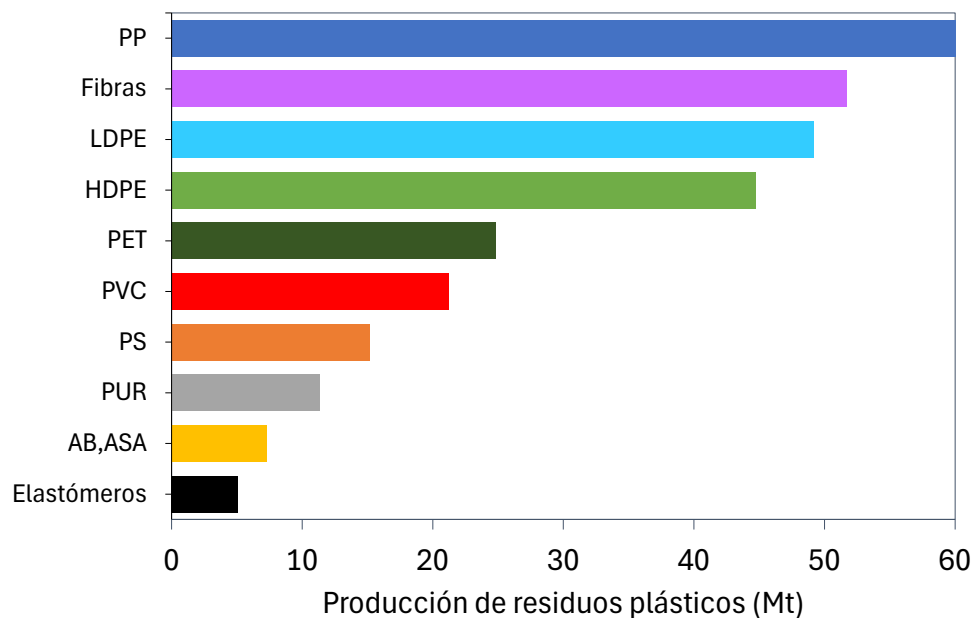


Figura 1.8. Producción global de residuos plásticos en 2019 en función de cada polímero. Leyenda: PP (polipropileno), LDPE (polietileno de baja densidad), HDPE (polietileno de alta densidad), PET (tereftalato de polietileno), PVC (cloruro de polivinilo), PS (poliestireno), PUR (poliuretano), AB (acrilonitrilo butadieno), ASA (acrilonitrilo estireno acrilato) [13]

Además, la persistencia de los plásticos en el medio ambiente es un problema crítico, ya que estos materiales no se degradan fácilmente y pueden permanecer en los ecosistemas durante siglos. La contaminación por plásticos ha alcanzado niveles alarmantes, afectando tanto a ambientes marinos como terrestres. Se estima que aproximadamente 8 millones de toneladas de plásticos terminan en los océanos cada año, causando daños a la vida marina, desde los microplásticos que son ingeridos por organismos marinos hasta grandes fragmentos que pueden atrapar o enredar a las especies [14].

En conclusión, aunque los plásticos siguen siendo materiales irremplazables en muchas aplicaciones debido a sus propiedades únicas, la búsqueda de soluciones sostenibles es esencial para enfrentar los problemas ambientales actuales. La sustitución de plásticos tradicionales por alternativas renovables y la mejora en las prácticas de gestión de residuos representan oportunidades clave para reducir el impacto ambiental y avanzar hacia una industria más sostenible. La producción de plásticos biodegradables y reciclables que mantengan las propiedades clave de los polímeros tradicionales (como resistencia, ligereza y versatilidad) será crucial para asegurar la sostenibilidad del sector. En este sentido, la industria está en una fase de transición hacia un modelo en el que los productos químicos se diseñen para tener un impacto ambiental mínimo durante todo su ciclo de vida.

1.2. ALTERNATIVAS SOSTENIBLES: BIORREFINERÍAS Y FURANOATO DE POLIETILENO

El futuro de la producción de productos químicos depende de la capacidad para sustituir las materias primas fósiles por fuentes alternativas sostenibles. Esta transición es clave no solo para hacer frente al agotamiento de los recursos, sino también para reducir los impactos medioambientales de la industria.

El enfoque en este campo abarca varias líneas de investigación que buscan diversificar las fuentes de productos químicos mediante el uso de recursos que sean más accesibles y tengan un menor impacto ambiental. Entre las alternativas más prometedoras se encuentran la valorización de biomasa lignocelulósica residual y los procesos de captura y utilización de CO₂ (CCU), que permiten transformar este gas de efecto invernadero en productos químicos útiles.

Actualmente, y como tecnologías emergentes, se está explorando cómo convertir el dióxido de carbono en compuestos como metanol, carbonatos cíclicos y otros precursores químicos, que pueden servir de base para fabricar plásticos y otros materiales. Asimismo, los residuos industriales y subproductos de otros procesos están siendo evaluados como fuentes para la producción de compuestos químicos.

Los procesos de biorrefinería están ganando interés en el desarrollo de alternativas viables para la sustitución tanto de los combustibles fósiles convencionales como para la fabricación de productos químicos de forma sostenible y con baja huella de carbono. El funcionamiento de la una biorrefinería se inspira de las refinerías tradicionales de petróleo, pero utiliza biomasa como materia prima para la producción de una amplia gama de productos químicos, materiales y energía, ya que es la fuente de carbono más abundante después del CO₂ atmosférico [15, 16]. La biomasa incluye desechos orgánicos como residuos agrícolas, subproductos forestales e incluso ciertos tipos de desechos industriales [16]. En la **Figura 1.9** se ilustran algunos de los diferentes productos que pueden obtenerse en una biorrefinería basada en biomasa lignocelulósica.

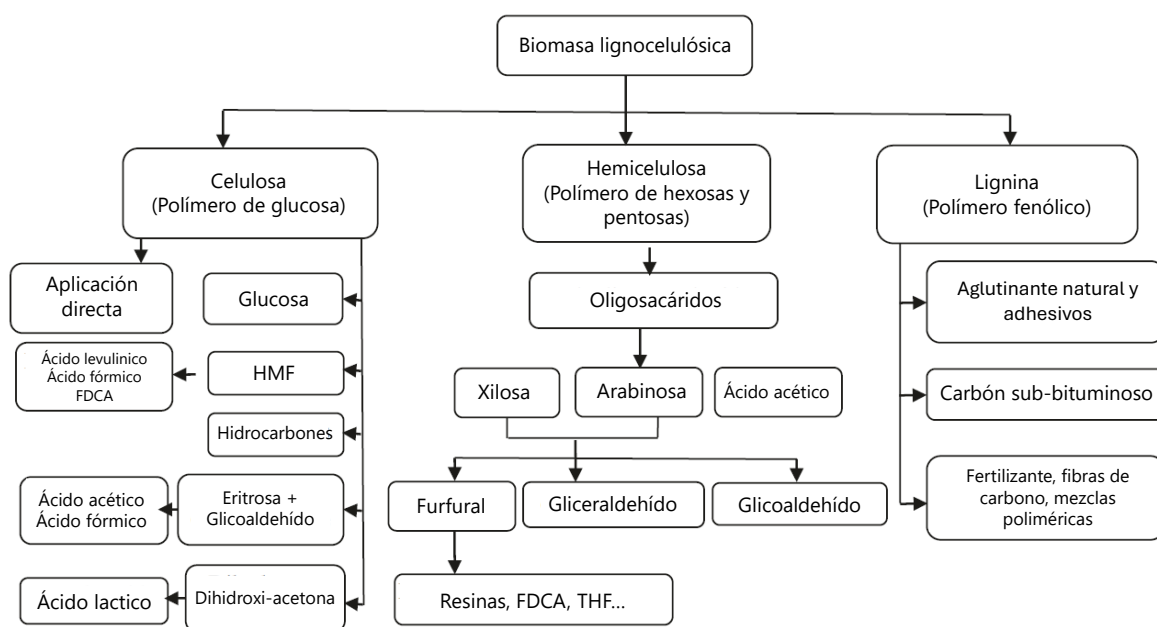


Figura 1.9. Representación de productos obtenidos en una biorrefinería basada en biomasa lignocelulósica. Adaptado de [18]

Comparadas con las refinerías tradicionales de petróleo, las biorrefinerías ofrecen varias ventajas significativas [19, 20]:

- **Sostenibilidad ambiental:** Las biorrefinerías utilizan recursos renovables y biodegradables (incluso residuos y materiales recuperados de residuos), reduciendo la dependencia de los combustibles fósiles y disminuyendo las emisiones de gases de efecto invernadero.
- **Diversificación de productos:** Las biorrefinerías pueden producir una amplia gama de productos, desde biocombustibles hasta productos químicos y biomateriales, lo que aumenta la versatilidad y la rentabilidad de la instalación.
- **Valorización de residuos:** Las biorrefinerías pueden utilizar una variedad de materias primas, incluidos los residuos agrícolas, forestales y alimentarios, convirtiéndolos en productos de valor añadido y reduciendo así la cantidad de residuos enviados a vertederos.
- **Menor dependencia de los mercados:** Al utilizar recursos renovables y locales, las biorrefinerías pueden reducir la dependencia de los precios volátiles del petróleo y promover la seguridad energética y económica a nivel local y regional.

Una de las vías de valorización de biomasa residual de mayor potencial industrial es la obtención de plásticos. Mediante el desarrollo de polímeros basados en moléculas derivadas de la biomasa es posible reducir la dependencia de los combustibles fósiles, disminuir las emisiones de carbono y contribuir a una economía circular. Este desarrollo es esencial para que la implementación de las políticas gubernamentales (prohibición de plásticos de un solo uso, aumento de la sostenibilidad del sector) sea factible sin suponer una ruptura drástica con el sistema económico actual. Actualmente, existen cuatro familias de plásticos, clasificados en función de su origen y su grado de biodegradabilidad, ver **Figura 1.10**.

La mayor parte de los plásticos tradicionales (polietileno, polipropileno, tereftalato de polietileno, etc.), tienen un origen fósil y son no biodegradables. Estos son los polímeros cuyo análisis de ciclo de vida demuestra un mayor impacto ambiental y, por lo tanto, aquéllos en los que la legislación y la industria deben focalizar los esfuerzos para su sustitución. Existe otra familia que, manteniendo un origen fósil, da lugar a plásticos biodegradables. En este grupo se incluyen, entre otros, los poliésteres alifáticos, plásticos ampliamente utilizados en el sector de paquetería. Ambas familias están llamadas a ser sustituidas por los bioplásticos, entendiendo como tal a todos los que tengan un origen basado en biomasa. Si bien no todos

ellos son 100% biodegradables, sí presentan un mayor grado de biodegradabilidad o, al menos, reciclabilidad, respecto a los plásticos convencionales.

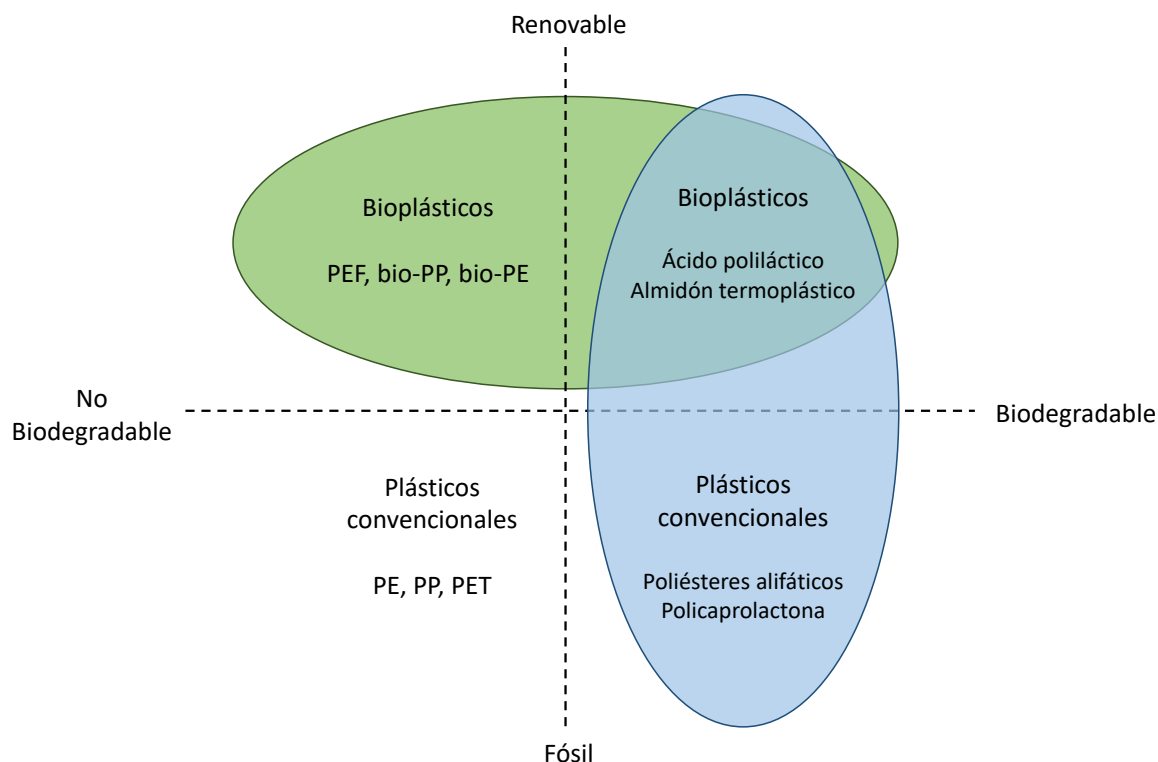


Figura 1.10. Clasificación de plásticos según su origen y capacidad de biodegradación [21]

Un ejemplo claro de sustitución prácticamente directa es el caso del tereftalato de polietileno (PET) y el furanoato de polietileno (PEF) [22]. El PET es un plástico convencional (de origen fósil y no biodegradable) utilizado principalmente para producir botellas y envases y constituye alrededor del 20% de la producción de plásticos a nivel mundial [22-24].

En la actualidad, el PET se produce utilizando etileno y xileno, ambos derivados de procesos de refinado del petróleo orientados principalmente a la producción de combustibles fósiles. Sin embargo, a medida que se impulsa la transición hacia un modelo de transporte más sostenible, donde se promueve el uso de vehículos eléctricos y se fomenta el transporte colectivo, la demanda de gasolina y gasóleo se verá reducida. Todo esto conllevará a una disminución en el refinado de petróleo, lo que resultará en una menor disponibilidad de olefinas y aromáticos como el etileno y el xileno. La disminución de estos subproductos podría plantear desafíos para la industria de los plásticos convencionales, aumentando la necesidad de alternativas sostenibles que no dependan del refinado de combustibles fósiles.

El furanoato de polietileno (PEF) surge como una alternativa renovable que, debido a su similitud estructural (**Figura 1.11**), genera un polímero de propiedades similares al PET y significativas ventajas medioambientales.

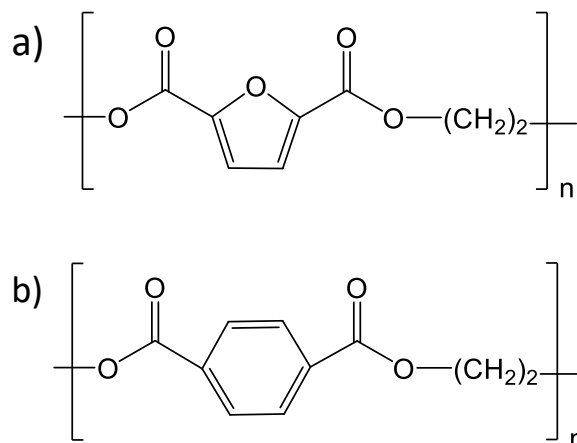


Figura 1.11. Comparación de la estructura de (a) PEF y (b) PET

El PEF se obtiene mediante la policondensación del bio-etilenglicol y el ácido 2,5-furandicarboxílico (FDCA). Ambos compuestos se obtienen a partir de biomasa lignocelulósica (**Figura 1.12**).

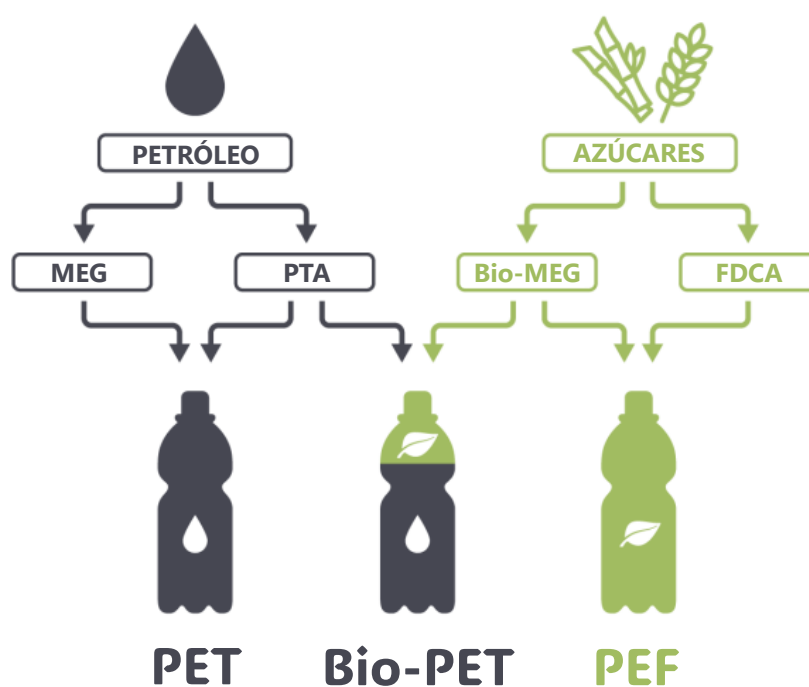


Figura 1.12. Composición de botellas de PEF, botellas multicapa de PEF y PET y botellas de PET

El FDCA y el ácido tereftálico (PTA), utilizado en la síntesis de PET y de origen no renovable, tienen propiedades químicas similares, lo que permite que el FDCA se utilice como un reemplazo directo en la síntesis de poliésteres [25]. Los poliésteres fabricados con FDCA pueden tener características comparables o incluso mejoradas. Destaca sobre todo la resistencia mecánica del PEF (comparable a la del PET) haciéndolo adecuado para aplicaciones que requieren durabilidad y robustez. Además, el PEF presenta excelentes propiedades de barrera frente a gases como oxígeno y dióxido de carbono, lo que lo convierte en una opción superior para el envasado de alimentos y bebidas, al preservar los alimentos frescos y extender la vida útil del producto.

Aunque el PEF no es completamente biodegradable en todas las condiciones, su capacidad para descomponerse en entornos específicos puede ayudar a mitigar la acumulación de residuos plásticos en el medio ambiente. También es reciclable, lo que facilita su integración en los sistemas de reciclaje existentes, ofreciendo una solución más sostenible en comparación con el PET. Además, su síntesis a partir de biomasa lignocelulósica representa un paso importante hacia una economía más sostenible y basada en recursos renovables.

1.3. BIOMASA LIGNOCELULÓSICA

La biomasa lignocelulósica está constituida principalmente por celulosa (40-60%), hemicelulosa (10-40%) y lignina (15-30%) formando un material compuesto que es resistente a la conversión química, un fenómeno comúnmente conocido como carácter recalcitrante de la biomasa (**Figura 1.13**) [26, 27]. La holocelulosa considera celulosa y hemicelulosa, es decir, engloba la parte de carbohidratos y contiene entre un 40-60% de oxígeno. La presencia de oxígeno hace que la biomasa sea una materia prima atractiva para producir productos químicos oxigenados de interés industrial que son costosos de sintetizar a partir de materias primas derivadas del petróleo [26].

Actualmente, uno de los mayores retos de la ingeniería química es avanzar hacia una industria capaz de implementar una conversión catalítica eficiente de la biomasa, transformando esta materia prima renovable en productos químicos, combustibles y energía de utilidad. Estos compuestos se pueden generar mediante procesos como la pirólisis y

gasificación, así como a través de fermentación o rutas químio-catalíticas avanzadas [27]. A largo plazo, el desarrollo de estas tecnologías promete contribuir a la creación de una economía más sostenible y menos dependiente de los recursos fósiles.

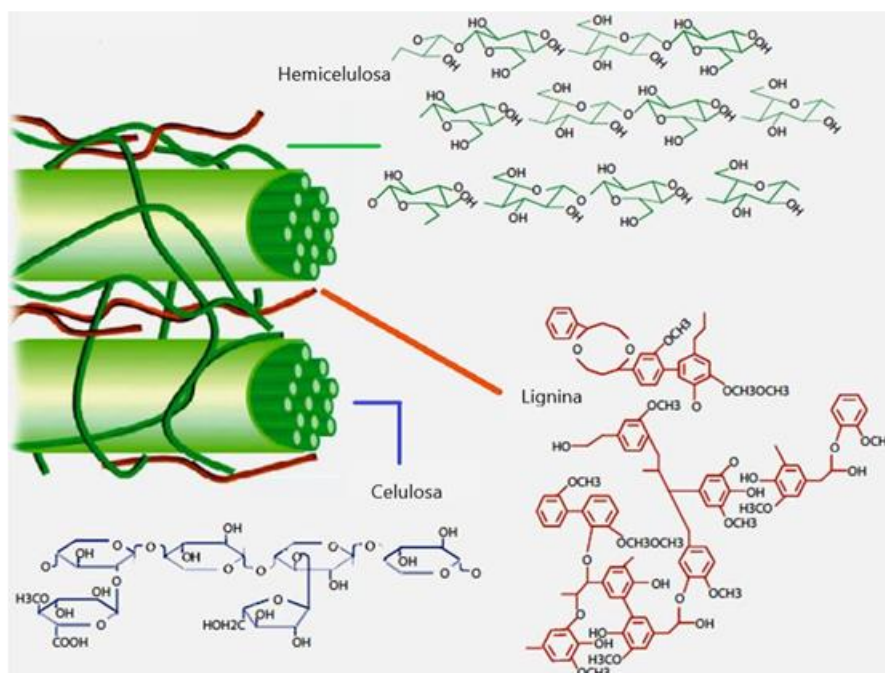


Figura 1.13. Representación esquemática de los constituyentes de la biomasa lignocelulósica

1.3.1. Celulosa

La celulosa es el polímero natural más abundante en la Tierra y se encuentra en la pared celular de las plantas. Es un homopolímero lineal compuesto por unidades repetidas de D-glucosa unidas mediante enlaces β -1,4-glucosídicos. Esta estructura confiere a la celulosa una alta resistencia y una naturaleza hidrofílica debido a los grupos hidroxilo presentes en sus enlaces. La celulosa tiene una complejidad química considerable, lo que dificulta su aislamiento y separación de otros componentes de la biomasa, como la hemicelulosa y la lignina [28].

La celulosa tiene múltiples aplicaciones industriales, como la producción de papel, textiles y productos químicos como el 5-hidroximetilfurfural (HMF) y el ácido levulínico (LA). La celulosa se obtiene principalmente a través de procesos de pretratamiento mecánico y químico que permiten su separación de otros componentes de la biomasa. Estos procesos incluyen el uso de disoluciones ácidas, alcalinas y enzimas para romper los enlaces entre la celulosa y otros biopolímeros [29].

1.3.2. Hemicelulosa

La hemicelulosa es un heteropolímero ramificado compuesto por una variedad de monosacáridos, incluyendo pentosas (como xilosa, arabinosa y ribosa) y hexosas (como glucosa, fructosa, galactosa y manosa), siendo la xilosa el componente predominante [30]. Este biopolímero se encuentra en la pared celular vegetal, donde está unida a la celulosa a través de enlaces de hidrógeno. La hemicelulosa es menos resistente a la hidrólisis en comparación con la celulosa, lo que facilita su degradación.

La hemicelulosa tiene aplicaciones potenciales en la producción de biocombustibles y productos químicos derivados de biomasa. Sin embargo, su desarrollo a nivel industrial presenta desafíos ya que su estructura compleja y heterogénea dificulta una conversión selectiva, y actualmente no posee un valor añadido elevado en comparación con otros biopolímeros [31]. La obtención de hemicelulosa implica el uso de métodos de pretratamiento y extracción específicos, como la hidrólisis ácida o alcalina, que permiten su separación de la celulosa y la lignina presentes en la biomasa lignocelulósica [30].

1.3.3. Lignina

La lignina es el principal componente polimérico restante en la biomasa lignocelulósica, representando aproximadamente el 20% en peso. Es un biopolímero polifenólico tridimensional que se encuentra en la pared celular de las plantas, proporcionando rigidez y resistencia estructural, esenciales para el sostenimiento de la planta. Además de su función estructural, la lignina actúa como una barrera protectora, ayudando a las plantas a resistir el ataque de microorganismos y a reducir la pérdida de agua, lo cual es vital para su supervivencia en condiciones ambientales diversas.

Tradicionalmente la lignina se quema para generar calor y energía ya que su conversión en coproductos adicionales sigue siendo un reto debido a su estructura altamente ramificada y aleatoria, lo que contribuye a su carácter recalcitrante y dificulta su conversión en productos útiles mediante técnicas convencionales [32]. Sin embargo, tiene potencial para ser utilizada en la producción de biocompuestos, productos químicos y materiales avanzados mediante procesos de valorización más innovadores [33]. La obtención de lignina implica métodos de extracción durante el proceso de *pulping*, como el método Kraft, que permiten su separación de la celulosa y la hemicelulosa [34].

1.4. VALORIZACIÓN DE RESIDUOS DE BIOMASA LIGNOCELULÓSICA

La Ley 7/2022, de 8 de abril, de residuos y suelos contaminados para una economía circular, define valorización como cualquier operación cuyo resultado principal sea que un residuo adquiera una finalidad útil, ya sea sustituyendo a otros materiales que se habrían utilizado para cumplir una función específica o preparándolo para cumplir esa función en un proceso industrial o en la economía en general. En este contexto, se están desarrollando cuatro tecnologías clave para la valorización de biomasa lignocelulósica: gasificación, pirólisis, licuefacción e hidrólisis [35, 36].

1.4.1. Gasificación

La gasificación es un proceso de oxidación parcial que convierte la alimentación orgánica en monóxido de carbono, dióxido de carbono e hidrógeno, por medio de una reacción a elevadas temperaturas ($>700\text{ }^{\circ}\text{C}$), sin que tenga lugar la combustión y controlando la cantidad de oxígeno o de vapor empleada. El resultado es un gas llamado gas de síntesis o *syngas* [35].

El gas de síntesis puede ser sometido a una combustión para la recuperación de energía térmica en forma de calor y/o vapor y electricidad. La energía derivada de la gasificación, mediante la combustión del gas de síntesis, se considera como una fuente de energía renovable si se emplea biomasa como materia prima. Por otro lado, el gas de síntesis puede ser utilizado para obtener diferentes productos químicos, destacando cinco rutas alternativas de valorización [38, 39]:

- Síntesis Fischer-Tropsch. Se trata de un proceso catalítico que ha sido utilizado desde 1920 para la producción de combustibles líquidos a partir del gas de síntesis derivado del carbón y del gas natural.
- Síntesis de alcoholes. Es también un proceso catalítico utilizado para producir metanol a partir del gas de síntesis derivado del reformado de vapor del gas natural o gas de síntesis a partir de carbón.
- Síntesis de alcoholes mixtos. Es un proceso catalítico que produce una mezcla de metanol, etanol, propanol, butanol y pequeñas cantidades de alcoholes más pesados.

- Síntesis de dimetil éter (DME). El dimetil éter se forma por eterificación de dos moléculas de metanol, con lo que se integra con la producción de este. Es un proceso catalítico a través del cual se consigue obtener un nuevo combustible que permite una combustión limpia debido a sus propiedades fisicoquímicas, como el alto índice de cetano y las bajas emisiones de combustión de hollín, CO, hidrocarburos y NO_x.
- Fermentación del gas de síntesis. Es un proceso biológico que utiliza microorganismos anaeróbicos para fermentar el gas de síntesis y producir etanol y otros compuestos químicos.

1.4.2. Pirólisis

La pirólisis es la despolimerización térmica de la materia orgánica en ausencia de oxígeno a temperaturas en torno a 500 °C. El requerimiento de calor para la pirólisis de materias primas lignocelulósicas se encuentra en el rango de 207-434 kJ/kg [40]. En este proceso se genera una mezcla compleja de productos gaseosos, líquidos y sólidos. El principal beneficio sobre la gasificación es que el combustible líquido generado puede almacenarse y transportarse fácilmente [41].

El calentamiento rápido de la biomasa en dicha atmósfera inerte da como resultado la producción de vapor orgánico compuesto por fragmentos de polímeros de celulosa, hemicelulosa y lignina. Estos vapores se pueden condensar para dar un líquido orgánico, comúnmente conocido como bio-aceite. Los gases no condensables abandonan el sistema de reacción y pueden usarse para proporcionar calor para la pirólisis. El sólido restante, conocido como bio-char, posee un alto contenido en carbono. La distribución del producto depende predominantemente de la composición de la biomasa lignocelulósica. El aceite de pirólisis es un material muy complejo (fuertemente ácido, muy heterogéneo) y precisa un refinado técnicamente complicado para ser utilizado como combustible, por lo que debe acondicionarse para emplearse en los motores actuales [40, 42].

1.4.3. Licuefacción

La licuefacción es una vía alternativa para la producción de bio-aceite, consiste en la descomposición térmica catalítica de moléculas grandes a especies inestables más cortas que se polimerizan nuevamente en un bio-aceite [43]. La biomasa se mezcla con agua y

catalizadores básicos como el carbonato de sodio, y el proceso se lleva a cabo a temperaturas más bajas que la pirólisis (250-450 °C) pero presiones más altas (5-20 atm). Estos factores se combinan para hacer que la licuefacción sea un proceso más costoso. El producto líquido obtenido contiene menos oxígeno (12-14%) que el bio-aceite producido por la pirólisis y generalmente requiere un procesamiento menos extenso [27, 44].

1.4.4. Hidrólisis

La hidrólisis en comparación con técnicas como la gasificación, pirólisis o licuefacción se lleva a cabo a temperaturas más bajas (100-250 °C) en fase acuosa. Su objetivo es romper las cadenas de celulosa y hemicelulosa para llegar a la unidad monomérica, en este caso, azúcares como la glucosa y la xilosa, principalmente [45]. Posteriormente, a través de diferentes técnicas catalíticas, se pueden transformar esos azúcares en productos plataforma, es decir, en compuestos que son la base para la obtención de otros más complejos de interés industrial, como HMF y furfural (FFL).

Como se indica anteriormente en el **apartado 1.3.1**, la celulosa es un polímero de glucosa ampliamente presente en las plantas, y representa una de las materias primas más abundantes y renovables para la producción de bioproductos. Se trata de un material higroscópico e insoluble en agua [46]. Sin embargo, la hidrólisis es uno de los procesos clave para la conversión de celulosa en productos químicos de valor añadido [47], ya que implica la ruptura de los enlaces glucosídicos que unen las unidades de glucosa en la cadena polimérica, generando así productos de menor peso molecular. Esta reacción puede llevarse a cabo mediante diversos métodos, como la hidrólisis ácida o la enzimática.

La hidrólisis enzimática se basa en la acción de enzimas celulolíticas, como las celulasas y hemicelulasas, que catalizan la descomposición de la celulosa en azúcares fermentables [48]. Por otro lado, la hidrólisis ácida utiliza ácidos diluidos, como el ácido sulfúrico o el ácido clorhídrico, para catalizar la ruptura de los enlaces glucosídicos, lo que genera la formación de azúcares monoméricos como la glucosa, así como productos secundarios como ácidos orgánicos y aldehídos [47]. Aunque la hidrólisis enzimática tiene ventajas en términos de selectividad y eficiencia energética, su implementación a gran escala puede verse limitada por los elevados costes asociados a la producción y purificación de las enzimas. En cambio, la hidrólisis ácida presenta menores costes, ya que la producción de los

ácidos utilizados como catalizadores es considerablemente más económica, y su velocidad de reacción es mayor, lo que permite completar el proceso en menos tiempo y con equipamientos más pequeños [49]. Además, se han investigado estrategias de pretratamiento de la celulosa para mejorar su accesibilidad a los agentes hidrolíticos, así como métodos de recuperación y reciclaje de los catalizadores ácidos [50].

Es importante destacar que la hidrólisis de la celulosa proporciona la base para el desarrollo de procesos más complejos que implican la utilización de biomasa lignocelulósica. A diferencia de la celulosa pura, la biomasa lignocelulósica contiene no solo celulosa, sino también hemicelulosa y lignina, lo que añade una complejidad adicional debido a la heterogeneidad de la materia prima y la necesidad de descomponer y valorizar múltiples componentes. Además, el sistema no ideal de la biomasa lignocelulósica introduce consideraciones adicionales en términos de cinética de reacción y transferencia de calor y materia, lo que requiere un enfoque integrado y multidisciplinario para su conversión eficiente.

1.5. OBTENCIÓN DE ÁCIDO 2,5-FURANDICARBOXÍLICO A PARTIR DE BIOMASA

Tras haber contextualizado la problemática medioambiental derivada de la sobreproducción de plásticos de origen fósil, así como la urgente necesidad de desarrollar alternativas sostenibles que minimicen el impacto ambiental, en esta Tesis Doctoral se detallan las distintas etapas del proceso de producción de FDCA (precursor de PEF) a partir de residuos de biomasa lignocelulósica.

Las etapas del proceso incluyen la hidrólisis de la biomasa tras su pretratamiento, obteniendo azúcares simples (glucosa, xilosa) y, posteriormente, la formación de aldehídos furánicos, como FFL y HMF. La oxidación de estos aldehídos produce FDCA y ácido furóico (FCA), compuesto que a su vez es sometido a una etapa adicional de carboxilación para completar la síntesis de FDCA.

Este proceso integrado no solo permite la conversión de un residuo abundante en un producto de alto valor añadido, sino que también se alinea con los principios de la economía

circular y la sostenibilidad industrial, proponiendo una alternativa viable a los plásticos convencionales. Las distintas etapas del proceso se muestran esquematizadas en la **Figura 1.14**, donde se ilustra cada fase del procedimiento para su mejor comprensión.

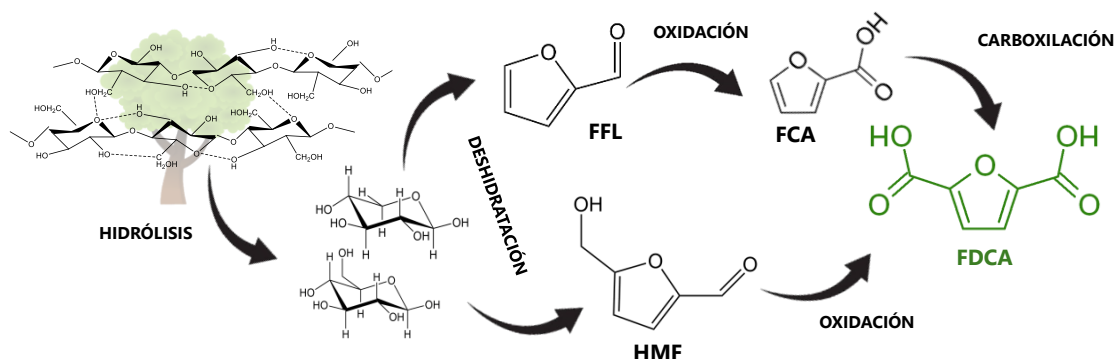


Figura 1.14. Secuencia de las diferentes etapas necesarias para la transformación de biomasa en FDCA.

1.5.1. Tratamientos previos de la biomasa lignocelulósica

La estructura recalcitrante de la biomasa lignocelulósica hace que su conversión directa hacia otros productos sea compleja. Por lo tanto, los pretratamientos son necesarios para permitir la separación efectiva de sus componentes y su posterior valorización independiente [51]. Entre los pretratamientos más comunes se encuentran la hidrólisis ácida, la hidrólisis alcalina, la explosión de vapor (*Steam Explosion*), la oxidación con oxígeno y el tratamiento con disolventes orgánicos [52].

- **Hidrólisis ácida:** En este proceso, la biomasa se trata con ácidos fuertes, como ácido sulfúrico o ácido clorhídrico, en condiciones controladas de temperatura y presión. El ácido rompe los enlaces químicos que mantienen unidas las fibras de celulosa, hemicelulosa y lignina, liberando así azúcares fermentables y compuestos fenólicos. Este método es efectivo para descomponer la hemicelulosa en azúcares simples, como la xilosa y la arabinosa, que luego pueden ser utilizados en la producción de biocombustibles o productos químicos [53].
- **Hidrólisis alcalina:** Similar a la hidrólisis ácida, este proceso implica el tratamiento de la biomasa con soluciones alcalinas, como hidróxido de sodio o hidróxido de potasio. La alcalinidad rompe los enlaces éster entre la lignina y los carbohidratos, facilitando la

separación de la lignina de la celulosa y la hemicelulosa. Además, la hidrólisis alcalina puede facilitar la despolimerización de la lignina en compuestos fenólicos de menor peso molecular, que son más fáciles de recuperar y utilizar en aplicaciones químicas [54].

- Explosión de vapor (*Steam Explosion*): En este proceso, la biomasa se somete a altas temperaturas y presiones en presencia de vapor de agua. La rápida expansión y contracción resultante de la liberación de la presión provoca la ruptura de las estructuras lignocelulósicas, aumentando la accesibilidad de los componentes de la biomasa. Este método es particularmente efectivo para la separación de la lignina de la celulosa y la hemicelulosa, sin degradar significativamente los azúcares fermentables [55].
- Pretratamientos oxidativos: En este proceso, la biomasa se trata con oxígeno a alta temperatura y presión en presencia de catalizadores metálicos. La oxidación química descompone los componentes de la biomasa, especialmente la lignina, en compuestos más simples y reactivos. Este método puede mejorar la extracción de lignina y aumentar la concentración de azúcares fermentables en la biomasa tratada [56].
- Tratamiento con disolventes orgánicos: En este proceso, la biomasa se trata con disolventes orgánicos, como etanol, metanol o acetona, que tienen afinidad con componentes específicos de la biomasa, como la lignina. Los disolventes disuelven selectivamente la lignina sin dañar significativamente la celulosa y la hemicelulosa, permitiendo su posterior recuperación y valorización [57].

La lignina, una vez separada de la celulosa y la hemicelulosa, puede ser sometida a diversos procesos para su valorización. Por ejemplo, la lignina se puede utilizar como materia prima para la producción de biocombustibles líquidos mediante procesos de pirólisis o gasificación. También puede ser transformada en productos químicos de alto valor mediante procesos de despolimerización, hidrogenación u oxidación controlada [32]. Sin embargo, todos estos procesos se encuentran fuera los objetivos de esta Tesis Doctoral.

1.5.2. Producción de furfural y 5-hidroximetilfurfural

El FFL es uno de los productos químicos renovables más antiguos producidos por el ser humano, cuya estructura se compone de un anillo de furano y un grupo aldehído, lo que lo convierte en una molécula reactiva y versátil. Tradicionalmente, ha sido utilizado en la fabricación de resinas, especialmente en tecnologías de fundición, y como disolvente en la

producción de lubricantes. Además, el FFL es una molécula plataforma clave para la síntesis de productos químicos basados en furanos, como el alcohol furfurílico, alcohol metilfurfurílico, furano, ácido furóico, furfurilamina y metilfurano (**Figura 1.15**). Estos derivados tienen un alto potencial en aplicaciones industriales, incluyendo la producción de biocombustibles, resinas y disolventes sostenibles [58]. Dada la baja valorización de esta fracción, las rutas centradas en el FFL ofrecen una ventaja adicional tanto desde la perspectiva de la economía circular como de la sostenibilidad [58].

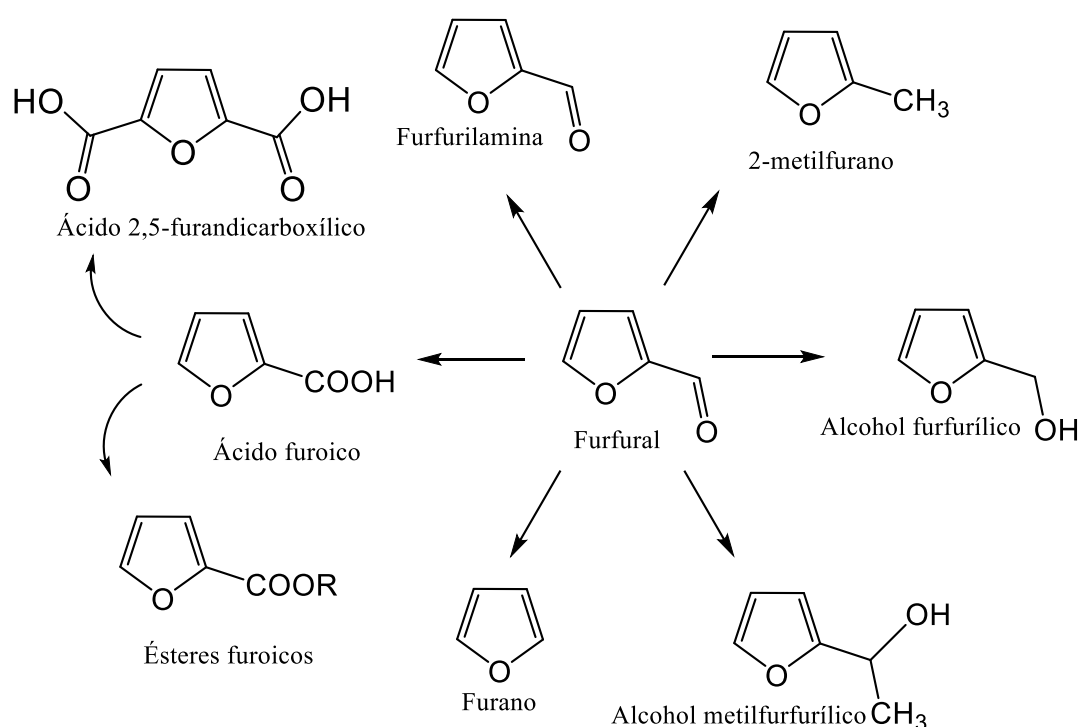


Figura 1. 15. Ejemplos de productos químicos derivados del furfural

El HMF, por su parte, presenta una estructura similar, con un anillo de furano al que están unidos un grupo aldehído y un grupo hidroxilo, lo que le confiere una gran reactividad y versatilidad en su uso industrial. Gracias a su estructura, puede transformarse en varios productos químicos y combustibles importantes debido a la presencia de los grupos funcionales C=O, C-O y el anillo de furano (**Figura 1.16**). El HMF es utilizado como materia prima para la síntesis de compuestos clave como el 2,5-diformilfurano (DFF) y el FDCA, a través de procesos de oxidación que permiten obtener productos de alto valor añadido. Tanto el DFF como el FDCA son fundamentales para la fabricación de productos farmacéuticos, fungicidas y polímeros de furano que tienen múltiples aplicaciones industriales. Como se indica anteriormente, el FDCA es de gran interés industrial por su papel en la producción de

PEF, un polímero renovable que tiene el potencial de sustituir al PET en la industria de los plásticos y que ofrece una alternativa más sostenible en la fabricación de envases y otros productos plásticos [59].

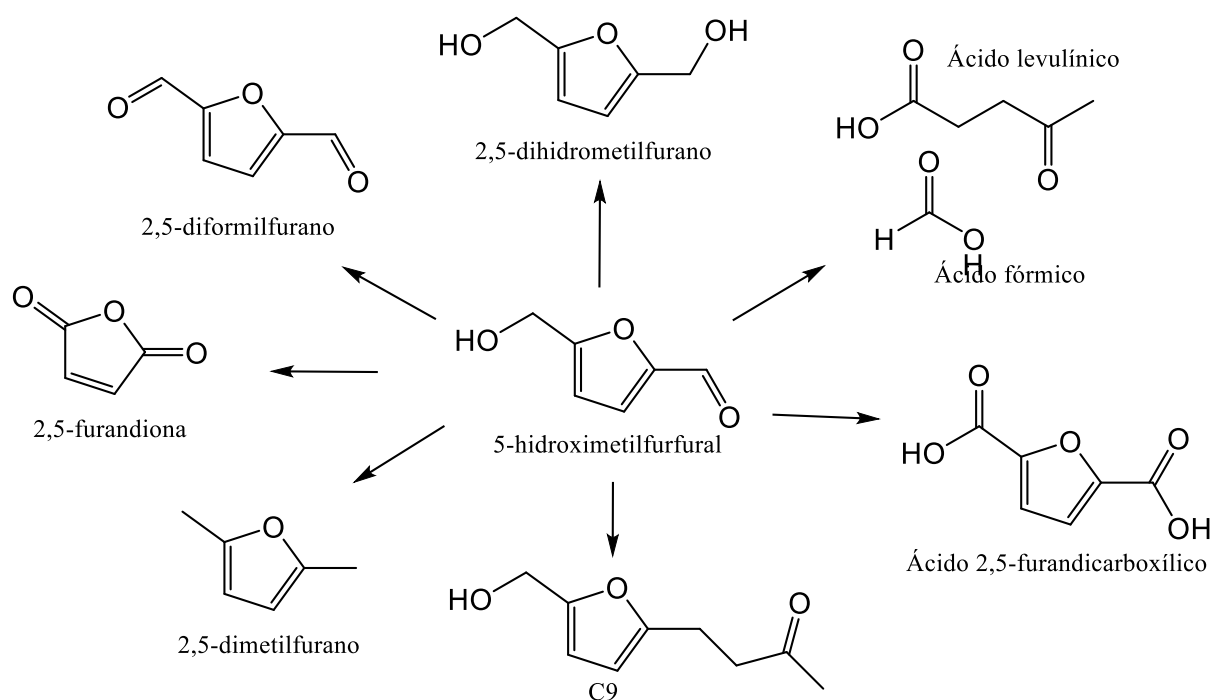


Figura 1. 16. Ejemplos de productos químicos derivados del 5-hidroximetilfurfural

La producción de FFL y HMF comienza con la hidrólisis de la biomasa hemicelulósica. Como se explica en el **apartado 1.4.4**, esta etapa puede llevarse a cabo mediante diferentes enfoques, incluyendo tratamientos ácidos, enzimáticos o combinados [60]. Una vez liberados los azúcares, el FFL y el HMF se generan mediante reacciones de deshidratación y condensación junto con el ácido levulínico (LA) y fórmico (FA) [26]. El FFL se produce a partir de la deshidratación de pentosas (principalmente xilosa) presente en la hemicelulosa, mientras que el HMF se forma a partir de la deshidratación de hexosas (principalmente glucosa) derivada de la celulosa (**Figura 1.17**) [53].

El FFL y el HMF emergen como un pilar en la valorización de la biomasa por su capacidad para transformarse en diferentes compuestos de alto valor añadido. La investigación en este campo continúa explorando nuevas rutas catalíticas y mejorando la eficiencia de los procesos, con el objetivo de maximizar el rendimiento y la pureza de los

productos derivados de la hidrólisis, lo que podría tener un impacto significativo en la industria de los materiales sostenibles. En la literatura se han propuesto diferentes catalizadores para llevar a cabo la hidrólisis, incluidos ácidos orgánicos e inorgánicos, sales, ácidos de Lewis y resinas de intercambio iónico [47], concluyendo que la isomerización de glucosa a fructosa (catalizada por ácidos de Lewis) es el paso limitante en la velocidad de reacción. Además de los cloruros metálicos (catálisis homogénea), se han probado zeolitas como ZSM-5 modificado con metales, zeolita Y o mordenita para obtener una buena actividad de isomerización [61, 62].

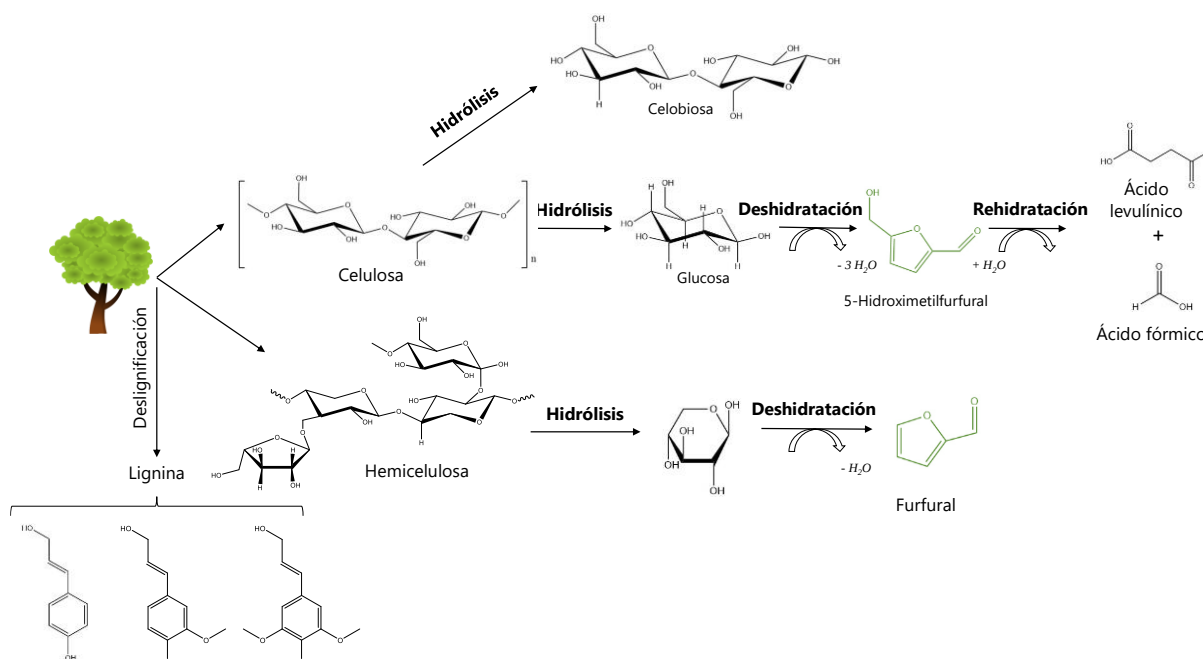


Figura 1.17. Esquema del proceso de hidrólisis de biomasa lignocelulósica

Por otro lado, cuando se utilizan ácidos de Brønsted, esta isomerización no tiene lugar y la deshidratación cíclica es termodinámicamente menos favorable. Además, la acidez de Brønsted promueve la degradación del HMF (ruptura del ciclo y rehidratación), obteniéndose productos como ácido levulínico (LA) y ácido fórmico (FA) [61]. Esto hace necesario un control estricto de las condiciones de reacción para minimizar la degradación indeseada y equilibrar la producción de los aldehídos de interés [26, 63]. La influencia de factores como la temperatura y el tiempo de reacción resulta clave para optimizar los rendimientos hacia HMF sin comprometer la estabilidad de los productos. En la **Tabla 1.1** se detallan las condiciones de operación y los tipos de catalizadores empleados en la hidrólisis de diferentes tipos de biomasa lignocelulósica encontrados en la literatura.

Tabla 1.1. Revisión de condiciones y resultados obtenidos en hidrólisis ácida de biomasa en la literatura.

Sustrato	Disolvente	Catalizador	T (°C)	t(h)	η glucosa (%)	η xilosa (%)	η HMF (%)	η FFL (%)	Ref.
MCC	H ₂ O	CP-SO ₃ H	120	10	93	-	-	-	[65]
Almidón	H ₂ O	CP-SO ₃ H	120	2	100	-	-	-	[65]
MCC	H ₂ O	H ₂ SO ₄	120	2	1	-	-	-	[65]
MCC molido	H ₂ O	Si ₃₃ C ₆₆ -823-SO ₃ H	150	24	50	-	0	-	[66]
MCC molido	H ₂ O	Sucrosa sulfonada	150	24	27	-	1	-	[66]
Hayas	H ₂ O	H ₂ SO ₄	145	1	76	74	2	6	[67]
Alamo	H ₂ O	H ₂ SO ₄	145	1	78	82	2	8	[67]
Algodón	[C ₂ mim]Cl	HCl	105	3	87	-	6	-	[68]
Maíz	[C ₂ mim]Cl	HCl	105	3	70	79	-	-	[68]
MCC	[C ₄ mim]Cl	H ₂ SO ₄	100	0.75	38	-	-	-	[69]
Eucalipto	[C ₄ mim]Cl/ChCl/oxálico	-	120	10	48	-	4	-	[70]
MCC de pino	[C ₄ mim]Cl/ChCl/oxálico	-	120	10	50	-	6	-	[70]
Maíz	[C ₄ mim]Cl/ChCl/oxálico	-	100	2	54	35	10	-	[70]
Maíz	ZnCl ₂ ·4·25H ₂ O	HCl	120	1	61	-	30	22	[71]
Algas	ZnCl ₂ ·4·25H ₂ O	HCl	120	1	49	-	35	29	[71]
Xilanos	ChCl/citríco/MIBK	AlCl ₃	140	0.5	-	-	-	69	[72]
Madera	ChCl/oxálico/MB	-	100	5	0	0	1	55	[73]

MCC, celulosa microcristalina; ChCl, Cloruro de colina
[C₂mim]Cl, 1-etil-3-metilimidazolium
[C₄mim]Cl, 1-butil-3-metilimidazolium

El uso combinado de zeolitas y ácidos minerales ha mostrado muy buenos resultados para transformar glucosa en HMF [62], pero su efecto en aquellas reacciones que combinan hidrólisis y deshidratación (como la obtención de HMF a partir del polímero) aún no ha sido estudiado, siendo una de las principales novedades de esta Tesis Doctoral.

A pesar de la gran cantidad de estudios en este campo, no se han abordado los efectos que conllevan los pretratamientos previos de la biomasa o de la celulosa en los resultados finales de la hidrólisis.

1.5.3. Oxidación de furfural para la obtención de ácido furoico

La producción industrial actual de FCA se basa en la reacción de Cannizzaro. Este método de síntesis está lejos de cumplir con los Principios de la Química Verde ya que se realiza en medios básicos fuertes, utilizado NaOH como catalizador básico de Brønsted, con todos los problemas derivados del uso de un catalizador homogéneo. El alcohol furfurílico (FOH) y el furoato de sodio se forman como resultado de esta reacción de desproporción por lo que esta ruta limita la selectividad máxima del FCA al 50% [74] (**Figura 1.18**).

La adición de un ácido es necesaria para neutralizar la solución y obtener ácido furóico, generalmente se emplea ácido sulfúrico y como resultado, se forma bisulfato de sodio. La temperatura óptima se encuentra en torno a 150 °C y debe controlarse meticulosamente porque la reacción de Cannizzaro es altamente exotérmica. La oligomerización del furfural en condiciones de Cannizzaro (pH muy alto, 150 °C) también es un inconveniente relevante [75].

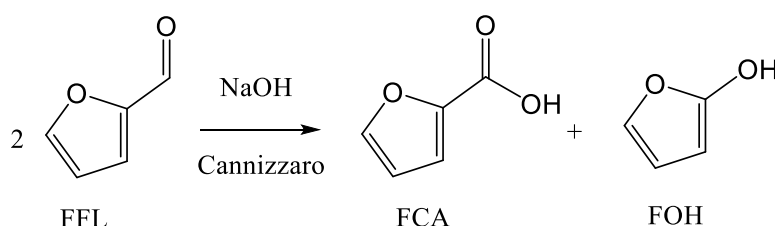


Figura 1.18. Esquema de la reacción de Cannizzaro

Como posibles alternativas al proceso industrial de síntesis de FCA, se han propuesto dos rutas prometedoras: la oxidación catalítica con peróxido de hidrógeno y la oxidación con aire u oxígeno.

Oxidación con peróxido de hidrógeno

El peróxido de hidrógeno es considerado un oxidante verde que no produce ningún residuo indeseado y que permite llevar a cabo la reacción de oxidación a temperaturas bajas ya que ambos reactivos (FFL y H_2O_2) se encuentran en fase líquida. La descomposición del H_2O_2 conduce a un proceso autocatalítico, aún más potenciado por los ácidos generados durante la oxidación (catálisis homogénea) [76]. Estas ventajas, así como el significativo crecimiento de la producción industrial de H_2O_2 en las últimas décadas y la posibilidad de generación *in situ* mediante métodos fotocatalíticos o electrocatalíticos justifican el creciente interés en la investigación de nuevos procesos de producción más verdes y nuevas aplicaciones de este oxidante industrial verde [77].

La oxidación del furfural utilizando H_2O_2 ha sido estudiada en la literatura, describiendo un complejo mecanismo de reacción caracterizado por una combinación de etapas paralelas y secuenciales (Figura 1.19). La literatura previa se ha centrado principalmente en la síntesis de ácido maleico [78, 79] y succínico [80], y, en menor medida, 2-(5H)-furanona (FN) [81] y ácido furóico [82].

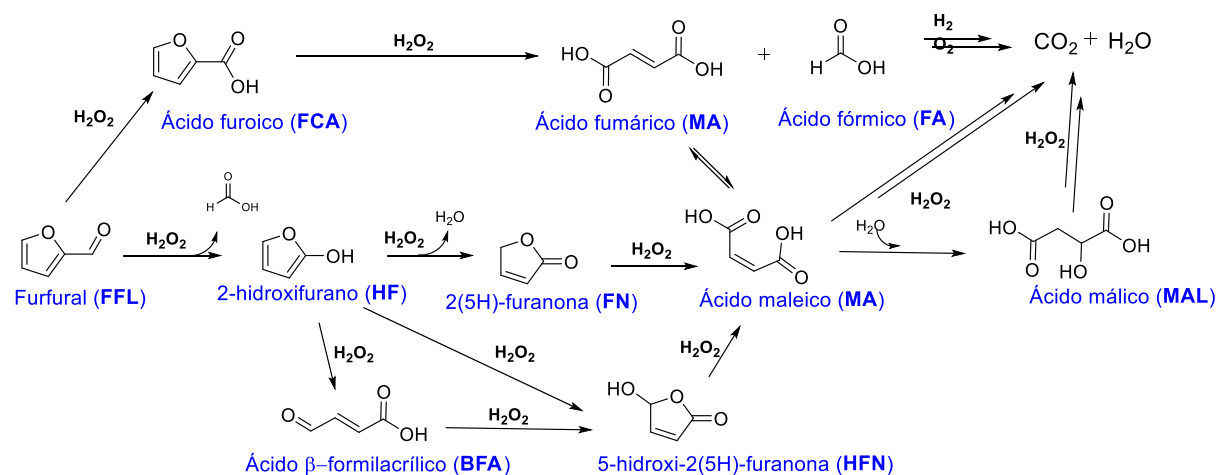


Figura 1.19. Esquema del mecanismo de reacción para la oxidación de FFL empleando H_2O_2

Entre los catalizadores basados en zeolitas, Palai *et al.* obtiene un rendimiento del 53% para producir ácido succínico al utilizar H_2O_2 como agente oxidante empleando como catalizador zeolita Sn-Beta. En este estudio se identificó la 2-(3H)-furanona como un intermedio clave. La zeolita Sn-Beta fue reutilizada durante varios ciclos, y los depósitos

orgánicos producidos se eliminan fácilmente calcinando el material. Sin embargo, en este estudio, la zeolita TS-1 fue más selectiva hacia la producción de ácido maleico (58%) [80].

Por otro lado, Murzin y colaboradores, en presencia de peróxido de hidrógeno, también tuvieron como producto principal el ácido succínico, mostrando una selectividad 50% frente a otros ácidos orgánicos como el FA y el MA utilizando como catalizador un ácido sulfónico soportado en un polímero fibroso (Smopex-101) [83]. En un estudio análogo con aluminosilicatos mesoporosos, Murzin y colaboradores obtienen un 19.5% de rendimiento de ácido succínico con 3MMAS. Con otros catalizadores como ZSM-5 y AlSi-SBA-15 tuvieron rendimientos de 17.8% y 16.4%, respectivamente [84].

En la mayoría de estos casos, se tienen selectividades inferiores al 5% de FCA, debido a la alta reactividad del H_2O_2 , a la coexistencia de diferentes rutas de reacción y a la naturaleza ácida de los catalizadores. En esta Tesis Doctoral, se evalúa otro enfoque mediante el uso de diferentes catalizadores con propiedades básicas para intentar favorecer la producción de FCA empleando una disolución tampón para minimizar la acción de los ácidos. Este nuevo enfoque no presenta bibliografía previa por lo que se considera un enfoque novedoso y prometedor. Se evalúan varios materiales como posibles catalizadores para la oxidación parcial del furfural utilizando H_2O_2 . Se utilizaron cuatro óxidos con diferentes propiedades catalíticas: TiO_2 y CeO_2 , que representan materiales redox, y MgAl y MgZr , como óxidos mixtos típicos con sitios ácido-básicos. Para mejorar la actividad catalítica, se prepararon materiales bifuncionales incorporando Au, Pd y Pt, tres de los metales más activos para oxidaciones [85, 86]. Estos cuatro soportes elegidos han sido propuestos previamente en diferentes estudios utilizando moléculas de plataforma lignocelulósica. Así, el CeO_2 ha sido probado con éxito en la oxidación selectiva de HMF, destacando el estrecho contacto entre el metal y el soporte obtenido, y el papel crucial de los defectos del soporte en la oxidación [87, 88]. El TiO_2 ha sido ampliamente utilizado como soporte para catalizadores bifuncionales en oxidaciones de HMF, revelando una fuerte interacción con las nanopartículas metálicas que altera las propiedades originales, aumentando el área de superficie y la concentración de sitios activos, lo que contribuye a una alta actividad, selectividad y estabilidad [89, 90]. También se consideraron óxidos mixtos derivados de hidrotalcitas (MgAl) y otros óxidos (incluidos Mg y Zr) para la oxidación de HMF [91, 92], principalmente utilizando Rh como fase activa.

A pesar de la escasa literatura sobre estos materiales en oxidaciones, se utilizan ampliamente en otras reacciones que involucran furfural, como la condensación [93] o la hidrogenación [94]. Por lo tanto, una buena actividad en esta reacción podría ampliar su versatilidad, aumentando el espectro de reacciones relacionadas con moléculas derivadas de biomasa que pueden catalizar.

Oxidación con aire u oxígeno

Al emplear oxígeno molecular para esta oxidación la selectividad hacia FCA es mucho más alta y el entorno es más fácilmente controlable debido a la oxidación selectiva. Sin embargo, esta reacción puede verse limitada por la transferencia de masa de oxígeno entre las fases gas-líquido, requiriendo condiciones más severas y necesitando catalizadores heterogéneos para la activación del oxígeno [95]. Para prevenir la desactivación catalítica inducida por ácidos, estas reacciones suelen llevarse a cabo en un medio básico fuerte (NaOH). La presencia de NaOH promueve las reacciones de Cannizzaro, mientras que el material sólido cataliza tanto la oxidación directa del aldehído como la oxidación secuencial del alcohol furfurílico a aldehído y del aldehído a ácido. Este enfoque requiere un control estricto de la temperatura para prevenir la oligomerización del FFL, que probablemente ocurra en condiciones muy básicas. Entre otros trabajos, Verdeguer y colaboradores muestran que se pueden lograr altas selectividades de FCA (92%) en presencia de un catalizador bimetálico PbPt [96]. Dowthwaite *et al.* obtiene rendimientos superiores al 93% con 1% AuPd/Mg(OH), un valor ligeramente superior al 76% obtenido con Au/MnO [97]. Sha y colaboradores logran altas selectividades (92%) hacia FCA con Ag₂O/CuO [98]. Un trabajo reciente propone diferentes catalizadores Au/Nb₂O₅, obteniendo conversiones moderadas (<50%) [99]. Como conclusión general de estos trabajos, se propone que Au es el metal noble óptimo para la oxidación de FFL, siendo más estable en un medio acuoso oxidante que Pt o Pd, y evitando rutas radicales de degradación de FFL, con el efecto positivo inherente en la selectividad y estabilidad del proceso [100].

A pesar de estos resultados prometedores, esta ruta sigue siendo contraria a los Principios de la Química Verde debido al uso de NaOH. Un enfoque alternativo considera trabajar en condiciones homogéneas sin base (pH no controlado). Varios trabajos obtienen mejoras claras concluyendo que la ausencia de NaOH debe ser compensada utilizando soportes básicos (MgO, CaO o materiales derivados de hidrotalcitas) para potenciar el

rendimiento catalítico [101, 102]. Como alternativa a este concepto, otros autores sugieren añadir un segundo metal (catalizadores bimetálicos) o desarrollar materiales tipo núcleo-corona, aumentando la complejidad del sistema catalítico [103, 104].

Sin embargo, existen dos inconvenientes relevantes relacionados con la estabilidad: la continua lixiviación del soporte debido a la formación de ácidos orgánicos y la desactivación de Au por la adsorción irreversible de ácido fórmico. Ambos problemas podrían ser minimizados utilizando una solución tampón que neutralice los ácidos obtenidos. Para lo cual no existe literatura previa sobre este enfoque, a pesar del equilibrio óptimo entre actividad, estabilidad y sostenibilidad que podría representar.

En esta Tesis Doctoral se aborda la oxidación parcial de FFL a FCA con O₂ utilizando catalizadores heterogéneos bifuncionales basados en Au como metal activo sobre dos soportes diferentes, MgAl y TiO₂. Además, se evitan las condiciones básicas fuertes sustituyéndolas por una disolución tampón.

1.5.4. Oxidación de 5-hidroximetilfurfural para la obtención de FDCA

La síntesis de FDCA a partir de HMF se ha estudiado principalmente a través de rutas electroquímicas y fotocatalíticas [105, 106], destacando el catalizador Au/TiO₂ como uno de los más prometedores debido a su alta actividad, estabilidad y selectividad debido a su capacidad para activar el oxígeno y adsorber HMF [107, 109]. En cuanto a la ruta termocatalítica, se ha investigado utilizando oxígeno molecular en presencia de catalizadores heterogéneos basados en Pt, Pd o Ru. Sin embargo, estos sistemas presentan una estabilidad o selectividad insuficiente [109-111]. En cambio, los catalizadores de oro, entre ellos el Au/TiO₂, son activos y más estables que el Pt y el Pd, alcanzando una selectividad casi total con conversiones de HMF superiores al 80% [112, 113].

La oxidación catalítica de HMF se define como un proceso de dos pasos, que sigue dos mecanismos diferentes según el grupo funcional que sufra la primera oxidación, transformándose en ácido 5-hidroximetil-2-furancarboxílico (HMFCa) en el caso del grupo aldehído, o 2,5-diformilfurano (DFF) si se trata del grupo hidroxilo (**Figura 1.20**).

La prevalencia de las rutas HMFCa o DFF está condicionada por diferentes factores, como el metal utilizado (Au promueve la ruta de HMFCa, mientras que otros metales nobles

favorecen la ruta de DFF [112]) y el disolvente empleado en la reacción (los disolventes orgánicos polares apróticos promueven la ruta de DFF, mientras que el agua y el entorno básico tienden a favorecer la ruta de HMFCa) [111, 114]. Además, las condiciones de temperatura y el pH pueden influir notablemente en la selectividad de cada ruta, al modificar la estabilidad y reactividad de los intermediarios formados, lo cual es clave para optimizar el proceso hacia el producto deseado.

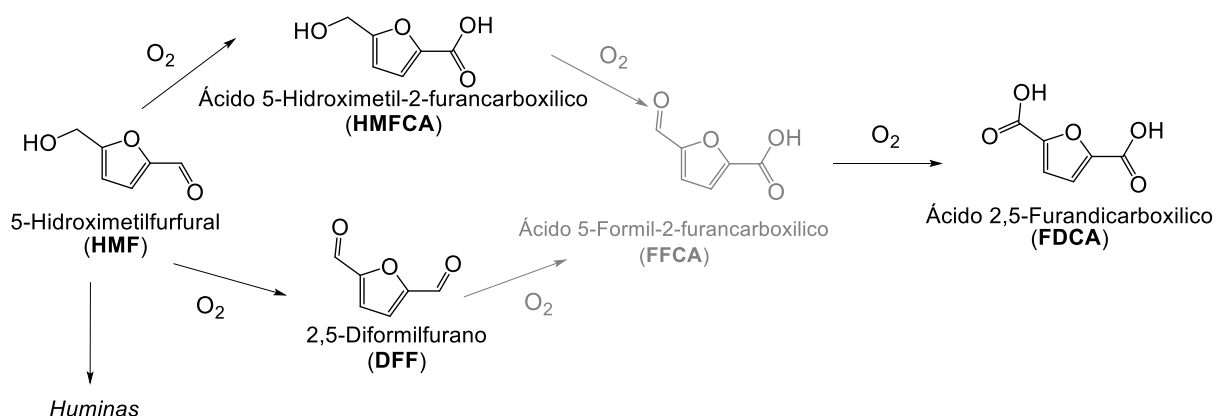


Figura 1.20. Mecanismo general de la oxidación de HMF para producir FDCA. Adaptado de [115].

Estudios previos demuestran los efectos positivos de la adición de bases homogéneas en el rendimiento de la oxidación de HMF, tanto activando el HMF para producir HMFCa [116, 117] como aumentando la solubilidad de los productos de reacción. Sin embargo, el entorno básico lleva a la formación de subproductos que no pueden ser fácilmente identificados, generalmente conocidos como huminas, con el subsiguiente efecto negativo en la selectividad y, en el caso de utilizar un catalizador heterogéneo, en la estabilidad [118]. A pesar de la influencia esperada de las condiciones de reacción en la formación de huminas, existe una brecha relevante en la literatura sobre estos aspectos. Los únicos estudios que abordan la prevención de huminas en la oxidación de HMF sugieren el uso de disolventes orgánicos [119], lo que plantea preocupaciones sobre la sostenibilidad del proceso.

La viabilidad económica es otro cuello de botella de esta ruta, ya que está restringida por la dificultad de aislar el HMF en la hidrólisis de biomasa ya que se trata de un aldehído inestable en un medio acuoso que tiende a descomponerse en ácido levulínico y ácido fórmico como productos finales [120, 121]. El desarrollo de un proceso en un solo paso que permita la oxidación *in situ* de HMF sería de gran interés, evitando su descomposición y reduciendo los costes totales del proceso. Sin embargo, las propiedades catalíticas opuestas

requeridas para la hidrólisis de azúcares (un proceso catalizado por ácido [122, 123]) y la oxidación de HMF (catálisis *redox* en condiciones alcalinas) hacen que este enfoque sea difícil. Algunos autores proponen un sistema bifásico donde la deshidratación de azúcares tiene lugar en medios acuosos y el HMF se extrae a una fase orgánica donde se lleva a cabo la oxidación, lo que implica desarrollos complejos de reactores y un control del proceso complicado [124]. Además, la mayoría de estos estudios proponen sistemas catalíticos complejos [125], o la oxidación se limita a producir DFF en lugar de FDCA [126].

En esta Tesis Doctoral se realiza un análisis integral del impacto de varias condiciones de reacción, incluyendo temperatura, presión de oxígeno, relación NaOH y concentración inicial de HMF, en la oxidación de HMF a FDCA sobre Au/TiO₂.

Por otro lado, la literatura explora extensamente la oxidación de FFL o HMF por separado, pero, como se mencionó anteriormente, en la reutilización directa de residuos lignocelulósicos, el HMF y el FFL se producen juntos generalmente en una relación de 1:2 [127, 128]. Además, ambos aldehídos tienen puntos de ebullición cercanos y polaridades similares, lo que complica su separación durante los procesos de extracción y purificación [129, 130]. El FFL, a pesar de ser producido a partir de la fracción minoritaria de hemicelulosa presente en la biomasa, es mucho más estable. Por el contrario, el HMF bajo condiciones de hidrólisis generalmente se descompone en LA y ácido fórmico. Este hecho abre una posible ruta inexplorada para la transformación conjunta de HMF y FFL mediante oxidación en ácidos furánicos como el FCA y FDCA utilizando un catalizador heterogéneo. Dado que, desde la perspectiva de la implementación industrial de la utilización de residuos de biomasa lignocelulósica, el estudio de la oxidación simultánea de FFL y HMF juega un papel clave, en esta Tesis Doctoral también se estudia la oxidación conjunta de ambos aldehídos a diferentes proporciones de NaOH utilizando Au/TiO₂.

1.5.5. Carboxilación de ácido furoico

En la búsqueda continua de métodos sostenibles y eficientes para la síntesis de compuestos orgánicos de alto valor añadido, los procesos de carboxilación se han convertido en una herramienta importante en la química moderna. Estos procesos permiten la introducción de grupos carboxilo (-COOH) en sustratos orgánicos, generando productos con

una amplia gama de aplicaciones industriales, que van desde la fabricación de polímeros hasta la síntesis de productos farmacéuticos.

La carboxilación también ha ganado interés en el contexto de la captura y utilización de dióxido de carbono (CO₂), un importante gas de efecto invernadero. Al convertir el CO₂ en compuestos orgánicos mediante procesos de carboxilación, no solo se puede mitigar su impacto ambiental al capturarlo, sino que también se puede transformar en productos químicos de valor añadido, contribuyendo así a la economía circular y a la reducción de la dependencia de recursos fósiles [131].

La incorporación de CO₂ en moléculas orgánicas se propuso por primera vez hace más de 100 años, como una aplicación particular de la Reacción de Grignard (**Figura 1.21**) [132]. Sin embargo, la disponibilidad limitada de los reactivos originales, así como su reactividad química y manipulación compleja, hacen que la fijación de CO₂ mediante este método sea poco atractiva para su implementación industrial.

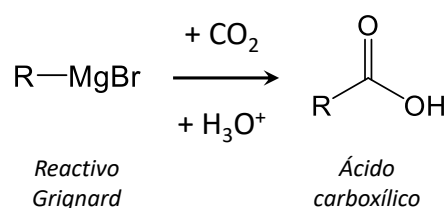


Figura 1.21. Esquema de la reacción de Grignard con CO₂

En este contexto, la producción de FDCA a partir de FCA es un proceso clave en la síntesis de polímeros de alto rendimiento y productos químicos bio-renovables. Este proceso puede llevarse a cabo mediante, carboxilación enzimática, carboxilación en discontinuo o carboxilación en lecho fijo.

Carboxilación enzimática de ácido furoico

La producción de FDCA a través de las rutas biocatalíticas ha ganado relevancia en los últimos años. La actividad carboxilativa de algunas enzimas de la familia de las descarboxilasas se identificó como una conclusión secundaria de los estudios de biodegradación [133, 134]. Estos resultados fueron el punto de partida para el estudio de

Payne y colaboradores, que demostró la capacidad de las enzimas HmF para carboxilar y producir FDCA [135].

Los resultados no son muy prometedores (0.3 % de rendimiento tras 12 h) y la reacción requiere un control estricto de las condiciones de reacción, ya que es muy sensible a la temperatura (50 °C es el óptimo), al pH (casi nula actividad fuera del rango neutro) y a la presión de CO₂ (se requieren 32 bar para observar resultados). Sin embargo, la sostenibilidad inherente de las reacciones enzimáticas, así como las posibilidades de recombinación e ingeniería de ADN, definen esta ruta biocatalítica como un campo prometedor para futuros estudios.

Carboxilación de ácido furoico en discontinuo

La carboxilación del FCA usando CO₂ y una base como reactivo se propuso por primera vez en 2016 [131]. Esta reacción es una aplicación particular de la síntesis de Kolbe-Schmitt, posiblemente la síntesis orgánica más antigua que usa CO₂, reportada en 1860. La reacción de Kolbe-Schmitt es una reacción en estado sólido que generalmente se lleva a cabo poniendo en contacto CO₂ con compuestos aromáticos activados por sustituyentes donadores de electrones, como cationes alcalinos. Aunque esta reacción se ha desarrollado para aromáticos de hidrocarburos, su mecanismo podría extenderse a otros compuestos heterocíclicos con características aromáticas, como piridinas o furano [136].

El trabajo pionero de Kanan y colaboradores [131] establece los pilares para estudios futuros, obteniendo conclusiones muy relevantes sobre el mecanismo y las condiciones de reacción. Investigaciones previas demuestran que los carbonatos pueden desprotonar enlaces C-H con valores de pKa de hasta 27 usando disolventes orgánicos y altas temperaturas [137, 138]. Considerando el alto pKa del C-H en la posición 5 del furano-2-carboxilato (≈ 35), la formación de FDCA mediante carboxilación con CO₂ es termodinámicamente desfavorable. Este inconveniente se soluciona mediante la formación inicial de un furoato metálico por la reacción del ácido furoico con una sal alcalina. Así, la reacción involucra dos sólidos y se lleva a cabo en condiciones sin disolvente. Estos sólidos deben fundirse para permitir la movilidad iónica necesaria para la correcta interacción entre los diferentes iones involucrados. Por lo tanto, el punto de fusión de los carbonatos es un

aspecto crítico para evitar la descomposición de los compuestos orgánicos (ácido furoico y productos intermedios de reacción o compuestos secundarios).

En este contexto, la mayoría de las sales alcalinas se descartan (temperaturas mucho mayores de 200 °C para fundirse), proponiendo Cs_2CO_3 como la mejor opción. Esta desprotonación da lugar a un átomo de carbono nucleofílico fuerte que podría reaccionar con el CO_2 débilmente electrófilo. Los mecanismos de reacción propuestos (**Figura 1.22**) resultan en un consumo neto de un equivalente de CO_2 por cada C-CO_2^- producido. Trabajar con una alta concentración de carbonatos garantiza la estabilización de la base conjugada de FDCA mediante apareamiento iónico. El FDCA se obtiene por protonación con HCl , mientras que el carbonato se recupera por electrodiálisis.

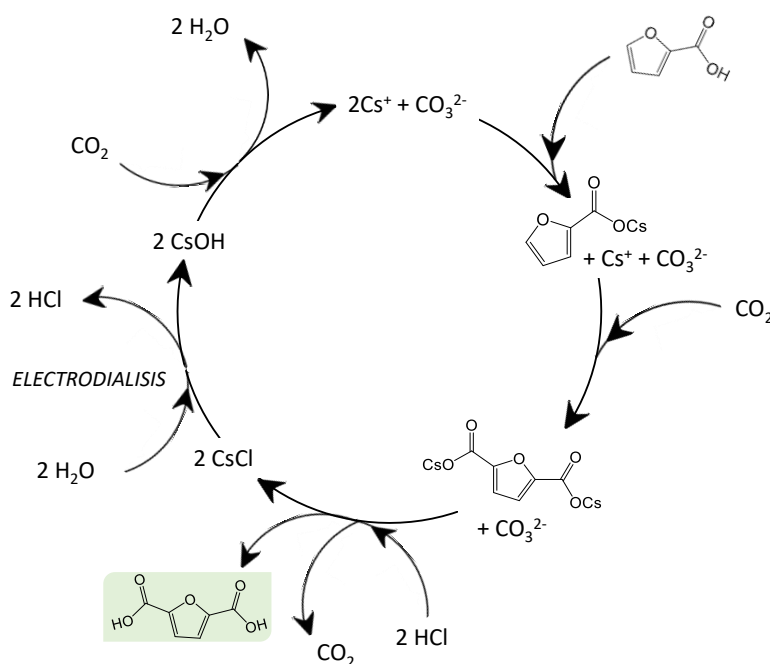


Figura 1.22. Esquema del mecanismo de reacción para obtener FDCA de manera selectiva mediante la carboxilación de ácido furoico y CO_2

Los mejores resultados propuestos en este trabajo corresponden a un rendimiento del 76% de FDCA^{2-} después de 12 h al calentar a 260 °C bajo un flujo de CO_2 de $40 \text{ mL} \cdot \text{min}^{-1}$, utilizando un 10% de exceso de Cs_2CO_3 . El acetato y el malonato se identifican como los principales productos de descomposición, limitando su producción al trabajar en un reactor por lotes presurizado (89% de rendimiento de FDCA^{2-} después de 7 h a 200 °C con 8 bar de CO_2) [131]. El papel limitado del Cs^+ (solo para reducir el punto de fusión de la sal) se corrobora

al sustituir este alcalino por sales de potasio (carbonato y carboxilato de potasio como co-sal). Empleando potasio se alcanzaron rendimientos superiores al 60% (por lo que Cs^+ no tiene un papel específico en el mecanismo), pero a temperaturas mucho más altas (320 °C) a las que las reacciones de descomposición no pueden ser evitadas. Como se esperaba debido al estado semilíquido del reactivo, la reacción ocurre en la interfaz gas-sólido. Los estudios de cambio de escala (de 1-10 a 100 mmol) resultan en rendimientos más bajos debido a la menor relación área superficial-volumen obtenida [131]. Estos resultados se justifican por problemas de transferencia del CO_2 hacia la sal y la eliminación del H_2O .

En un enfoque diferente, Nocito y colaboradores comparan la actividad de diferentes carbonatos más baratos, tratando de obtener más evidencias del mecanismo de reacción y los intermediarios involucrados, concluyendo que los carbonatos inorgánicos, especialmente aquellos con cationes monovalentes, son las especies más activas, observando una actividad creciente a medida que la densidad de carga en los cationes disminuye [139]. Este estudio también demuestra la correlación de actividad-punto de fusión de los carbonatos y propone el uso de difuroato de cobre ($\text{Cu}(\text{F})_2$) como una alternativa al Cs. Una comparación completa entre la carboxilación de $\text{Cu}(\text{F})_2$ y FCA demuestra un mayor rendimiento al usar el complejo de cobre (selectividad del 89% frente al 70%, después de 6 h a 220 °C, 6 MPa de CO_2).

Por otro lado, otros autores proponen la carboxilación de derivados del furano utilizando catálisis homogénea, empleando sales de Cu y Pd. Sin embargo, este enfoque se basa en la síntesis de FDCA a través de un proceso multietapa que involucra reacciones en cascada: bromación, esterificación, carboxilación e hidrólisis. Los principales avances en este tema se resumen en una revisión de Drault *et al.* [140].

Carboxilación de ácido furoico en lecho fijo

Tratando de mejorar estos resultados y garantizar la escalabilidad del proceso, Dick y colaboradores llevaron a cabo la carboxilación del furoato en un reactor de lecho fijo utilizando carbonato con diferentes mezclas de cationes. Se obtuvieron resultados muy prometedores a pequeña escala utilizando una mezcla en relación 2:1 de K^+/Cs^+ , alcanzando un 89 % de selectividad de FDCA después de 24 horas a 260-285°C con 8 bares de CO_2 [141]. Estos resultados son relevantes para mejorar la rentabilidad del proceso, ya que emplea K^+ cuyo precio es más asequible que el Cs^+ , a pesar de la recuperación teórica propuesta

mediante electrodiálisis. La reacción equivalente bajo presión estática no fue eficiente, produciendo una mezcla enriquecida en productos de descomposición. Se concluyó que la eliminación de H_2O suprime la descomposición y mejora el rendimiento de FDCA [131].

En base a estos resultados, Zhou y colaboradores propusieron en 2019 la producción directa de FDCA a partir de HMF y FFL [142]. Desarrollaron un catalizador metálico soportado (complejo de Co/Zn-lignina sobre un *single-atom* de Co soportado en carbono dopado con nitrógeno, Co SAs/N@C) que, en presencia de Cs_2CO_3 , produce la oxidación simultánea de HMF y FFL, obteniendo FDCA y FCA, respectivamente. Dado que el Cs_2CO_3 actúa como base facilitando la deshidrogenación oxidativa del furfural (no se observa reacción en ausencia de este carbonato), se utilizó el mismo sistema para transformar directamente el FCA en FDCA. Después de 36 horas a 260°C , se obtuvo un rendimiento del 71.1 % de FDCA a partir del producto de oxidación de FFL con una selectividad cercana al 83 %. Estos resultados muestran una alta similitud con aquellos optimizados al usar FCA puro.

Wang y colaboradores realizaron un estudio completo sobre las condiciones de reacción en reactores de flujo de lecho fijo, analizando el efecto de Cs_2CO_3 y la relación FA-Cs, la temperatura, el tiempo de reacción y la presión de CO_2 sobre el rendimiento de FDCA [143], obteniendo resultados prometedores en concordancia con los valores reportados por otros autores. En este estudio, se alcanza un máximo de producción de FDCA con una relación molar de 3:5 (FDCA: Cs_2CO_3) (50.6 % de rendimiento a 270°C después de 3 horas), mientras que con excesos superiores la actividad se reduce. Los resultados por encima de 270°C muestran una descomposición de FCA-Cs en acetato, malonato y otros compuestos. El tiempo de reacción también es relevante, ya que a tiempos prolongados se genera tanta agua en el sistema de reacción que afecta la disociación de los reactivos, mientras que parte del Cs_2CO_3 se disuelve. Ambos fenómenos dificultan la reacción, definiendo un máximo a 3 horas cuando la reacción se lleva a cabo a 280°C con 8 bares de CO_2 .

En resumen, diferentes estudios demuestran que la carboxilación heterogénea del ácido furúico es factible en ausencia de disolvente. Además de las ventajas mencionadas, esta reacción en fase sólido-gas se recomienda sobre la de fase líquida, ya que el uso de sales de metales alcalinos en lugar de catalizadores de metales de transición permite realizar la reacción utilizando CO_2 de pureza relativamente baja (calidad industrial), debido a que las sales de metales alcalinos son mucho más tolerantes a las impurezas que los metales de

transición. Sin embargo, según el estado actual de la técnica, el proceso debe mejorarse sustituyendo del cesio por un elemento más económico o regenerando completamente la sal carbonatada para garantizar su total reutilización. Además, para una producción a escala industrial más grande, se deben mejorar las cinéticas de reacción, así como el control de algunos parámetros, como la transferencia de materia. Este tema se ha desarrollado en **Capítulo 4.6** de esta Tesis Doctoral.

Sin embargo, a pesar de los avances significativos en los procesos de carboxilación y la captura de CO₂, aún persisten desafíos importantes que deben abordarse de cara a futuro. Estos incluyen la mejora de la selectividad hacia los productos deseados, la optimización de la eficiencia energética y la escalabilidad de los procesos a nivel industrial.

1.6. REFERENCIAS

- [1] Annual emissions of carbon dioxide (CO₂) by fuel or industry type (<https://ourworldindata.org/emissions-by-fuel>) Acceso: Agosto 2024
- [2] Per capita plastic waste (<https://ourworldindata.org/plastic-pollution>) Acceso: Agosto 2024
- [3] Objetivos de desarrollo sostenible (<https://www.un.org/sustainabledevelopment/es/2015/09/la-asamblea-general-adopta-la-agenda-2030-para-el-desarrollo-sostenible/>) Acceso: Agosto 2024
- [4] Naciones unidas: Acción por el clima (<https://www.un.org/es/climatechange/paris-agreement>) Acceso: Agosto 2024
- [5] Plásticos - Situación en 2022 (<https://plasticseurope.org/es/wp-content/uploads/sites/4/2023/02/PLASTICOS-SITUACION-2022-esp.pdf>) Acceso: Agosto 2024
- [6] COP 28: What Was Achieved and What Happens Next? (<https://unfccc.int/cop28/5-key-takeaways>) Acceso: Agosto 2024
- [7] Ollila, The Greenhouse Effect Definition, *Physical Science International Journal* **2019** (23) 1-5. <https://doi.org/10.9734/psij/2019/v23i230149>
- [8] El efecto invernadero – Un modelo sobre el cambio climático (<https://crea-portaldemedios.siemens-stiftung.org/vieworig/107114>). Acceso: Agosto 2024
- [9] K. Md. Zulfequar Ahmad, Causes and Consequences of Greenhouse Effect & Its Catastrophic Problems for Earth, *International Journal of Sustainability Management and Information Technologies* **2017** (3) 34-39. <https://doi.org/10.11648/j.ijsmi.20170304.11>
- [10] CO₂ and Greenhouse gas emissions (<https://ourworldindata.org/co2-and-greenhouse-gas-emissions>) Acceso: Julio 2024
- [11] Statistical Review of World Energy (<https://ourworldindata.org/grapher/oil-proved-reserves?time=latest>) Acceso: Agosto 2024

- [12] Annual plastic production between 1950 and 2019 and plastic use projections (<https://ourworldindata.org/grapher/global-plastic-production-projections>) Acceso:
- [13] Global Plastics Outlook - Plastics waste in 2019 by region, polymer and application (<https://ourworldindata.org/grapher/plastic-waste-polymer>) Acceso: Julio 2024
- [14] M.G. Kibria, N.I. Masuk, R. Safayet, H.Q. Nguyen, M. Mourshed, Plastic Waste: Challenges and Opportunities to Mitigate Pollution and Effective Management, *International Journal of Environmental Research* **2023** (17) 20. <https://doi.org/10.1007/s41742-023-00507-z>
- [15] T. Chaturvedi, A.I. Torres, G. Stephanopoulos, M.H. Thomsen, J.E. Schmidt, Developing Process Designs for Biorefineries—Definitions, Categories, and Unit Operations, *Energies* **2020** (13). <https://doi.org/10.3390/en13061493>
- [16] J.M.R. Gallo, M.A. Trapp, The chemical conversion of biomass-derived saccharides: An overview, *Journal of the Brazilian Chemical Society* **2017** (28) 1586-1607. <https://doi.org/10.21577/0103-5053.20170009>
- [17] Y. Duan, A. Tarafdar, V. Kumar, P. Ganeshan, K. Rajendran, B. Shekhar Giri, R. Gómez-García, H. Li, Z. Zhang, R. Sindhu, P. Binod, A. Pandey, M.J. Taherzadeh, S. Sarsaiya, A. Jain, M. Kumar Awasthi, Sustainable biorefinery approaches towards circular economy for conversion of biowaste to value added materials and future perspectives, *Fuel* **2022** (325) 124846. <https://doi.org/10.1016/j.fuel.2022.124846>
- [18] A.F. Ferreira, Biorefinery Concept, *Biorefineries: Targeting Energy, High Value Products and Waste Valorisation*, **2017**, 1-20. https://doi.org/10.1007/978-3-319-48288-0_1
- [19] E. de Jong, G. Jungmeier, Chapter 1 - Biorefinery Concepts in Comparison to Petrochemical Refineries, *Industrial Biorefineries & White Biotechnology*, **2015**, 3-33. <https://doi.org/10.1016/B978-0-444-63453-5.00001-X>
- [20] Gupta, T. Sahni, S. Kumar, Biorefineries: An Analogue to Petroleum Refineries, *Paddy Straw Waste for Biorefinery Applications*, **2024**, 1-29. https://doi.org/10.1007/978-981-99-8224-0_1
- [21] Bio-based and biodegradable plastics (<https://plasticseurope.org/sustainability/climate/circular-feedstocks/bio-based-and-biodegradable-plastics/>). Acceso: Agosto 2024
- [22] L. Dai, O. Karakas, Y. Cheng, K. Cobb, P. Chen, R. Ruan, A review on carbon materials production from plastic wastes, *Chemical Engineering Journal* **2023** (453) 139725. <https://doi.org/10.1016/j.cej.2022.139725>
- [23] G. Tang, W. Qiao, Z. Wang, F. Liu, L. He, M. Liu, W. Huang, H. Wu, C. Liu, Waste plastic to energy storage materials: a state-of-the-art review, *Green Chemistry* **2023** (25) 3738-3766. <http://doi.org/10.1039/D2GC04927A>
- [24] Q.-L. Li, R. Shan, S.-X. Wang, H.-R. Yuan, Y. Chen, Production of carbon nanotubes via catalytic pyrolysis of waste plastics over Ni/Al₂O₃ catalyst: The influence of plastic types, *Journal of Analytical and Applied Pyrolysis* **2024** (177) 106318. <https://doi.org/10.1016/j.jaap.2023.106318>
- [25] H. Zhou, Y. Ren, B. Yao, Z. Li, M. Xu, L. Ma, X. Kong, L. Zheng, M. Shao, H. Duan, Scalable electrosynthesis of commodity chemicals from biomass by suppressing non-Faradaic transformations, *Nature Communications* **2023** (14) 5621. <http://doi.org/10.1038/s41467-023-41497-y>

-
- [26] G. Gómez Millán, S. Hellsten, J. Llorca, R. Luque, H. Sixta, A.M. Balu, Recent Advances in the Catalytic Production of Platform Chemicals from Holocellulosic Biomass, *ChemCatChem* **2019** (11) 2022-2042. <https://doi.org/10.1002/cctc.201801843>
- [27] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Catalytic conversion of biomass to biofuels, *Green Chemistry* **2010** (12) 1493-1513. <https://doi.org/10.1039/C004654J>
- [28] K. Huang, W. Won, K.J. Barnett, Z.J. Brentzel, D.M. Alonso, G.W. Huber, J.A. Dumesic, C.T. Maravelias, Improving economics of lignocellulosic biofuels: An integrated strategy for coproducing 1,5-pentanediol and ethanol, *Applied Energy* **2018** (213) 585-594. <https://doi.org/10.1016/j.apenergy.2017.11.002>
- [29] F. Hussin, N.N. Hazani, M. Khalil, M.K. Aroua, Environmental life cycle assessment of biomass conversion using hydrothermal technology: A review, *Fuel Processing Technology* **2023** (246) 107747. <https://doi.org/10.1016/j.fuproc.2023.107747>
- [30] J. Rao, Z. Lv, G. Chen, F. Peng, Hemicellulose: Structure, chemical modification, and application, *Progress in Polymer Science* **2023** (140) 101675. <https://doi.org/10.1016/j.progpolymsci.2023.101675>
- [31] C. T, S. Das, P. Das, V.D. Veeranki, A.A. Prabhu, Re-routing the hemicellulosic fraction of lignocellulosic biomass toward value added products: A pragmatic bio refinery approach, *Journal of Environmental Chemical Engineering* **2024** (12) 111971. <https://doi.org/10.1016/j.jece.2024.111971>
- [32] R. Saini, A. Kaur, J.K. Saini, A.K. Patel, S. Varjani, C.-W. Chen, R.R. Singhanian, C.-D. Dong, Trends in Lignin Biotransformations for Bio-Based Products and Energy Applications, *BioEnergy Research* **2023** (16) 88-104. <https://doi.org/10.1007/s12155-022-10434-0>
- [33] C.G. Yoo, X. Meng, Y. Pu, A.J. Ragauskas, The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review, *Bioresource Technology* **2020** (301) 122784. <https://doi.org/10.1016/j.biortech.2020.122784>
- [34] R.-C. Sun, Lignin Source and Structural Characterization, *ChemSusChem* **2020** (13) 4385-4393. <https://doi.org/10.1002/cssc.202001324>
- [35] I.U. Haq, K. Qaisar, A. Nawaz, F. Akram, H. Mukhtar, X. Zohu, Y. Xu, M.W. Mumtaz, U. Rashid, W.A. Ghani, T.S. Choong, Advances in Valorization of Lignocellulosic Biomass towards Energy Generation, *Catalysts* **2021** (11). <https://doi.org/10.3390/catal11030309>
- [36] F. Güleç, A. Parthiban, G.C. Umenweke, U. Musa, O. Williams, Y. Mortezaei, H. Suk-Oh, E. Lester, C.C. Ogbaga, B. Gunes, J.A. Okolie, Progress in lignocellulosic biomass valorization for biofuels and value-added chemical production in the EU: A focus on thermochemical conversion processes, *Biofuels, Bioproducts and Biorefining* **2024** (18) 755-781. <https://doi.org/10.1002/bbb.2544>
- [37] Ö. Tezer, N. Karabağ, A. Öngen, C.Ö. Çolpan, A. Ayol, Biomass gasification for sustainable energy production: A review, *International Journal of Hydrogen Energy* **2022** (47) 15419-15433. <https://doi.org/10.1016/j.ijhydene.2022.02.158>
- [38] M. Ram, M.K. Mondal, Chapter 13 - Biomass gasification: a step toward cleaner fuel and chemicals, *Biofuels and Bioenergy*, **2022**, 253-276. <https://doi.org/10.1016/B978-0-323-85269-2.00008-3>
- [39] L.J.R. Nunes, Biomass gasification as an industrial process with effective proof-of-concept: A comprehensive review on technologies, processes and future developments, *Results in Engineering* **2022** (14) 100408. <https://doi.org/10.1016/j.rineng.2022.100408>
-

- [40] V. Dhyani, T. Bhaskar, A comprehensive review on the pyrolysis of lignocellulosic biomass, *Renewable Energy* **2018** (129) 695-716. <https://doi.org/10.1016/j.renene.2017.04.035>
- [41] A.N. Amenaghawon, C.L. Anyalewechi, C.O. Okieimen, H.S. Kusuma, Biomass pyrolysis technologies for value-added products: a state-of-the-art review, *Environment, Development and Sustainability* **2021** (23) 14324-14378. <https://doi.org/10.1007/s10668-021-01276-5>
- [42] Y. Zhang, Y. Liang, S. Li, Y. Yuan, D. Zhang, Y. Wu, H. Xie, K. Brindhadevi, A. Pugazhendhi, C. Xia, A review of biomass pyrolysis gas: Forming mechanisms, influencing parameters, and product application upgrades, *Fuel* **2023** (347) 128461. <https://doi.org/10.1016/j.fuel.2023.128461>
- [43] M. El Bast, N. Allam, Y. Abou Msallem, S. Awad, K. Loubar, A review on continuous biomass hydrothermal liquefaction systems: Process design and operating parameters effects on biocrude, *Journal of the Energy Institute* **2023** (108) 101260. <https://doi.org/10.1016/j.joei.2023.101260>
- [44] E. Ocampo, V.V. Beltrán, E.A. Gómez, L.A. Ríos, D. Ocampo, Hydrothermal liquefaction process: Review and trends, *Current Research in Green and Sustainable Chemistry* **2023** (7) 100382. <https://doi.org/10.1016/j.crgsc.2023.100382>
- [45] R. Agrawal, A. Verma, R.R. Singhania, S. Varjani, C. Di Dong, A. Kumar Patel, Current understanding of the inhibition factors and their mechanism of action for the lignocellulosic biomass hydrolysis, *Bioresource Technology* **2021** (332) 125042. <https://doi.org/10.1016/j.biortech.2021.125042>
- [46] T.H. Mokhothu, M.J. John, Review on hygroscopic aging of cellulose fibres and their biocomposites, *Carbohydrate Polymers* **2015** (131) 337-354. <https://doi.org/10.1016/j.carbpol.2015.06.027>
- [47] S. Kang, J. Fu, G. Zhang, From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis, *Renewable and Sustainable Energy Reviews* **2018** (94) 340-362. <https://doi.org/10.1016/j.rser.2018.06.016>
- [48] A.A. Vaidya, K.D. Murton, D.A. Smith, G. Dedual, A review on organosolv pretreatment of softwood with a focus on enzymatic hydrolysis of cellulose, *Biomass Conversion and Biorefinery* **2022** (12) 5427-5442. <http://doi.org/10.1007/s13399-022-02373-9>
- [49] C.A. Hubbell, A.J. Ragauskas, Effect of acid-chlorite delignification on cellulose degree of polymerization, *Bioresource Technology* **2010** (101) 7410-7415. <https://doi.org/10.1016/j.biortech.2010.04.029>
- [50] Z. Zhou, D. Liu, X. Zhao, Conversion of lignocellulose to biofuels and chemicals via sugar platform: An updated review on chemistry and mechanisms of acid hydrolysis of lignocellulose, *Renewable and Sustainable Energy Reviews* **2021** (146) 111169. <https://doi.org/10.1016/j.rser.2021.111169>
- [51] X. Shen, R. Sun, Recent advances in lignocellulose prior-fractionation for biomaterials, biochemicals, and bioenergy, *Carbohydrate Polymers* **2021** (261) 117884. <https://doi.org/10.1016/j.carbpol.2021.117884>
- [52] W. Schutyser, T. Renders, S. Van den Bosch, S.F. Koelewijn, G.T. Beckham, B.F. Sels, Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading, *Chemical Society Reviews* **2018** (47) 852-908. <http://doi.org/10.1039/C7CS00566K>
- [53] K. Świątek, S. Gaag, A. Klier, A. Kruse, J. Sauer, D. Steinbach, Acid Hydrolysis of Lignocellulosic Biomass: Sugars and Furfurals Formation, *Catalysts* **2020** (10). <https://doi.org/10.3390/catal10040437>

-
- [54] V. Oriez, J. Peydecastaing, P.-Y. Pontalier, Lignocellulosic Biomass Mild Alkaline Fractionation and Resulting Extract Purification Processes: Conditions, Yields, and Purities, *Clean Technologies* **2020** (2) 91-115. <https://doi.org/10.3390/cleantechnol2010007>
- [55] Y. Yu, J. Wu, X. Ren, A. Lau, H. Rezaei, M. Takada, X. Bi, S. Sokhansanj, Steam explosion of lignocellulosic biomass for multiple advanced bioenergy processes: A review, *Renewable and Sustainable Energy Reviews* **2022** (154) 111871. <https://doi.org/10.1016/j.rser.2021.111871>
- [56] H. Luo, E.P. Weeda, M. Alherech, C.W. Anson, S.D. Karlen, Y. Cui, C.E. Foster, S.S. Stahl, Oxidative Catalytic Fractionation of Lignocellulosic Biomass under Non-alkaline Conditions, *Journal of the American Chemical Society* **2021** (143) 15462-15470. <https://doi.org/10.1021/jacs.1c08635>
- [57] P. Paulsen Thoresen, H. Lange, U. Rova, P. Christakopoulos, L. Matsakas, Role and importance of solvents for the fractionation of lignocellulosic biomass, *Bioresource Technology* **2023** (369) 128447. <https://doi.org/10.1016/j.biortech.2022.128447>
- [58] M. Kabbour, R. Luque, Chapter 10 - Furfural as a platform chemical: From production to applications, *Biomass, Biofuels, Biochemicals*, **2020**, 283-297. <https://doi.org/10.1016/B978-0-444-64307-0.00010-X>
- [59] H. Xia, S. Xu, H. Hu, J. An, C. Li, Efficient conversion of 5-hydroxymethylfurfural to high-value chemicals by chemo- and bio-catalysis, *RSC Advances* **2018** (8) 30875-30886. <http://doi.org/10.1039/C8RA05308A>
- [60] E. Cousin, K. Namhaed, Y. Pérès, P. Cognet, M. Delmas, H. Hermansyah, M. Gozan, P.A. Alaba, M.K. Aroua, Towards efficient and greener processes for furfural production from biomass: A review of the recent trends, *Science of The Total Environment* **2022** (847) 157599. <https://doi.org/10.1016/j.scitotenv.2022.157599>
- [61] C. Moreau, R. Durand, A. Roux, D. Tichit, Isomerization of glucose into fructose in the presence of cation-exchanged zeolites and hydrotalcites, *Applied Catalysis A: General* **2000** (193) 257-264. [https://doi.org/10.1016/S0926-860X\(99\)00435-4](https://doi.org/10.1016/S0926-860X(99)00435-4)
- [62] Galadima, A. Masudi, O. Muraza, Conversion of cellulose to glucose and further transformation into fuels over solid acid catalysts: A mini review, *Microporous and Mesoporous Materials* **2022** (336) 111846. <https://doi.org/10.1016/j.micromeso.2022.111846>
- [63] D. Garcés, E. Díaz, S. Ordóñez, Aqueous Phase Conversion of Hexoses into 5-Hydroxymethylfurfural and Levulinic Acid in the Presence of Hydrochloric Acid: Mechanism and Kinetics, *Industrial & Engineering Chemistry Research* **2017** (56) 5221-5230. <https://doi.org/10.1021/acs.iecr.7b00952>
- [64] D. Garcés, L. Faba, E. Díaz, S. Ordóñez, Aqueous-Phase Transformation of Glucose into Hydroxymethylfurfural and Levulinic Acid by Combining Homogeneous and Heterogeneous Catalysis, *ChemSusChem* **2019** (12) 924-934. <https://doi.org/10.1002/cssc.201802315>
- [65] L. Shuai, X. Pan, Hydrolysis of cellulose by cellulase-mimetic solid catalyst, *Energy & Environmental Science* **2012** (5) 6889-6894. <https://doi.org/10.1039/C2EE03373A>
- [66] S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C.J. Gommers, B. Goderis, P.A. Jacobs, B.F. Sels, Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose, *Green Chemistry* **2010** (12) 1560-1563. <https://doi.org/10.1039/CoGC00235F>
- [67] M.D. Kaufman Rechulski, M. Källdström, U. Richter, F. Schüth, R. Rinaldi, Mechanocatalytic Depolymerization of Lignocellulose Performed on Hectogram and Kilogram Scales, *Industrial*
-

- & *Engineering Chemistry Research* **2015** (54) 4581-4592. <https://doi.org/10.1021/acs.iecr.5b00224>
- [68] J.B. Binder, R.T. Raines, Fermentable sugars by chemical hydrolysis of biomass, *Proceedings of the National Academy of Sciences* **2010** (107) 4516-4521. <https://doi.org/10.1073/pnas.0912073107>
- [69] C. Li, Z.K. Zhao, Efficient Acid-Catalyzed Hydrolysis of Cellulose in Ionic Liquid, *Advanced Synthesis & Catalysis* **2007** (349) 1847-1850. <https://doi.org/10.1002/adsc.200700259>
- [70] Bodachivskyi, U. Kuzhiumparambil, D. Bradley G. Williams, High Yielding Acid-Catalysed Hydrolysis of Cellulosic Polysaccharides and Native Biomass into Low Molecular Weight Sugars in Mixed Ionic Liquid Systems, *ChemistryOpen* **2019** (8) 1316-1324. <https://doi.org/10.1002/open.201900283>
- [71] Bodachivskyi, U. Kuzhiumparambil, D.B.G. Williams, The role of the molecular formula of ZnCl₂·nH₂O on its catalyst activity: a systematic study of zinc chloride hydrates in the catalytic valorisation of cellulosic biomass, *Catalysis Science & Technology* **2019** (9) 4693-4701. <https://doi.org/10.1039/C9CY00846B>
- [72] R. Brière, P. Loubet, E. Glogic, B. Estrine, S. Marinkovic, F. Jérôme, G. Sonnemann, Life cycle assessment of the production of surface-active alkyl polyglycosides from acid-assisted ball-milled wheat straw compared to the conventional production based on corn-starch, *Green Chemistry* **2018** (20) 2135-2141. <https://doi.org/10.1039/C7GC03189K>
- [73] Bodachivskyi, U. Kuzhiumparambil, D.B.G. Williams, Catalytic Valorization of Native Biomass in a Deep Eutectic Solvent: A Systematic Approach toward High-Yielding Reactions of Polysaccharides, *ACS Sustainable Chemistry & Engineering* **2020** (8) 678-685. <https://doi.org/10.1021/acssuschemeng.9b06528>
- [74] F. Deng, A.S. Amarasekara, Catalytic upgrading of biomass derived furans, *Industrial Crops and Products* **2021** (159) 113055. <https://doi.org/10.1016/j.indcrop.2020.113055>
- [75] Sádaba, M. Ojeda, R. Mariscal, J.L.G. Fierro, M.L. Granados, Catalytic and structural properties of co-precipitated Mg–Zr mixed oxides for furfural valorization via aqueous aldol condensation with acetone, *Applied Catalysis B: Environmental* **2011** (101) 638-648. <https://doi.org/10.1016/j.apcatb.2010.11.005>
- [76] S. Eaimsumang, S. Wongkasemjit, S. Pongstabodee, S.M. Smith, S. Ratanawilai, N. Chollacoop, A. Luengnaruemitchai, Effect of synthesis time on morphology of CeO₂ nanoparticles and Au/CeO₂ and their activity in oxidative steam reforming of methanol, *Journal of Rare Earths* **2019** (37) 819-828. <https://doi.org/10.1016/j.jre.2018.11.010>
- [77] R. Ciriminna, L. Albanese, F. Meneguzzo, M. Pagliaro, Hydrogen Peroxide: A Key Chemical for Today's Sustainable Development, *ChemSusChem* **2016** (9) 3374-3381. <https://doi.org/10.1002/cssc.201600895>
- [78] D.Y. Murzin, E. Bertrand, P. Tolvanen, S. Devyatkov, J. Rahkila, K. Eränen, J. Wärnå, T. Salmi, Heterogeneous Catalytic Oxidation of Furfural with Hydrogen Peroxide over Sulfated Zirconia, *Industrial & Engineering Chemistry Research* **2020** (59) 13516-13527. <https://doi.org/10.1021/acs.iecr.oco2566>
- [79] Q. Yu, R. Bai, F. Wang, Q. Zhang, Y. Sun, Y. Zhang, L. Qin, Z. Wang, Z. Yuan, A sustainable system for maleic acid synthesis from biomass-derived sugar, *Journal of Chemical Technology & Biotechnology* **2020** (95) 751-757. <https://doi.org/10.1002/jctb.6260>
- [80] Y.N. Palai, A. Shrotri, A. Fukuoka, Selective Oxidation of Furfural to Succinic Acid over Lewis Acidic Sn-Beta, *ACS Catalysis* **2022** (12) 3534-3542. <https://doi.org/10.1021/acscatal.1c05348>

-
- [81] V. Zvarych, A. Nakonechna, M. Marchenko, O. Khudiyi, V. Lubenets, L. Khuda, O. Kushniryk, V. Novikov, Hydrogen Peroxide Oxygenation of Furan-2-carbaldehyde via an Easy, Green Method, *Journal of Agricultural and Food Chemistry* **2019** (67) 3114-3117. <http://doi.org/10.1021/acs.jafc.8b06284>
- [82] J. Thuriot-Roukos, R. Khadraoui, S. Paul, R. Wojcieszak, Raman Spectroscopy Applied to Monitor Furfural Liquid-Phase Oxidation Catalyzed by Supported Gold Nanoparticles, *ACS Omega* **2020** (5) 14283-14290. <http://doi.org/10.1021/acsomega.0c00091>
- [83] D.Y. Murzin, F. Saleem, J. Warnå, T. Salmi, Kinetic modelling of heterogeneous catalytic oxidation of furfural with hydrogen peroxide to succinic acid, *Chemical Engineering Journal* **2020** (382) 122811. <https://doi.org/10.1016/j.cej.2019.122811>
- [84] N.D. Shcherban, R.Y. Barakov, S.A. Sergiienko, K. Eränen, J. Wärnå, D.Y. Murzin, Furfural Oxidation with Hydrogen Peroxide Over ZSM-5 Based Micro-Mesoporous Aluminosilicates, *Catalysis Letters* **2022** (152) 2920-2932. <https://doi.org/10.1007/s10562-021-03899-9>
- [85] C. Ampelli, G. Centi, C. Genovese, G. Papanikolaou, R. Pizzi, S. Perathoner, R.J. van Putten, K.J.P. Schouten, A.C. Gluhoi, J.C. van der Waal, A Comparative Catalyst Evaluation for the Selective Oxidative Esterification of Furfural, *Topics in Catalysis* **2016** (59) 1659-1667. <https://doi.org/10.1007/s11244-016-0675-y>
- [86] T. Pirmohamed, J.M. Dowding, S. Singh, B. Wasserman, E. Heckert, A.S. Karakoti, J.E.S. King, S. Seal, W.T. Self, Nanoceria exhibit redox state-dependent catalase mimetic activity, *Chemical Communications* **2010** (46) 2736-2738. <https://doi.org/10.1039/B922024K>
- [87] Lolli, R. Amadori, C. Lucarelli, M.G. Cutrufello, E. Rombi, F. Cavani, S. Albonetti, Hard-template preparation of Au/CeO₂ mesostructured catalysts and their activity for the selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, *Microporous and Mesoporous Materials* **2016** (226) 466-475. <https://doi.org/10.1016/j.micromeso.2016.02.014>
- [88] O. Casanova, S. Iborra, A. Corma, Biomass into Chemicals: Aerobic Oxidation of 5-Hydroxymethyl-2-furfural into 2,5-Furandicarboxylic Acid with Gold Nanoparticle Catalysts, *ChemSusChem* **2009** (2) 1138-1144. <https://doi.org/10.1002/cssc.200900137>
- [89] T. Xie, S. Yue, T. Su, M. Song, W. Xu, Y. Xiao, Z. Yang, C. Len, D. Zhao, High selective oxidation of 5-hydroxymethyl furfural to 5-hydroxymethyl-2-furan carboxylic acid using Ag-TiO₂, *Molecular Catalysis* **2022** (525) 112353. <https://doi.org/10.1016/j.mcat.2022.112353>
- [90] Y. Cao, X. Liu, S. Iqbal, P.J. Miedziak, J.K. Edwards, R.D. Armstrong, D.J. Morgan, J. Wang, G.J. Hutchings, Base-free oxidation of glucose to gluconic acid using supported gold catalysts, *Catalysis Science & Technology* **2016** (6) 107-117. <https://doi.org/10.1039/C5CY00732A>
- [91] Y.Y. Gorbaney, S. Kegnæs, A. Riisager, Effect of Support in Heterogeneous Ruthenium Catalysts Used for the Selective Aerobic Oxidation of HMF in Water, *Topics in Catalysis* **2011** (54) 1318. <https://doi.org/10.1007/s11244-011-9754-2>
- [92] F. Nocito, M. Ventura, M. Aresta, A. Dibenedetto, Selective Oxidation of 5-(Hydroxymethyl)furfural to DFF Using Water as Solvent and Oxygen as Oxidant with Earth-Crust-Abundant Mixed Oxides, *ACS Omega* **2018** (3) 18724-18729. <https://doi.org/10.1021/acsomega.8b02839>
- [93] L. Faba, E. Díaz, S. Ordóñez, Aqueous-phase furfural-acetone aldol condensation over basic mixed oxides, *Applied Catalysis B: Environmental* **2012** (113-114) 201-211. <https://doi.org/10.1016/j.apcatb.2011.11.039>
- [94] R. López-Asensio, J.A. Cecilia-Buenestado, C. Herrera-Delgado, M.Á. Larrubia-Vargas, C. García-Sancho, P.J. Maireles-Torres, R. Moreno-Tost, Mixed Oxides Derived from
-

- Hydrotalcites Mg/Al Active in the Catalytic Transfer Hydrogenation of Furfural to Furfuryl Alcohol, *Catalysts* **2023** (13). <https://doi.org/10.3390/catal13010045>
- [95] M. Douthwaite, X. Huang, S. Iqbal, P.J. Miedziak, G.L. Brett, S.A. Kondrat, J.K. Edwards, M. Sankar, D.W. Knight, D. Bethell, G.J. Hutchings, The controlled catalytic oxidation of furfural to furoic acid using AuPd/Mg(OH)₂, *Catalysis Science & Technology* **2017** (7) 5284-5293. <https://doi.org/10.1039/C7CY01025G>
- [96] P. Verdeguer, N. Merat, L. Rigal, A. Gaset, Optimization of experimental conditions for the catalytic oxidation of furfural to furoic acid, *Journal of Chemical Technology & Biotechnology* **1994** (61) 97-102. <https://doi.org/10.1002/jctb.280610203>
- [97] C.P. Ferraz, A.G. Da Silva, T.S. Rodrigues, P.H. Camargo, S. Paul, R. Wojcieszak, Furfural Oxidation on Gold Supported on MnO₂: Influence of the Support Structure on the Catalytic Performances, *Applied Sciences* **2018** (8). <https://doi.org/10.3390/app8081246>
- [98] Q. Tian, D. Shi, Y. Sha, CuO and Ag₂O/CuO Catalyzed Oxidation of Aldehydes to the Corresponding Carboxylic Acids by Molecular Oxygen, *Molecules* **2008** (13) 948-957. <http://doi.org/10.3390/molecules13040948>
- [99] M. Lin, C. Mochizuki, T. Ishida, Y. Zhang, M. Haruta, T. Murayama, Effect of poly(N-vinylpyrrolidone) ligand on catalytic activities of Au nanoparticles supported on Nb₂O₅ for CO oxidation and furfural oxidation, *Catalysis Today* **2023** (410) 143-149. <https://doi.org/10.1016/j.cattod.2022.03.034>
- [100] R. Wojcieszak, C.P. Ferraz, J. Sha, S. Houda, L.M. Rossi, S. Paul, Advances in Base-Free Oxidation of Bio-Based Compounds on Supported Gold Catalysts, *Catalysts* **2017** (7). <http://doi.org/10.3390/catal7110352>
- [101] Z. Ren, Y. Yang, S. Wang, X. Li, H. Feng, L. Wang, Y. Li, X. Zhang, M. Wei, Pt atomic clusters catalysts with local charge transfer towards selective oxidation of furfural, *Applied Catalysis B: Environmental* **2021** (295) 120290. <https://doi.org/10.1016/j.apcatb.2021.120290>
- [102] C.P. Ferraz, S. Navarro-Jaén, L.M. Rossi, F. Dumeignil, M.N. Ghazzal, R. Wojcieszak, Enhancing the activity of gold supported catalysts by oxide coating: towards efficient oxidations, *Green Chemistry* **2021** (23) 8453-8457. <https://doi.org/10.1039/D1GC02889H>
- [103] Y. Wu, Z. Guo, C. Sun, Y. Yang, Q. Li, Integrated experimental and DFT analysis on the efficient and green upgrading of agroforestry biomass derived furan chemicals over NiMoO₄-CNTs-CF electrocatalyst with bi-catalytic sites, *Industrial Crops and Products* **2022** (187) 115492. <https://doi.org/10.1016/j.indcrop.2022.115492>
- [104] F. Nocito, N. Ditaranto, D. Linsalata, M. Naschetti, R. Comparelli, M. Aresta, A. Dibenedetto, Selective Aerobic Oxidation of Furfural into Furoic Acid over a Highly Recyclable MnO₂@CeO₂ Core-Shell Oxide: The Role of the Morphology of the Catalyst, *ACS Sustainable Chemistry & Engineering* **2022** (10) 8615-8623. <https://doi.org/10.1021/acssuschemeng.2c02341>
- [105] H. Luo, J. Barrio, N. Sunny, A. Li, L. Steier, N. Shah, I.E.L. Stephens, M.-M. Titirici, Progress and Perspectives in Photo- and Electrochemical-Oxidation of Biomass for Sustainable Chemicals and Hydrogen Production, *Advanced Energy Materials* **2021** (11) 2101180. <https://doi.org/10.1002/aenm.202101180>
- [106] C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural, *Chemical Society Reviews* **2020** (49) 4273-4306. <https://doi.org/10.1039/DoCS00041H>

- [107] W. Yu, Y. Wang, H. Zhang, Q. Zhang, S. Wang, Z. Liu, G. Yang, F. Peng, Mechanistic Insights into the Selective Oxidation of 5-Hydroxymethylfurfural over Au/TiO₂ Catalysts under Photoexcited and Dark States, *ACS Sustainable Chemistry & Engineering* **2023** (11) 13116-13125. <https://doi.org/10.1021/acssuschemeng.3c03289>
- [108] H. Li, S. Wang, M. Wang, Y. Gao, J. Tang, S. Zhao, H. Chi, P. Zhang, J. Qu, F. Fan, C. Li, Enhancement of Plasmon-Induced Photoelectrocatalytic Water Oxidation over Au/TiO₂ with Lithium Intercalation, *Angewandte Chemie International Edition* **2022** (61) e202204272. <https://doi.org/10.1002/anie.202204272>
- [109] X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, Y. Wang, Base-Free Aerobic Oxidation of 5-Hydroxymethyl-furfural to 2,5-Furandicarboxylic Acid in Water Catalyzed by Functionalized Carbon Nanotube-Supported Au-Pd Alloy Nanoparticles, *ACS Catalysis* **2014** (4) 2175-2185. <https://doi.org/10.1021/cs5003096>
- [110] S. Hameed, L. Lin, A. Wang, W. Luo, Recent Developments in Metal-Based Catalysts for the Catalytic Aerobic Oxidation of 5-Hydroxymethyl-Furfural to 2,5-Furandicarboxylic Acid, *Catalysts* **2020** (10). <https://doi.org/10.3390/catal10010120>
- [111] P. Verdeguer, N. Merat, A. Gaset, Oxydation catalytique du HMF en acide 2,5-furane dicarboxylique, *Journal of Molecular Catalysis* **1993** (85) 327-344. [https://doi.org/10.1016/0304-5102\(93\)80059-4](https://doi.org/10.1016/0304-5102(93)80059-4)
- [112] Villa, M. Schiavoni, S. Campisi, G.M. Veith, L. Prati, Pd-modified Au on Carbon as an Effective and Durable Catalyst for the Direct Oxidation of HMF to 2,5-Furandicarboxylic Acid, *ChemSusChem* **2013** (6) 609-612. <https://doi.org/10.1002/cssc.201200778>
- [113] C.A. Antonyraj, N.T.T. Huynh, S.-K. Park, S. Shin, Y.J. Kim, S. Kim, K.-Y. Lee, J.K. Cho, Basic anion-exchange resin (AER)-supported Au-Pd alloy nanoparticles for the oxidation of 5-hydroxymethyl-2-furfural (HMF) into 2,5-furan dicarboxylic acid (FDCA), *Applied Catalysis A: General* **2017** (547) 230-236. <https://doi.org/10.1016/j.apcata.2017.09.012>
- [114] L. Yu, H. Chen, Z. Wen, M. Jin, Z. Ma, X. Ma, Y. Sang, M. Chen, Y. Li, Highly selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over an α -MnO₂ catalyst, *Catalysis Today* **2021** (367) 9-15. <https://doi.org/10.1016/j.cattod.2020.10.037>
- [115] Z. Li, L. Zhao, B. Li, S. Bian, J. Wang, H. Zhang, C. Zhao, Base metal catalyzed oxidation of 5-hydroxy-methyl-furfural to 2,5-furan-dicarboxylic acid: A review, *Catalysis Today* **2023** (408) 64-72. <https://doi.org/10.1016/j.cattod.2022.09.002>
- [116] B.N. Zope, D.D. Hibbitts, M. Neurock, R.J. Davis, Reactivity of the Gold/Water Interface During Selective Oxidation Catalysis, *Science* **2010** (330) 74-78. <https://doi.org/10.1126/science.1195055>
- [117] T. Mallat, A. Baiker, Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts, *Chemical Reviews* **2004** (104) 3037-3058. <https://doi.org/10.1021/cr0200116>
- [118] D. Yan, J. Xin, Q. Zhao, K. Gao, X. Lu, G. Wang, S. Zhang, Fe-Zr-O catalyzed base-free aerobic oxidation of 5-HMF to 2,5-FDCA as a bio-based polyester monomer, *Catalysis Science & Technology* **2018** (8) 164-175. <https://doi.org/10.1039/C7CY01704A>
- [119] S. Liu, Y. Zhu, Y. Liao, H. Wang, Q. Liu, L. Ma, C. Wang, Advances in understanding the humins: Formation, prevention and application, *Applications in Energy and Combustion Science* **2022** (10) 100062. <https://doi.org/10.1016/j.jaecs.2022.100062>
- [120] P. Rapado, D. Garcés, L. Faba, S. Ordóñez, Zeolite-assisted acid hydrolysis of cellulose: Optimization of reaction conditions and chemical pretreatments for enhancing HMF yields,

- Industrial Crops and Products* **2024** (212) 118309. <https://doi.org/10.1016/j.indcrop.2024.118309>
- [121] R. Wojcieszak, I. Itabaiana, Engineering the future: Perspectives in the 2,5-furandicarboxylic acid synthesis, *Catalysis Today* **2020** (354) 211-217. <https://doi.org/10.1016/j.cattod.2019.05.071>
- [122] Q.N.B. Nguyen, H.A.N. Le, P.D. Ly, H.B. Phan, P.H. Tran, One-step synthesis of 2,5-diformylfuran from monosaccharides by using lanthanum(iii) triflate, sulfur, and DMSO, *Chemical Communications* **2020** (56) 13005-13008. <https://doi.org/10.1039/DoCC05582D>
- [123] W. Wei, G. Lyu, W. Jiang, Z. Chen, S. Wu, High-efficiency synthesis of 5-hydroxymethylfurfural and 2,5-diformylfuran from fructose over magnetic separable catalysts, *Journal of Colloid and Interface Science* **2021** (602) 146-158. <https://doi.org/10.1016/j.jcis.2021.05.161>
- [124] G. Yi, S.P. Teong, Y. Zhang, The Direct Conversion of Sugars into 2,5-Furandicarboxylic Acid in a Triphasic System, *ChemSusChem* **2015** (8) 1151-1155. <https://doi.org/10.1002/cssc.201500118>
- [125] F. Wang, L. Jiang, J. Wang, Z. Zhang, Catalytic Conversion of Fructose and 5-Hydroxymethylfurfural into 2,5-Diformylfuran over SBA-15 Supported Ruthenium Catalysts, *Energy & Fuels* **2016** (30) 5885-5892. <https://doi.org/10.1021/acs.energyfuels.6b01148>
- [126] Z. Yang, W. Qi, R. Su, Z. He, 3D Flower-like Micro/Nano Ce–Mo Composite Oxides as Effective Bifunctional Catalysts for One-Pot Conversion of Fructose to 2,5-Diformylfuran, *ACS Sustainable Chemistry & Engineering* **2017** (5) 4179-4187. <https://doi.org/10.1021/acssuschemeng.7b00175>
- [127] D. Steinbach, A. Kruse, J. Sauer, Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production- A review, *Biomass Conversion and Biorefinery* **2017** (7) 247-274. <https://doi.org/10.1007/s13399-017-0243-0>
- [128] Y. Zhao, K. Lu, H. Xu, L. Zhu, S. Wang, A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion, *Renewable and Sustainable Energy Reviews* **2021** (139) 110706. <https://doi.org/10.1016/j.rser.2021.110706>
- [129] S.P. Verevkin, V.N. Emel'yanenko, E.N. Stepurko, R.V. Ralys, D.H. Zaitsau, A. Stark, Biomass-Derived Platform Chemicals: Thermodynamic Studies on the Conversion of 5-Hydroxymethylfurfural into Bulk Intermediates, *Industrial & Engineering Chemistry Research* **2009** (48) 10087-10093. <https://doi.org/10.1021/ie901012g>
- [130] V.N. Emel'yanenko, A. Dabrowska, M.O. Hertel, H. Scheuren, K. Sommer, Vapor Pressures, Enthalpies of Vaporization, and Limiting Activity Coefficients in Water at 100 °C of 2-Furaldehyde, Benzaldehyde, Phenylethanal, and 2-Phenylethanol, *Journal of Chemical & Engineering Data* **2007** (52) 468-471. <https://doi.org/10.1021/jeo60406c>
- [131] Banerjee, G.R. Dick, T. Yoshino, M.W. Kanan, Carbon dioxide utilization via carbonate-promoted C–H carboxylation, *Nature* **2016** (531) 215-219. <https://doi.org/10.1038/nature17185>
- [132] D.M. Dalton, T. Rovis, C–H carboxylation takes gold, *Nature Chemistry* **2010** (2) 710-711. <https://doi.org/10.1038/nchem.815>
- [133] M.M. Cajnko, U. Novak, M. Grilc, B. Likozar, Enzymatic conversion reactions of 5-hydroxymethylfurfural (HMF) to bio-based 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA) with air: mechanisms, pathways and synthesis selectivity, *Biotechnology for Biofuels* **2020** (13) 66. <https://doi.org/10.1186/s13068-020-01705-z>

- [134] B. Lupa, D. Lyon, M.D. Gibbs, R.A. Reeves, J. Wiegel, Distribution of genes encoding the microbial non-oxidative reversible hydroxyarylic acid decarboxylases/phenol carboxylases, *Genomics* **2005** (86) 342-351. <https://doi.org/10.1016/j.ygeno.2005.05.002>
- [135] K.A.P. Payne, S.A. Marshall, K. Fisher, M.J. Cliff, D.M. Cannas, C. Yan, D.J. Heyes, D.A. Parker, I. Larrosa, D. Leys, Enzymatic Carboxylation of 2-Furoic Acid Yields 2,5-Furandicarboxylic Acid (FDCA), *ACS Catalysis* **2019** (9) 2854-2865. <https://doi.org/10.1021/acscatal.8bo4862>
- [136] J.A. Gibson, W. Kynaston, A.S. Lindsey, The infrared spectra of some pyridones and quinolones and their behaviour in the Kolbe–Schmitt reaction, *Journal of the Chemical Society (Resumed)* **1955** 4340-4344. <https://doi.org/10.1039/JR9550004340>
- [137] Y. Dingyi, Z. Yugen, The direct carboxylation of terminal alkynes with carbon dioxide, *Green Chemistry* **2011** (13) 1275-1279. <https://doi.org/10.1039/CoGC00819B>
- [138] K. Kudo, M. Shima, Y. Kume, F. Ikoma, S. Mori, N. Sugita, Carboxylation of Cesium 2-Naphthoate in the Alkali Metal Molten Salts of Carbonate and Formate with CO₂ under High Pressure, *Journal of the Japan Petroleum Institute* **1995** (38) 40-47. <https://doi.org/10.1627/jpi1958.38.40>
- [139] F. Nocito, N. Ditaranto, A. Dibenedetto, Valorization of C₅ polyols by direct carboxylation to FDCA: Synthesis and characterization of a key intermediate and role of carbon dioxide, *Journal of CO₂ Utilization* **2019** (32) 170-177. <https://doi.org/10.1016/j.jcou.2019.04.013>
- [140] F. Drault, Y. Snoussi, S. Paul, I. Itabaiana Jr, R. Wojcieszak, Recent Advances in Carboxylation of Furoic Acid into 2,5-Furandicarboxylic Acid: Pathways towards Bio-Based Polymers, *ChemSusChem* **2020** (13) 5164-5172. <https://doi.org/10.1002/cssc.202001393>
- [141] G.R. Dick, A.D. Frankhouser, A. Banerjee, M.W. Kanan, A scalable carboxylation route to furan-2,5-dicarboxylic acid, *Green Chemistry* **2017** (19) 2966-2972. <https://doi.org/10.1039/C7GC01059A>
- [142] H. Zhou, H. Xu, X. Wang, Y. Liu, Convergent production of 2,5-furandicarboxylic acid from biomass and CO₂, *Green Chemistry* **2019** (21) 2923-2927. <https://doi.org/10.1039/C9GC00869A>
- [143] Y.-G. Wang, C.-Y. Guo, J. Shen, Y.-Q. Sun, Y.-X. Niu, P. Li, G. Liu, X.-Y. Wei, A sustainable and green route to furan-2,5-dicarboxylic acid by direct carboxylation of 2-furoic acid and CO₂, *Journal of CO₂ Utilization* **2021** (48) 101524. <https://doi.org/10.1016/j.jcou.2021.101524>



2. OBJETIVOS



El objetivo de esta Tesis Doctoral es el desarrollo y optimización de un proceso catalítico que permita la obtención de ácido 2,5-furandicarboxílico (FDCA) a partir de biomasa residual mediante una secuencia de tres etapas en serie que incluye la hidrólisis ácida de biomasa, la oxidación de los aldehídos y la carboxilación del ácido furoico. Dada la complejidad del proceso a estudiar, se han establecido objetivos parciales (agrupados según las etapas del proceso) que, conjuntamente, permiten avanzar en la comprensión y aplicación de procesos sostenibles para la producción de materiales biodegradables y biocompatibles, en este caso un monómero para la obtención de bioplásticos, a partir de materias primas renovables e incluyendo una última etapa de captura de CO₂.

Hidrólisis ácida de biomasa lignocelulósica:

- Optimización de las condiciones de operación para maximizar la obtención de 5-hidroximetilfurfural (HMF) a partir de celulosa microcristalina. Se utilizará este polímero comercial como estándar para determinar el mecanismo y el modelo cinético del proceso de hidrólisis con catálisis homogénea y heterogénea, mediante un estudio riguroso sobre la influencia de la temperatura, concentración de catalizador y tiempo de reacción. Igualmente, se analizará la influencia de diferentes pretratamientos que permitan una degradación parcial de la estructura recalcitrante de la celulosa, favoreciendo la producción de HMF.

- Optimización de las condiciones de operación para maximizar la obtención de furfural (FFL) y HMF a partir de serrín de pino. Se evaluará la extrapolación de las condiciones óptimas definidas con anterioridad a una matriz real, serrín de pino. En base a los resultados experimentales, se estudiará en profundidad la influencia de los principales parámetros de operación en la productividad de los aldehídos de interés (pretratamientos, temperatura, carga catalítica), haciendo hincapié en las diferencias obtenidas respecto a los estudios previos con celulosa, de forma que se determine el papel de la lignina y la hemicelulosa en el proceso.

Oxidación de furfural y HMF:

- Desarrollo del mecanismo de reacción y optimización de las condiciones de operación para maximizar la obtención de ácido furoico a partir de furfural. Se llevará a cabo un estudio sistemático y detallado de la oxidación catalítica de furfural empleando dos tipos de oxidantes, peróxido de hidrógeno y oxígeno molecular. La actividad de diversos catalizadores de metales nobles soportados sobre materiales con diferentes propiedades ácidas, básicas y redox se analizará en función de las condiciones de reacción (temperatura, presión, concentración de furfural y pH), permitiendo determinar el mecanismo y las etapas cinéticamente controlantes en este proceso.
- Optimización de las condiciones de operación para maximizar la obtención de ácido 2,5-furandicarboxílico a partir de 5-hidroximetilfurfural y fructosa. Los estudios referidos a la oxidación del HMF partirán de las conclusiones obtenidas durante la oxidación de furfural (catalizador y agente oxidante). En este caso, dada la mayor inestabilidad química del HMF (formación de huminas, tendencia a la descomposición), se reevaluarán las condiciones de operación (temperatura, presión), con especial atención al pH. Una vez optimizada esta etapa, se explorará la posibilidad de obtener el FDCA directamente a partir de fructosa, mediante un proceso en una sola etapa, analizando la aplicabilidad de los mecanismos y resultados cinéticos obtenidos en los estudios individuales de hidrólisis y oxidación.
- Producción simultánea de ácido furoico (FCA) y FDCA a partir de mezclas de furfural y HMF. Se evaluará la oxidación simultánea de ambos aldehídos, en un avance hacia un sistema realista en el cual se pudiera prescindir de la etapa de purificación tras la hidrólisis.

Tomando como punto de partida los resultados obtenidos en las optimizaciones individuales, se realizarán las adaptaciones necesarias en términos de composición de la mezcla (ratio FFL/HMF y grado de dilución) y condiciones de operación.

Carboxilación de ácido furoico:

- Selección de rutas químicas para la carboxilación de FCA a FDCA. Se llevará a cabo un análisis crítico de las diferentes rutas y condiciones de reacción para llevar a cabo la carboxilación de ácido furoico haciendo hincapié en las ventajas y desventajas de cada enfoque. Ello permitirá identificar posibles oportunidades para desarrollar estrategias de mejora que permitan aumentar la eficacia del proceso o simplificar las condiciones de operación para aumentar la sostenibilidad de esta etapa.
- Desarrollo de nuevas estrategias para la carboxilación. Se plantearán experimentos a baja presión para facilitar el acople de la reacción a un sistema de captura de CO₂. En otra línea de trabajo, se propondrá una configuración en fase líquida, evaluando posibles disolventes y planteando la posible sustitución total o parcial del cesio, metal utilizado en bibliografía para generar la sal fundente que encarece significativamente el proceso.



3. METODOLOGÍA EXPERIMENTAL

3.1. REACTIVOS Y CATALIZADORES COMERCIALES

Para el desarrollo de esta Tesis Doctoral se han empleado diferentes reactivos y catalizadores comerciales. Como reactivos se emplean: celulosa microcristalina (Sigma Aldrich, CAS: 9004-34-6), serrín de pino (carpintería local), fructosa ($\geq 99.5\%$, Panreac Applichem), furfural ($\geq 99\%$, Sigma Aldrich), 5-hidroximetilfurfural ($\geq 99\%$, Sigma Aldrich), ácido furoico ($\geq 98\%$, Sigma Aldrich) y carbonato de cesio ($\geq 99\%$, Sigma Aldrich). Como catalizadores se emplean: HCl (49-51%, Panreac Applichem) y zeolita β (Zeolyst International, CP814E, $\text{SiO}_2/\text{Al}_2\text{O}_3=25$).

3.2. SÍNTESIS DE CATALIZADORES

En este apartado de la Tesis Doctoral se describen las síntesis de los catalizadores no comerciales utilizados a lo largo de la tesis, agrupados por apartados según las etapas del proceso en las que son utilizados (hidrólisis y oxidación).

3.2.1. Catalizadores empleados en las reacciones de hidrólisis

En los experimentos de hidrólisis se emplea zeolita β comercial. Esta zeolita comercial se suministra en su forma catiónica NH_4^+ , la cual no es activa desde el punto de vista catalítico. Para activarla, se somete a un tratamiento térmico en mufla con un gradiente de temperatura de $1\text{ }^\circ\text{C min}^{-1}$ hasta $550\text{ }^\circ\text{C}$, manteniendo esta temperatura constante durante 12 horas para eliminar los grupos funcionales NH_4^+ y obtener así la forma protonada y activa para este tipo

de reacciones. Este protocolo de activación ha sido previamente utilizado por otros autores en la bibliografía [1].

3.2.2. Catalizadores empleados para los estudios de oxidación

Para llevar a cabo las reacciones de oxidación de FFL, se ha realizado una selección de catalizadores bifuncionales (metal + soporte) sintetizados en el laboratorio. En concreto, en base a la bibliografía se utilizan cuatro soportes con diferentes propiedades catalíticas: TiO_2 y CeO_2 como ejemplos de materiales redox [2,3], y MgAl y MgZr como óxidos mixtos típicos con sitios ácidos y básicos [4,5]. Para potenciar la actividad catalítica, se preparan materiales bifuncionales (con una carga metálica de un 1% en peso) con Au , Pd y Pt , tres de los metales más utilizados en oxidaciones [6,7]. En base a los resultados obtenidos, se selecciona Au/TiO_2 como el catalizador con mejores resultados sobre el cual se continua la investigación de oxidación de HMF. A continuación, se detalla el protocolo seguido para la síntesis de los soportes y el procedimiento experimental utilizado para la impregnación de los metales en la superficie de estos.

- Óxido de titanio (TiO_2). El óxido de titanio utilizado para llevar a cabo estas reacciones posee un 25% de la fase cristalina rutilo y un 75% de anatasa, se trata de un material comercial con un 99% de pureza adquirido en Sigma Aldrich. Para activar la superficie del material se somete a un proceso de calcinación en flujo de aire durante 2h con una rampa de 5°C min^{-1} hasta 500°C [8].
- Óxido de cerio (CeO_2). El óxido de cerio se sintetiza de acuerdo con el procedimiento propuesto por Eaimsumang *et al.* a partir de una sal precursora, en este caso nitrato de amonio y cerio (IV) [9]. Junto a esta sal, se utiliza un surfactante catiónico, el bromuro de hexadeciltrimetilamonio (CTAB), que ayuda a la correcta síntesis del óxido de cerio. Se utiliza una mezcla con una relación molar 2:3 respectivamente. Esta mezcla se disuelve en agua y amoníaco en disolución al 28%, empleándose un ratio volumétrico 5:1. La disolución resultante se introduce en un reactor discontinuo de tanque agitado (Autoclave Engineers EZE Seal), donde se le somete a agitación suave y se aumenta la temperatura hasta 100°C durante 2 h. Posteriormente, el sólido se lava con agua desionizada y acetona y se filtra para posteriormente secarse durante 24 h en un horno a 80°C . El material una vez seco se tamiza y se calcina en una mufla a 400°C durante 4h para así obtener el CeO_2 .

- Óxido mixto de magnesio y aluminio ($\text{MgO-Al}_2\text{O}_3$). La síntesis de este soporte se realiza siguiendo un procedimiento de co-precipitación a sobresaturación (pH 10-12) controlada con ultrasonidos desarrollado por Larina *et al.* [10]. Se emplea un reactor de vidrio que posee un encamisado de agua suspendido sobre un baño de ultrasonidos. Se añaden gota a gota disoluciones 1 M de $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 98%) y $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich, 99%) en proporción 2:1 sobre 200 ml de una disolución tampón que contiene NaOH 1.6 M y Na_2CO_3 0.1 M bajo agitación vigorosa a una temperatura de 85°C. Posteriormente, la mezcla se somete a un proceso de envejecimiento a 85°C durante 24 h en un baño con agitación leve. El sólido resultante se filtra y se lava para eliminar los restos de sales o iones Na^+ y se tamiza entre 50-80 μm . Las hidrotalcitas resultantes se calcinan a 700 °C durante 5 h en flujo de aire para obtener óxidos mixtos.
- Óxido mixto de magnesio y zirconio (MgO-ZrO_3). Este soporte se sintetiza empleando la técnica sólido-gel propuesta por Aramendía y colaboradores [11]. Se disuelven 51 g de $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ y 4g de $\text{Zr}(\text{NO}_3)_2$ (Sigma Aldrich, 98%) en agua desionizada lo que supone una relación $\text{Mg/Zr}=4$. La mezcla se agita a temperatura ambiente y se agrega NaOH (25% en peso) hasta alcanzar un pH de 10 mientras se forma un sólido blanquecino. El gel resultante se envejece a 85 °C durante 24h en un baño con agitación leve y posteriormente se filtra y se lava hasta obtener un pH de 7 para eliminar todos los iones de las disoluciones empleadas que hayan podido quedar retenidos sobre la superficie del catalizador. El gel obtenido se seca a 100 °C durante 24h y se tamiza para obtener un tamaño de partícula homogéneo (50-80 μm). Finalmente, se calcina el sólido en un flujo de aire en exceso hasta 600 °C con una rampa de 5 °C min^{-1} que se mantiene durante 3h.

Impregnación de la fase metálica: Pd, Pt y Au

Los catalizadores modificados con Pd y Pt (1% en peso como carga metálica teórica) se preparan utilizando el método de impregnación seca. Esta técnica se basa en disolver el precursor metálico en un volumen de agua desionizada igual al volumen de poros del material utilizado como soporte. La adicción se hace gota a gota y agitando el catalizador constantemente para evitar sobresaturaciones locales del metal. Sin necesidad de lavado previo, el sólido resultante se seca en una estufa a 100°C durante 24h. Concretamente, se utiliza $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ como precursor de Pd y $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ como precursor de Pt (ambos

adquiridos por Sigma Aldrich, >99.99%). Los catalizadores obtenidos se calcinan en aire a la misma temperatura que se calcina cada soporte previamente y se reducen en flujo de H_2 a 400 °C durante 4 h (en todos los casos, temperatura se alcanza con una rampa de 5 °C·min⁻¹)

El Au se deposita con una concentración de un 1% en peso en los diferentes soportes mediante el método de deposición-precipitación utilizando $HAuCl_4 \cdot 3H_2O$ (Sigma Aldrich, 99%) como precursor en presencia de urea [8]. Todos los catalizadores se calcinan durante 3 h a la misma temperatura que sus correspondientes soportes (es decir, 400, 500, 600 y 700 °C para CeO_2 , TiO_2 , $MgZr$ y $MgAl$, respectivamente). Para garantizar la reducción del metal, los catalizadores se reducen en H_2 durante 4 h, a 300 °C con una rampa de 5 °C·min⁻¹ [12].

3.3. TÉCNICAS DE CARACTERIZACIÓN DE LOS MATERIALES UTILIZADOS

Una vez preparados los diferentes materiales se debe proceder con su caracterización para relacionar sus propiedades morfológicas, superficiales y fisicoquímicas con su actividad catalítica. Para ello, se emplean diversas técnicas espectroscópicas y analíticas cuyo fundamento teórico se detalla a continuación junto la descripción del equipo y del procedimiento experimental empleado en cada caso.

3.3.1. Técnicas de adsorción-desorción

Cuando una molécula de gas se encuentra con una superficie sólida, puede rebotar o quedar fijada sobre la superficie, es decir, sufrir adsorción. Se define la adsorción como el proceso de unión de una molécula gaseosa sobre la superficie de un sólido. Por el contrario, la desorción es el proceso inverso a la adsorción. Se distingue entre dos comportamientos en la adsorción: la fisisorción y quimisorción. En la adsorción física o fisisorción, las moléculas del gas se mantienen unidas a la superficie del sólido por medio de fuerzas de Van der Waals (interacciones dipolares). Este hecho define todas las características propias de la fisisorción ya que se trata de una interacción débil. Es un proceso exotérmico en el que las moléculas fisisorbidas mantienen su naturaleza química. Además, la fisisorción se puede producir en multicapas, es decir, sobre una capa de gas fisisorbida puede adsorberse otra. Por otro lado, en el caso de la adsorción química o quimisorción, las moléculas de gas se mantienen unidas

a la superficie formando un enlace químico fuerte por lo que se trata de una interacción más fuerte que la fisisorción. Las entalpías de quimisorción son mucho mayores que las de fisisorción y del orden de las que se liberan en la formación de enlaces químicos, es decir, semejante a una reacción química. Dado que implica la formación de un enlace entre adsorbato y el adsorbente, el proceso se detiene tras la formación de una monocapa sobre la superficie.

Durante el desarrollo de esta Tesis Doctoral, se han realizado ensayos de fisisorción y quimisorción de los catalizadores empleados. Ambos tipos de técnicas se han llevado a cabo en el mismo equipo, en concreto en un Micromeritics ASAP 2020, que dispone de la posibilidad de realizar ambos análisis (**Figura 3.1**).



Figura 3.1. Equipos utilizados para la fisisorción de nitrógeno (A) y para la quimisorción de H_2 y CO (B). Micromeritics ASAP 2020

Fisorción de nitrógeno

La técnica de fisisorción de gases es la más extendida para la determinación de áreas superficiales y distribución de tamaños de poros en sólidos. Esta técnica se basa en la adsorción generalmente de nitrógeno a 77 K. Las isothermas obtenidas (representación del volumen de nitrógeno fisisorbido en el sólido respecto a la presión relativa de nitrógeno) corresponden al proceso de adsorción y desorción del gas en el sólido, produciéndose histéresis cuando la isoterma de adsorción no coincide con la de desorción. Los sólidos se pueden clasificar en función del tipo de isothermas que presenten. Las isothermas de adsorción, mayoritariamente, se pueden agrupar en seis tipos diferentes (**Figura 3.2**):

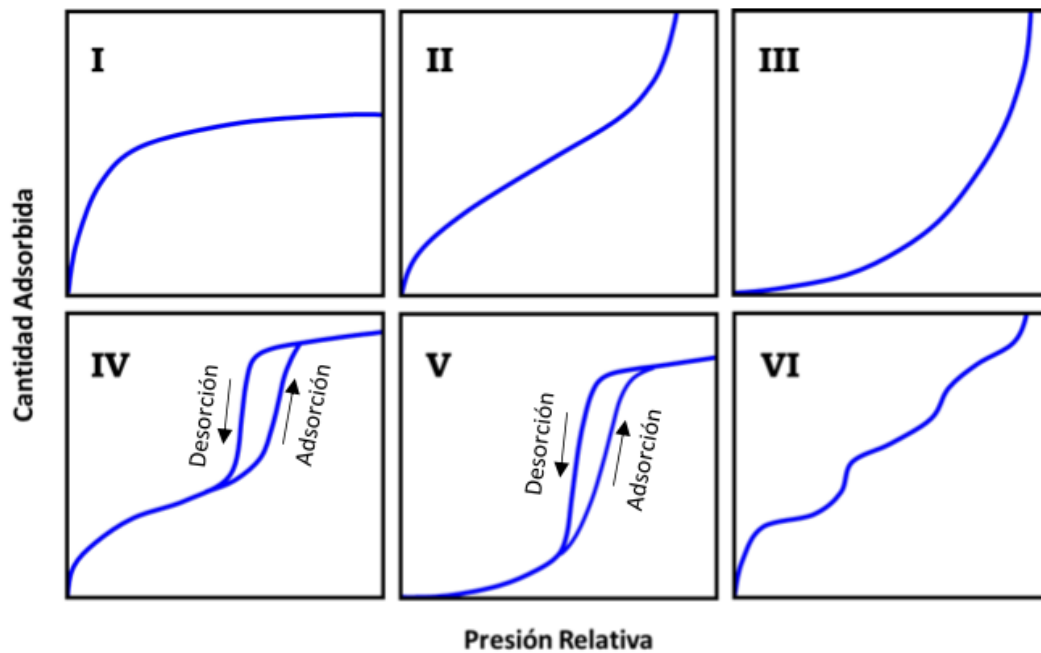


Figura 3.2. Isotermas de adsorción. Adaptada de Sing *et al.* [13]

- Isotherma de tipo I. denominado isoterma de Langmuir, corresponde a una adsorción en monocapa. La cantidad adsorbida aumenta con P hasta alcanzar un valor límite correspondiente al recubrimiento de la superficie por una monocapa. Es la isoterma característica de los sólidos microporosos.
- Isotherma de tipo II. es indicativo de una adsorción física en multicapa. El rápido ascenso inicial corresponde a la formación de la primera capa, que tiene en este caso una constante de formación mayor que para el resto de las capas. Al seguir aumentando la presión se forma la segunda capa de moléculas adsorbidas, seguida de otras más. Características de los materiales macroporosos.
- Isotherma de tipo III. corresponde también a una adsorción física en multicapas, pero donde la constante de equilibrio de formación de la primera capa es igual que para las siguientes, es decir, donde la interacción entre adsorbato y adsorbente es baja.
- Isotherma de tipo IV. La máxima extensión de la adsorción se produce antes de alcanzar la presión de saturación. Típica de materiales mesoporosos. Se produce un ciclo de histéresis debido a la condensación en los macroporos.
- Isotherma de tipo V. Se corresponde con una adsorción débil que presenta un ciclo de histéresis debido a la condensación. Es una variación de la isoterma tipo III.

➤ Isoterma de tipo VI. Es un tipo de adsorción en escalones donde cada escalón representa una capa fisisorbida. Este tipo de adsorción ocurre solo para sólidos con una superficie no porosa muy uniforme, es poco frecuente.

Durante procedimiento experimental, se debe pesar el tubo que contiene la muestra y llevar a cabo a un proceso de desgasificación a vacío hasta 10 mm de Hg y a una temperatura que permita eliminar las impurezas de los poros del material (250 °C durante 4h). A continuación, se pesa de nuevo el tubo de muestra y se especifica la masa empleada después de la desgasificación. La masa inicial debe garantizar un mínimo de 200 m² de superficie específica para asegurar la máxima sensibilidad y el funcionamiento óptimo del equipo. El análisis se lleva a cabo 77 K y aplica automáticamente las distintas presiones parciales de nitrógeno hasta alcanzar el equilibrio, que se corresponde con el momento en el que la presión en el interior del tubo portamuestras no varía. Es decir, el momento en el que, para dicha presión parcial, el adsorbente no admite más adsorbato en su superficie. Una vez finalizado el análisis, se emplea el rango de presiones de $0.05 < P/P_0 < 0.35$ para determinar la superficie específica a través de la teoría de Brunauer, Emmet y Teller (BET) y aplica el modelo de Barret, Joyner y Halenda (BJH) a la curva de desorción de nitrógeno para obtener el volumen y el diámetro de mesoporos.

Quimisorción de hidrógeno y CO

La quimisorción es el término que se aplica a la interacción de superficies sólidas con gases cuando esta da lugar a la formación de enlaces químicos. Esta técnica se emplea para el cálculo de la dispersión metálica (**Ec 3.1**) y el tamaño de la cristalita en los catalizadores de metal reducido soportados, mediante adsorción específica de determinados gases. Durante el desarrollo de esta Tesis Doctoral se han empleado dos moléculas sonda para la realización de los experimentos de quimisorción H₂ y CO. Si bien la quimisorción con H₂ es la técnica más extendida, la quimisorción con CO es más adecuada para analizar Au y Pt.

$$\gamma(\%) = \frac{\frac{V_m}{V_{mol}}}{\frac{M_{\%}}{W_a}} \cdot F_s \cdot 100 \quad [3.1]$$

donde " V_m " es el volumen de gas quimisorbido en cm_3/g ; " V_{mol} " el volumen molar de dicho gas (en las mismas unidades); " F_s " el factor estequiométrico de la reacción de quimisorción; " M " el porcentaje de metal activo expresado en gramos de metal activo por cada gramo de muestra, y " W_a " el peso atómico del metal activo.

Esta técnica permite cuantificar la cantidad de H_2 o CO quimisorbida en cada átomo metálico. Con el objetivo de determinar este parámetro, se realiza un experimento para observar la cantidad de gas adsorbida a distintas presiones. Gracias a la formación de un enlace químico entre la molécula de adsorbato y un sitio activo en la superficie del adsorbente, el número de átomos activos (metálicos) se puede determinar simplemente midiendo la cantidad del gas adsorbido, si se conoce el factor estequiométrico (F_s) entre el gas y el metal en el proceso de adsorción (**Tabla 3.1**).

Tabla 3.1. Factores estequiométricos utilizados para determinar la dispersión metálica mediante quimisorción (F_s) [14,15]

Metal	Coefficiente $F_{S \text{ H}_2}$	Metal	Coefficiente $F_{S \text{ CO}}$
Pd	1	Pd	1
Pt	1	Pt	1
Au	0.2-0.9	Au	1
Ru	2	Ru	2
Rh	2	Rh	2

Dependiendo de la naturaleza del metal y los gases, así como de las condiciones de operación, pueden coexistir especies de enlaces fuertes y débiles en la superficie del metal, lo cual influye en la extensión y tipo de interacción de quimisorción que se establece. En ciertos casos, la quimisorción puede ser en parte reversible. La cantidad de hidrógeno quimisorbido reversiblemente se determina entonces mediante mediciones de readsorción, después de la evacuación del gas a la misma temperatura. Es decir, se realizan dos isotermas que representan la adsorción total y reversible, y la adsorción irreversible viene dada por la diferencia entre ambas, tal y como se observa en la **Figura 3.3**. Este análisis detallado es decisivo para comprender los mecanismos de adsorción y desorción en procesos catalíticos específicos.

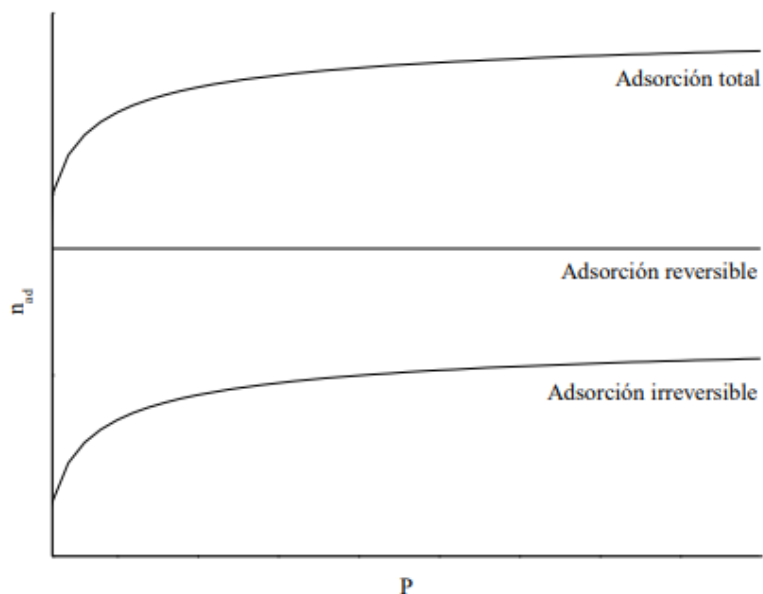


Figura 3.3. Determinación del volumen de la monocapa. Isothermas de adsorción total, reversible e irreversible

A partir de la dispersión metálica también es posible calcular el tamaño de cristalita (**Ec.3.2**). Para ello se considera una morfología esférica o semiesférica de las partículas metálicas. “ A_{sm} ” representa el área activa por gramo de metal puro y “ ρ ” la densidad del metal.

$$d = \frac{6}{A_{sm} \cdot \rho \cdot \gamma} \cdot 100 \quad [3.2]$$

3.3.2. Técnicas de reacción o desorción a temperatura programada

Las técnicas a temperatura programada se emplean para determinar propiedades fisicoquímicas de los materiales. Principalmente, se ha utilizado para analizar la reducibilidad de los metales nobles empleados en este trabajo (y, con ello, determinar la temperatura a la que debe realizarse la reducción de los mismos), y para determinar la concentración y fortaleza de los centros activos ácido, base y redox. Para realizar estos análisis, se han utilizado tres variantes:

➤ Desorción de NH_3/CO_2 a temperatura programada (TPD): Estos ensayos se utilizan para caracterizar centros ácidos o básicos de los catalizadores. Se llevan a cabo mediante adsorción de NH_3 o CO_2 a temperatura ambiente, y el estudio de su desorción en función de la temperatura (monitorizado mediante espectrómetro de masas). Con este tipo de análisis

se obtiene información sobre la acidez (desorción de NH_3) y basicidad (desorción del CO_2). En ambos casos, un calibrado previo permite cuantificar la totalidad de los centros, mientras que la deconvolución de las curvas obtenidas permite la clasificación de los centros por dureza en función de la temperatura de desorción.

Para la realización de estos ensayos se realiza una previa limpieza de la superficie con helio para eliminar la humedad adsorbida en el material (200°C , 1 h). Tras esta etapa, una vez alcanzada la temperatura ambiente, se satura la muestra con el gas sonda deseado durante 20 min. El posible exceso de gas se elimina de forma natural con un tiempo de estabilización de la señal mientras se mantiene el flujo de He y la temperatura ambiente (tiempo aproximado 2 h, asegurando en cada análisis haber alcanzado la línea base en la señal).

Finalmente, la desorción de la molécula sonda se monitoriza con un programa de temperatura que alcanza los 900°C con una rampa de $5^\circ\text{C}\cdot\text{min}^{-1}$. A pesar de estas condiciones generales, sólo se consideran las señales obtenidas hasta la temperatura de preparación de los materiales, para asegurar que no se consideran posibles degradaciones.

➤ Reducción a temperatura programada (TPR): Este tipo de ensayos se emplean para la caracterización de catalizadores que contengan un metal susceptible de ser reducido. En este caso, se monitoriza el consumo de H_2 que conlleva dicha reducción, siendo también relevante la temperatura a la cual ocurre dicha reacción (indicativo de la mayor o menor tendencia a reducirse/oxidarse). Tras limpiar la superficie del material durante 1 h a 200°C en flujo de He, se recupera la temperatura ambiente y, con una rampa de $5^\circ\text{C}\cdot\text{min}^{-1}$ se monitoriza la señal de H_2 hasta alcanzar los 500°C (temperatura máxima de reducción de los materiales considerados en este estudio).

➤ Oxidación a temperatura programada (TPO): Se utiliza para la caracterización de los depósitos carbonosos adsorbidos sobre las superficies catalíticas tras las diferentes reacciones. El programa es análogo al realizado para los TPR, pero sustituyendo el H_2 por O_2 y monitorizando las señales de CO y CO_2 que se producirían por la combustión de dichos depósitos. Igualmente, la temperatura a la que ocurren estas oxidaciones indica la fortaleza relativa de los depósitos carbonosos.

Para llevar a cabo este tipo de ensayos, se ha empleado un Autochem 2910 de Micromeritics de la Universidad de Oviedo como el que se muestra en la **Figura 3.4** que permite realizar análisis de materiales sólidos a temperatura programada en un rango de temperaturas de -20° a 1000 °C. Puede trabajar con 5 gases diferentes: He, CO₂, NH₃/He, H₂/Ar y O₂/He. Está equipado con un espectrómetro de masas (modelo Pfeiffer Omnistar Vacuum GSD 301) que permite seguir la señal de los diferentes gases empleados.



Figura 3.4. Equipo utilizado para la adsorción a temperatura programada. Autochem 2910 de Micromeritics

3.3.3. Difracción de rayos X (DRX)

La difracción de rayos X es una técnica analítica versátil y no destructiva que se utiliza para analizar propiedades físicas, como la composición de fases, la estructura cristalina de los catalizadores.

La técnica se basa en el fenómeno de difracción, es decir, se refiere al fenómeno de dispersión de ondas cuando pasan a través de una rendija o apertura estrecha, mientras que la extensión de la dispersión depende del tamaño de la rendija. Cuando los rayos X pasan a través de una estructura cristalina, son difractados por las diversas capas atómicas o moleculares dentro de ese cristal. Estos rayos difractados sufren interferencias constructivas o destructivas. Las interferencias constructivas constituyen el fundamento de la técnica y son aquellas que tienen lugar cuando se suman los efectos de dos ondas “en fase”, es decir, cuando la longitud de onda de los rayos X utilizados es del mismo orden de magnitud de la distancia entre los átomos en una red cristalina se generan picos que dan lugar a un patrón de difracción que se puede analizar de varias maneras; la más popular es la aplicación ley de Bragg (**Ec. 3.3**).

$$n \cdot \lambda = 2 \cdot d \cdot \sin\theta$$

[3.3]

donde “n” es un número entero; “λ”, la longitud de onda de la radiación incidente; “θ”, el ángulo de difracción; y “d”, la distancia entre planos de átomos del cristal.

Además, La aproximación de Scherrer (**Ec. 3.4**) se emplea para la estimación del tamaño promedio de cristal cuando la red cristalina no tiene deformación y la muestra está compuesta mayoritariamente de pequeños cristales.

$$\beta = \frac{K \cdot \lambda}{L \cdot \cos \theta} \quad [3.4]$$

donde: “L” es el tamaño medio de los cristales, “λ” es la longitud de onda, “θ” es el ángulo de Bragg, “β” es la anchura a media altura del pico (en radianes, FWHM) y K es la constante de Scherrer que depende de la forma del cristal y del método utilizado para calcular el tamaño (0.9).

En un difractómetro de rayos X, las diferentes fases cristalinas muestran diferentes patrones de difracción. La identificación de fases se puede realizar mediante la comparación de los patrones de difracción obtenidos de muestras desconocidas con los patrones de las bases de datos de referencia. Para la medición de los espectros se ha utilizado el difractómetro Philips PW1710 de los Servicios Científico-Técnicos de la Universidad de Oviedo (**Figura 3.5**). Se emplea como radiación incidente la line K-α de cobre (λ=1.54 Å) con un voltaje y una corriente del tubo de 45kV y 40mA, en un intervalo de 2θ comprendido entre 5.01 y 115°, con una velocidad de barrido de 2°min⁻¹.

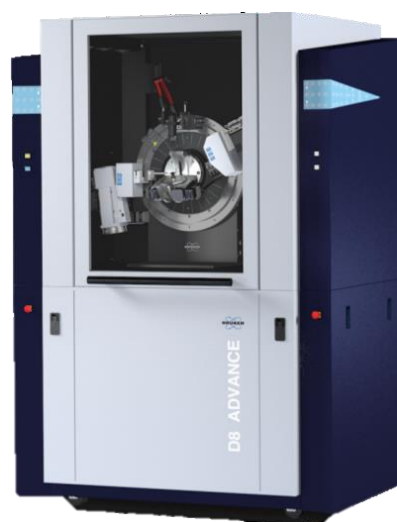


Figura 3.5. Equipo empleado para llevar a cabo los análisis de difracción de rayos X para polvo cristalino. Philips PW1710

Esta técnica se ha utilizado para determinar las fases cristalinas o parcialmente amorfas existentes en los diferentes materiales, así como para calcular el tamaño de cristalita metálica en el caso de los catalizadores de metal soportado.

3.3.4. Análisis elemental

El análisis elemental se puede utilizar para determinar la cantidad de carbono, hidrógeno, nitrógeno, azufre y oxígeno de los diferentes materiales mediante el empleo de la oxidación instantánea y completa de muestras a través de la combustión en un horno a 1200°C y posterior reducción, convirtiendo cada sustancia orgánica e inorgánica en un producto de combustión (CO₂, H₂O, N₂O y SO₂). Posteriormente, el análisis de dichos gases se realiza empleando una columna de cromatografía para separarlos y un detector de conductividad térmica (TCD). El contenido de cada elemento en la muestra tiene una relación directa con la concentración de cada uno de estos gases.

La determinación del contenido en carbono, hidrógeno, nitrógeno y azufre de la celulosa y del serrín, frescos y tras los pretratamientos, se ha llevado a cabo empleando un analizador elemental C, H, N, S Elemental Vario EL disponible en los Servicios Científico-Técnicos de la Universidad de Oviedo.

3.3.5. Espectrometría de masas con plasma acoplado inductivamente (ICP-MS)

La espectrometría de masas con plasma acoplado inductivamente (ICP-MS, por sus siglas en inglés) es una técnica de análisis multielemental que permite determinar y cuantificar la mayoría de los elementos de la tabla periódica a nivel de traza que tengan un potencial de ionización menor que el potencial de ionización del argón. Se basa en el acoplamiento de un método para generar iones (plasma acoplado inductivamente) y un método para separar y detectar los iones (espectrómetro de masas). Esta técnica se ha utilizado para determinar la composición elemental de los diferentes catalizadores.

La muestra, en forma líquida, es transportada por medio de una bomba peristáltica hasta el sistema nebulizador donde es transformada en aerosol gracias a la acción de gas argón. Dicho aerosol es conducido a la zona de ionización que consiste en un plasma generado al someter un flujo de gas argón a la acción de un campo magnético oscilante inducido por una corriente de alta frecuencia. En el interior del plasma se pueden llegar a

alcanzar temperaturas de hasta 8000 K. En estas condiciones, los átomos presentes en la muestra son ionizados. Los iones pasan al interior del filtro cuadrupolar a través de una interfase de vacío creciente, allí son separados según su relación carga/masa. Cada una de las

masas sintonizadas llegan al detector donde se evalúa su abundancia en la muestra. Para los análisis de ICP-MS realizados se ha empleado el espectrómetro de masas de cuadrupolo tipo ICP-MS con celda de colisión (modelo HP 7500c de Agilent) disponible en los Servicios Científico Técnicos de la Universidad de Oviedo.

3.3.6. Análisis termogravimétrico

Los análisis termogravimétricos consisten en un grupo de técnicas que monitorizan los cambios en la masa de una muestra sólida con el tiempo mientras se somete a variaciones de temperatura, lo que puede relacionarse con cambios tanto físicos como químicos del material. Una característica fundamental de esta técnica es que permite la cuantificación de la ganancia o pérdida de masa de la muestra debido a procesos de, por ejemplo, descomposición, reducción, adsorción o desorción. En este caso, los ensayos termogravimétricos se han realizado siempre en N₂ con el objetivo de caracterizar las celulosas microcristalinas y pretratadas, el serrín (para establecer la temperatura en la que pierden el agua completamente y conocer la temperatura máxima a la que puede llevarse a cabo las reacciones sin descomponer el material térmicamente) y las sales de ácido furoico (para determinar la estabilidad y, con ello, la temperatura máxima para las reacciones de carboxilación).

El dispositivo experimental (**Figura 3.6**) consiste en una termobalanza conectada a un recipiente que contiene la muestra (crisol de platino) dentro de un horno y a un controlador de temperatura perteneciente a la casa comercial TA Instruments (modelo TGA 55). La configuración del horno, la colocación de la muestra y los puntos de entrada y salida de gas minimizan el ruido en la señal. El programa de temperatura empleado puede incluir etapas de calentamiento, enfriamiento, periodos isotérmicos o una combinación. En el caso del desarrollo de esta Tesis Doctoral, se ha utilizado



Figura 3.6. Equipo utilizado para los ensayos termogravimétricos (TGA 55)

un programa de temperatura que consta de una rampa de calentamiento de $5^{\circ}\text{C}\cdot\text{min}^{-1}$ desde 25°C hasta 900°C con un flujo de nitrógeno.

3.3-7. Espectroscopía infrarroja de reflexión difusa por transformada de Fourier (DRIFT)

La espectroscopía infrarroja de reflexión difusa (DRIFT) implica la captura y análisis de la radiación difusa reflejada en todas las direcciones por la muestra objeto de estudio cuando se le aplica un haz de radiación infrarroja. Al incidir el haz infrarrojo en la muestra, puede ser reflejado por su superficie o transmitido a través de ella. La energía transmitida puede encontrarse con otra partícula, donde puede ser reflejada nuevamente o transmitida hacia otra partícula diferente. Este proceso de transmisión y reflectancia puede repetirse múltiples veces en una misma muestra, lo que aumenta significativamente el recorrido del haz incidente. La reflexión difusa ocurre en todas las direcciones del espacio y se recopila utilizando un sistema de espejos orientados hacia el detector correspondiente. Los espejos concentradores, dirigen la radiación reflejada hacia el detector, capturando exclusivamente la radiación difusa. La intensidad de la reflexión puede expresarse, mediante la transformación empírica de Kubelka-Munk. Los picos o bandas observados a diferentes longitudes de onda se relacionan con las vibraciones de ciertos enlaces químicos presentes en la muestra cuando se expone a radiación infrarroja.

La asignación de estas bandas de absorbancia a cada tipo de enlace puede lograrse mediante referencia bibliográfica o análisis de estándares conocidos. Esta técnica, por tanto, facilita el estudio de la modificación o ruptura de enlaces existentes en el material, así como la formación de nuevos enlaces tras tratamientos o reacciones químicas. Además, la incorporación de un accesorio conocido como cámara catalítica permite el flujo controlado de gases sobre la muestra y una precisa regulación mediante una bomba de vacío. Además, dispone de un controlador de temperatura lo que permite el estudio de enlaces rotos o generados durante una reacción química o proceso de adsorción a temperaturas específicas. Para llevar a cabo estas mediciones, se emplea un espectrómetro Agilent Technologies Cary 600 Series FTIR Spectrometer perteneciente al Instituto Fritz-Haber de la sociedad alemana Max Planck de Berlín (**Figura 3.7**), equipado con un detector MCT/A, capaz de capturar el espectro infrarrojo en el rango de $700\text{-}4000\text{ cm}^{-1}$.

El equipo está configurado con una resolución de 2 cm^{-1} y realiza 256 escaneos consecutivos para obtener cada espectro. Antes de la adsorción de CO, las muestras se secaron a 150°C en vacío. La adsorción de CO se llevó a cabo isotérmicamente a temperatura ambiente, con una adición gradual de CO en el rango de presión de 0,025 a 18 mbar, seguido de una evacuación escalonada. Mediante espectroscopía DRIFT, se ha evaluado posibles causas de desactivación del Au en reacciones de oxidación.



Figura 3.7. Equipo utilizado para la espectroscopía infrarroja de reflexión difusa por transformada de Fourier (DRIFT), Agilent Technologies Cary 600 Series FTIR Spectrometer

3.3.8. Espectroscopía Raman

La espectroscopía Raman es una técnica de dispersión de luz, mediante la cual una molécula dispersa la luz incidente desde una fuente de luz láser de alta intensidad. La mayor parte de la luz dispersada tiene la misma longitud de onda (o color) que la fuente del láser y no proporciona información útil; esto se denomina Dispersión de Rayleigh. Sin embargo, una pequeña cantidad de luz (normalmente $1 \cdot 10^{-7} \%$) se dispersa en diferentes longitudes de onda (o colores), que dependen de la estructura química del analito; esto se denomina dispersión Raman.

El procedimiento de medida es el siguiente: un haz de luz monocromático, de frecuencia ν_0 , incide sobre la muestra, dispersándose de manera elástica (dispersión Rayleigh) en su mayor parte, pero existiendo una cantidad de luz que ha sido dispersada inelásticamente, y por tanto presenta un cambio en su frecuencia. Estos cambios en la frecuencia son característicos de la naturaleza química y del estado físico de la muestra, y por tanto son los datos que permiten identificar distintos compuestos y características moleculares. Microscópicamente, este efecto se puede describir como una excitación de la nube electrónica de la molécula debido a la interacción con el fotón incidente. Este provoca que la excitación de la molécula a un estado excitado virtual luego emite otro fotón con el

objetivo de regresar al estado fundamental. Sin embargo, si el choque ha sido inelástico y se ha perdido o ganado energía, la molécula no volverá exactamente al mismo estado, sino que se encontrará en un estado rotacional o vibracional distinto del inicial. La diferencia de energía entre estos estados es lo que modifica la frecuencia del fotón emitido. Según la frecuencia de los fotones dispersados, se pueden distinguir los siguientes casos (**Figura 3.8**).

- **Dispersión Rayleigh.** Cuando el choque es elástico, la frecuencia del fotón incidente y emitido es la misma, y por tanto no hay ninguna variación energética. Este proceso no proporciona información espectroscópica.
- **Dispersión Raman-Stokes.** Si el choque es inelástico, y la frecuencia del fotón emitido es menor, quiere decir que ha transferido energía a la molécula, la cual se encontrará ahora en un estado vibracional o rotacional superior al inicial.
- **Dispersión Raman Anti-Stokes.** También para choques inelásticos, pero con frecuencias mayores del fotón. En este caso, la molécula no se encontraba en el estado fundamental, y al proporcionar energía al fotón, decae al estado de mínima energía.

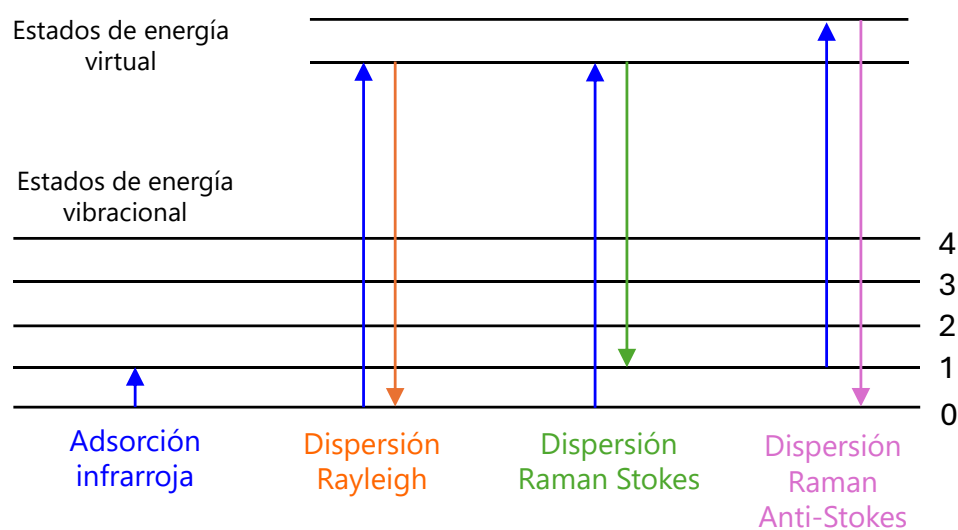


Figura 3.8. Diagrama de nivel de energía mostrando los estados implicados en la señal de Raman

Con esta técnica se puede analizar la composición química de diferentes materiales inorgánicos sin destruir las muestras y sin preparación especial. Los ensayos se realizaron en un microscopio WITec alpha300 R perteneciente al Instituto Fritz-Haber de la sociedad alemana Max Planck de Berlín, equipado con un espectrómetro UHTS300S VIS, un objetivo Zeiss EC Epiplan 10x / 0.25 y láseres WITec de 488 y 633 nm. Cada espectro se registró con una potencia de láser de 4 mW, un tiempo de integración de 0,5 s y 100 acumulaciones. Esta

técnica se emplea para identificar posibles depósitos carbonos en la superficie de los catalizadores tras las diferentes reacciones estudiadas en esta Tesis Doctoral.

3.3.9. Microscopía electrónica

La microscopía electrónica analizar los materiales a escalas muy pequeñas que van más allá de lo que la microscopía óptica tradicional puede alcanzar. Mientras que la microscopía óptica utiliza luz visible para magnificar y visualizar muestras, la microscopía electrónica emplea haces de electrones para lograr una resolución mucho mayor. La microscopía electrónica se divide principalmente en dos formas: microscopía electrónica de transmisión (TEM) y microscopía electrónica de barrido (SEM).

Microscopía electrónica de barrido

El microscopio electrónico de barrido (SEM, *Scanning Electron Microscope*) es un instrumento muy versátil, permite la observación y caracterización superficial de materiales orgánicos e inorgánicos, dando información morfológica y de composición química rápida, eficiente y simultáneamente del material analizado. Su versatilidad está dada en su alta resolución (de 20 a 50 Å) y apariencia tridimensional de las imágenes.

Estos microscopios trabajan con un haz de electrones para generar la imagen y en condiciones de alto vacío (10^{-6} torr), las partes esenciales del microscopio son: columna de electrones, consola de controles y sistema de adquisición de imágenes. En la parte superior de la columna se encuentra el emisor de electrones, que genera un haz de electrones, éste es conducido y dirigido por lentes electromagnéticas, el sistema de deflexión mueve el haz en forma de “zig zag” para hacer un barrido superficial del material, produciendo señales por la interacción del haz con el espécimen. Estas señales (rayos secundarios, rayos retro-dispersados y rayos X entre otros) son colectadas por detectores y cada uno de ellos nos brindan información específica, los rayos secundarios producen imágenes SEI (*Secondary Electron Image*) de morfología superficial de la muestra, los electrones retrodispersados producen imágenes con diferente brillantez en función de la composición química y topografía de la superficie BEI (*Backscattered Electron Image*) y los Rayos X, EDS (*Energy Dispersive Spectrometer*) obtiene información cualitativa de composición química de la muestra de manera rápida y eficiente, realizando un análisis semi-cuantitativo de los elementos detectados.

Los análisis SEM realizados se han realizado en un microscopio electrónico de barrido modelo FEI/Philips SXL30S FEG disponible en los Servicios Científico-Técnicos de la Universidad de Oviedo. (Figura 3.9). Se requieren dos condiciones para analizar muestras en un SEM: que se encuentren libres de humedad y sean conductoras. Las muestras no conductoras necesitan un recubrimiento metálico para su observación, por ello se recubren con una capa de oro cuando se quiere realizar análisis químico por EDS. Durante el desarrollo de esta Tesis Doctoral, se caracteriza mediante análisis SEM la superficie de la celulosa microcristalina y del serrín, tanto fresco como después de los pretratamientos.



Figura 3.9. Microscopio electrónico de barrido FEI/Philips SXL30S FEG

Microscopía electrónica de transmisión

Las aplicaciones de esta técnica son numerosas, entre ellas destaca el análisis de materiales nanoestructurados. Los análisis TEM realizados, se han llevado a cabo en un microscopio modelo TALOS F200X perteneciente al Instituto Fritz-Haber de la sociedad alemana Max Planck de Berlín y en un microscopio modelo JEOL-JEM 2100F perteneciente a los Servicios Científico-Técnicos de la Universidad de Oviedo (Figura 3.10).



Figura 3.10. Microscopios electrónicos de transmisión utilizados durante el desarrollo de la Tesis Doctoral. A la izquierda TALOS F200X, a la derecha JEOL-JEM 2100F

Durante el desarrollo de esta Tesis Doctoral se ha empleado para caracterizar la morfología de los diferentes tipos catalizadores bifuncionales empleados. Realizando micrografías TEM podemos distinguir la morfología del soporte de la morfología de las partículas soportadas y nos permite medir el tamaño de las partículas metálicas presentes, así como las dispersiones metálicas de las mismas en cada material.

En este tipo de microscopios, al tratarse de una muestra en polvo esta debe soportarse sobre una gradilla impregnada con nanofibras de carbono o con una membrana de silicona que permita la adhesión de la muestra. En ocasiones si la integración entre la gradilla y la muestra no es óptima, se debe preparar una suspensión del material, sonicarla varios minutos y finalmente añadir una gota en la gradilla para evitar que el material se desprenda en el interior del microscopio. Posteriormente, se introduce la muestra en el microscopio y se irradia con un haz de electrones de densidad de corriente uniforme. Los electrones interactúan fuertemente con los átomos de la muestra mediante dispersión elástica e inelástica. Por lo tanto, la muestra debe ser muy delgada, típicamente del orden de 5 a 100 nm. Un sistema de lentes condensadoras de tres o cuatro etapas permite la variación de la apertura de iluminación y el área de la muestra iluminada. Para obtener la imagen, la distribución de intensidad electrónica detrás de la muestra se visualiza con un sistema de lentes, compuesto de tres a ocho lentes en una cámara que permite aumentar la imagen hasta un millón de veces.

3.4. EQUIPO Y PROCEDIMIENTOS EXPERIMENTALES PARA LOS ESTUDIOS EN REACCIÓN

En este apartado de la presente Tesis Doctoral, se detalla el dispositivo experimental y el procedimiento utilizado para todos los estudios catalíticos en discontinuo (hidrólisis, oxidación y carboxilación).

3.4.1. Pretratamientos de celulosa y serrín de pino

En las reacciones de hidrólisis se emplean como reactivos celulosa microcristalina (MCC) y serrín de pino. Estos reactivos se someten a pretratamientos con el fin de debilitar su estructura para facilitar su conversión y, en el caso del serrín de pino, para eliminar la lignina.

Pretratamientos de la celulosa microcristalina

Se llevan a cabo pretratamientos ácidos (HCl, HNO₃) y oxidantes (H₂O₂) de la celulosa para reducir su grado de cristalinidad [16, 17]. Los reactivos empleados se adquieren en Sigma Aldrich con una pureza del 49% de HCl, el 68% de HNO₃ y del 30% de H₂O₂. Estos pretratamientos, se realizan a temperatura ambiente, consisten en atacar 10 g de celulosa microcristalina con disoluciones de 250 mL de HCl, HNO₃ y H₂O₂ de diferente concentración (1, 5, 10 y 68% en peso en el caso de los ácidos; 5 y 10% en peso en el caso del peróxido de hidrógeno) durante 6 horas. Transcurrido este tiempo, las muestras de celulosa pretratada se filtran para retirar el líquido remanente y se lavan con agua destilada hasta pH neutro para garantizar la ausencia de ácido o peróxido de hidrógeno en la muestra filtrada ya que estos compuestos pueden interferir en el posterior proceso de hidrólisis.

Pretratamientos de la biomasa lignocelulósica

Durante el desarrollo de esta Tesis Doctoral, se estudia la influencia de dos tipos de pretratamientos para reducir el contenido de lignina de la biomasa lignocelulósica: el pretratamiento oxidativo y el pretratamiento reductivo. El pretratamiento oxidativo se realiza de acuerdo con el procedimiento propuesto en la literatura por *Yu et al.* [18]. Se basa en utilizar como reactivos clorito de sodio (NaClO₂, Sigma Aldrich, ≥99%) y ácido acético (Sigma Aldrich, ≥99%) en relación masa/volumen 3:1. Inicialmente, se introducen 15 gramos de serrín de pino natural junto con 600 ml de agua destilada en un matraz de bola equipado con un condensador y un baño de agua termostatizado. Una vez que se alcanza la temperatura deseada (80 °C), se añaden 7.5 g de ácido acético y cada 30 minutos durante un total de 4h se añaden 22.5 g de clorito de sodio. Una vez finalizado el proceso, el serrín deslignificado se extrae y se lava con agua destilada hasta que el filtrado es de color transparente y finalmente se lava 3 veces más. Por último, el serrín deslignificado se seca en una estufa a 110 °C y se tamiza para obtener un tamaño de partícula de 200 µm.

Por otro lado, el pretratamiento reductivo se realiza de acuerdo con el procedimiento propuesto por *Van den Bosch et al.* [19]. En este caso, el pretratamiento se realiza en un reactor discontinuo de tanque agitado (Autoclave Engineers EZE Seal) en el que se introducen 10 gramos de serrín de pino natural junto con un catalizador comercial 5% Ru/C y 200 ml de metanol. Posteriormente, se purga la atmosfera del reactor con N₂ para eliminar el

O₂ del interior, se presuriza con H₂ hasta 25 bar a temperatura ambiente y se calienta hasta 150 °C. La reacción transcurre durante 6h con una agitación de 700 rpm. Finalmente, se recupera el sólido de la reacción filtrándolo, se lava con agua destilada, se seca en una estufa a 110 °C y se tamiza a 200 µm.

3.4.2. Reacciones de hidrólisis y oxidación

Para llevar a cabo las reacciones de hidrólisis de biomasa y oxidación de aldehídos se emplea el reactor ilustrado en la **Figura 3.11**. Está fabricado por Autoclave Engineers, es el modelo Eze Seal y consta de una vasija de acero inoxidable (SS316L) de 500 mL de capacidad. Además, tiene una vasija adicional interna de titanio para poder emplear catalizadores ácidos a pH bajo, como en el caso de la hidrólisis, evitando así posibles efectos de corrosión y proporcionando, mediante el empleo de titanio, una buena conductividad térmica. Presenta un sistema de calefacción por encamisado compuesto por una manta calefactora eléctrica de cerámica de 550W de potencia y la posibilidad de incorporar un serpentín de refrigeración interna. Permite la regulación de la temperatura mediante un sistema compuesto por dos controladores PID unidos a dos termopares tipo K, uno de ellos situado en el interior del reactor por lo que permite medir la temperatura real de la reacción; mientras que el segundo permite regular la temperatura de la manta calefactora mediante la variación de la potencia suministrada a la misma. La temperatura máxima de trabajo está limitada a 250°C. La agitación viene proporcionada por un agitador magnético de turbina controlado a través de un tacómetro que permite medir la velocidad de giro. El intervalo de agitación está comprendido entre 100 y 1400 rpm.

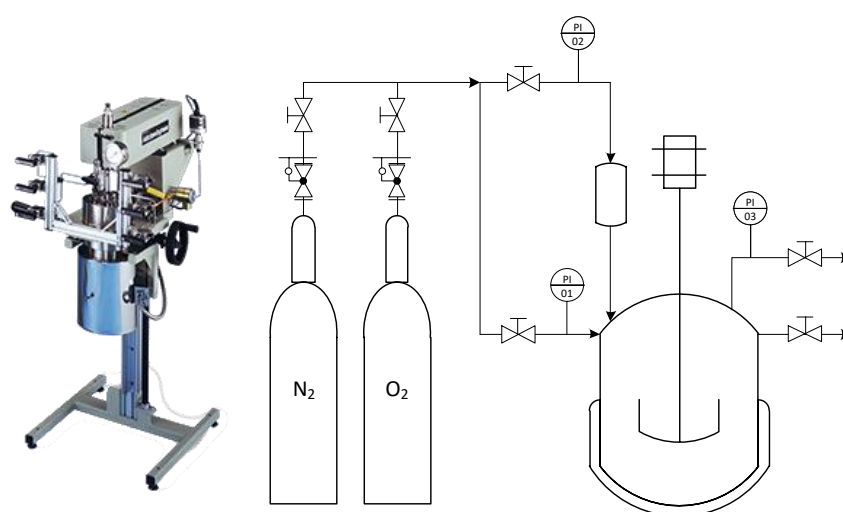


Figura 3.11. Dispositivo experimental y diagrama de flujo de Autoclave Engineers

El equipo permanece cerrado gracias a un sistema de cremallera, que, junto con una junta tórica, proporcionan estanqueidad para poder trabajar en presiones de hasta 100 bar. Dispone de un sistema de seguridad para evitar sobrepresiones compuesto por una válvula de alivio y un disco de ruptura. Por otro lado, el sistema de cierre de cremallera no permite abrir el reactor si está presurizado. Para poder extraer contenido de dentro del reactor mientras se encuentra presurizado, el dispositivo dispone de una salida de toma de muestra para recoger muestras. Esta tubería dispone de un filtro metálico que evita la pérdida de reactivo o catalizador durante la toma de muestra. Por otro lado, al reactor se le ha acoplado un sistema de alimentación adicional en su parte superior con el objetivo de poder inyectar el catalizador o el agente oxidante empleado una vez que el reactor ha alcanzado la temperatura de operación permitiendo establecer así perfectamente el tiempo de inicio de reacción.

Para llevar a cabo las reacciones se introducen los reactivos junto con el disolvente en el reactor discontinuo, se cierra el reactor empleando un sistema de manivela y se coloca la cremallera para garantizar la estanqueidad y la imposibilidad de abrir el reactor durante la reacción. A continuación, se elimina el aire del interior del reactor desplazándolo con nitrógeno u oxígeno en función de la reacción estudiada y se aumenta la presión hasta la presión de operación detallada en cada caso en el capítulo correspondiente de esta Tesis Doctoral. Se comprueba que la presión se mantiene estable y se activa la agitación y la manta calefactora. Una vez que se alcanza la temperatura de operación, con ayuda del dispositivo de alimentación adicional se agregan los catalizadores. En el caso de la hidrólisis de celulosa o biomasa lignocelulósica, a través del embudo de alimentación se añade la zeolita β y el HCl. Cuando se llevan a cabo reacciones de oxidación de FFL, el peróxido se introduce de forma análoga.

En las reacciones de hidrólisis, se emplea como reactivo una suspensión acuosa del 25% de celulosa (sin tratar o pretratada según los experimentos), y un 4% de zeolita β . En las reacciones de hidrólisis de serrín, se emplea un 1.5% de serrín en suspensión en cada ensayo. La reacción transcurre a 10 bar de N_2 . La concentración de ácido, así como la temperatura, dependen del experimento y se especifican en el Capítulo 4 de esta Tesis Doctoral.

Para las reacciones de oxidación de furfural con peróxido de hidrógeno, se emplea como reactivo 250ml de una disolución acuosa al 0.5M de furfural y 1.5M de H_2O_2 . En las

reacciones de oxidación con O_2 , se alimenta el reactor con una disolución acuosa 0.5 M de FFL el pH de la disolución inicial es 4.8 y se modifica empleando una disolución tampón $KHCO_3$ para ajustarlo a pH 8. En el caso de oxidación de HMF, se emplea como reactivo una disolución acuosa de HMF y NaOH (Sigma Aldrich, 99%) con diferentes concentraciones (de 0.1 a 0.01 M) y relaciones relativas (de 4:1 a 1:1) en función del experimento. En los estudios de oxidación de mezclas, se introduce en el autoclave una solución acuosa de HMF y FFL a la concentración inicial deseada y NaOH. En todas las reacciones de oxidación introduce una carga de catalizador de un 0.2%. Las presiones en cada caso se indican en la sección de resultados (Capítulo 4).

3.4.3. Reacciones de carboxilación

En las reacciones de carboxilación se emplea un reactor análogo, pero de menor volumen (50 ml, Parr 4590) y se plantean experimentos en ausencia de disolvente en los cuales se introducen 0.05 moles de la sal correspondiente, furoato de cesio (F-Cs) o difuroato de cobre ($Cu(F)_2$), y 0.05 moles de carbonato de cesio en el reactor previamente calentado (150 °C). A continuación, se cierra el reactor, se presuriza con CO_2 y se lleva con ayuda de una manta calefactora a la temperatura deseada. Cuando se emplean disolventes se introducen en el reactor 30ml de una disolución de F-Cs o $Cu(F)_2$ y Cs_2CO_3 en relación 1:1 y posteriormente se presuriza y se calienta hasta 170 °C.

3.5. TÉCNICAS DE ANÁLISIS

Para la cuantificación de los productos de reacción de las muestras obtenidas del reactor de forma periódica, se han empleado diferentes técnicas de cromatografía. Esta técnica se basa en el principio de la retención selectiva, que consiste en el distinto comportamiento de los componentes de una mezcla sobre un soporte específico alojado en una columna de cromatografía. Cuanto más fuertemente se adsorbe un soluto, más lentamente atraviesa la columna y por lo tanto mayor será su tiempo de retención.

Debido a la naturaleza de los procesos estudiados y al hecho de trabajar empleando agua como disolvente, para el análisis cualitativo de las muestras se han empleado dos tipos de cromatografía: cromatografía de gases (GC) y cromatografía de líquidos (HPLC).

3.5.1. Análisis mediante cromatografía de gases

En este tipo de cromatografía, la muestra se volatiliza y se inyecta en la columna, fluyendo a través de esta con un flujo controlado de gas portador, generalmente helio. En función de la interacción de los diferentes reactivos y productos los componentes se separan a lo largo de la columna y finalmente llegan al detector que genera una señal en función de la concentración del producto químico que se puede relacionar con un calibrado para obtener el valor exacto de concentración. En este trabajo se ha utilizado en concreto un detector de espectrometría de masas (MS). En concreto, durante el desarrollo de esta Tesis Doctoral, se empleó un GC-MS Shimadzu, modelo GC-MS QP2010 Plus Instrument, equipado con una columna capilar tipo TRB-5MS de 30 metros de longitud como el que se muestra en la **Figura 3.12.**



Figura 3.12. Cromatógrafo de gases empleado para identificación de compuestos. GC-MS QP2010 Plus Instrument.

Para obtener un espectro de masas, las moléculas gaseosas o las especies desorbidas de fases condensadas se ionizan, los iones se aceleran en un campo eléctrico y a continuación, se separan según su relación masa/carga (m/z). Cada ion que llega al detector pasa por un multiplicador de electrones que mediante una serie de dinodos desencadena una cascada de electrones antes de llegar al ánodo, donde se mide la corriente dando lugar al espectro de masas donde se representa la abundancia iónica de cada componente en función de la relación m/z . Un pico se puede identificar comparando su espectro con los de una librería de espectros guardados en el ordenador. El espectro de masas es extremadamente sensible. La

espectrometría de masas requiere un alto vacío, para evitar las colisiones moleculares durante la separación de iones. Mediante una rampa de temperatura se consigue que eluyan todos los compuestos evitando así que algunos queden retenidos en el interior de la columna, y una separación de picos más o menos uniforme. Para el análisis se empleó un volumen de inyección de 1 µL de muestra, una columna de polaridad media: CP-Sil 5CB de 15 metros de longitud y 0,15 mm de espesor. Los detalles del método se muestran a continuación, en las **Tablas 3.2-4.**

Tabla 3.2. Parámetros empleados en el método de análisis en GC.

Inyección	Temperatura de inyección (°C)	250
	Presión (bar)	0.99
	Flujo total (mL·min ⁻¹)	43.9
Columna	Flujo en columna (mL·min ⁻¹)	1.35
	Ratio de Split	31.4
	Gas portador	Helio
Detector	Tipo	FID
	Temperatura (°C)	250
	Make up (N ₂ /aire, mL·min ⁻¹)	30
	Flujo de H ₂ (mL·min ⁻¹)	40
	Flujo de aire (mL·min ⁻¹)	400

Tabla 3.3. Rampa de temperaturas empleado en el análisis mediante GC-MS de las muestras de hidrólisis.

Rampa (°C·min ⁻¹)	Temperatura (°C)	Tiempo (min)
-	35	2
0.5	37	0
20	82	0
10	190	5
10	220	15
25	260	3
	Tiempo total	46.65

Tabla 3.4. Rampa de temperaturas empleado en el análisis mediante GC-MS de las muestras de oxidación.

Rampa (°C·min ⁻¹)	Temperatura (°C)	Tiempo (min)
-	33	2
0.5	37	0
10	44	0
12	62	0
4	100	5
30	250	2
Tiempo total		28.70

Una vez obtenidos los correspondientes valores de concentración a partir de las áreas de cada pico en los cromatogramas de cada uno de los reactivos y productos, se aplica la metodología detallada en cada uno de los capítulos de resultados de esta Tesis Doctoral para el cálculo de selectividades, rendimientos, conversiones y balances al carbono.

3.5.2. Análisis mediante cromatografía de líquidos

La cromatografía de líquidos de alta eficacia (HPLC) utiliza una presión elevada para forzar al disolvente a que pase por una columna que contiene partículas muy finas, consiguiendo así separaciones de gran resolución. Los equipos típicos de HPLC constan de un sistema de suministro de disolvente, una válvula de inyección de muestra, una columna de alta presión, un detector y un ordenador para controlar el equipo y visualizar los resultados además de un horno para controlar la temperatura de la columna.

Para los análisis llevados a cabo, se ha empleado un detector de índice de refracción (RID) ya que responde casi a cualquier soluto, permitiendo la identificación simultánea de azúcares, aldehídos y ácidos. Consta de dos compartimentos de 5 a 10 mL, a través de uno pasa disolvente puro y a través del otro la muestra. Para eliminar la radiación infrarroja (que calentaría la muestra), se hace pasar luz visible colimada (paralela) a través de la celda, con disolvente puro en los dos compartimentos, y se dirige a la fotocélula mediante una placa de deflexión. Cuando a la celda entra un soluto de diferente índice de refracción, el haz se desvía y la señal dada por la fotocélula varía.

Los detectores de índice de refracción no sirven para llevar a cabo una elución con gradientes, porque es imposible ajustar exactamente la muestra y la referencia mientras varía la composición del disolvente.

En este caso, el equipo empleado ha sido un cromatógrafo de líquidos de alta eficacia HPL Agilent-1200 como el que se muestra en la **Figura 3.13**, equipado con un desgasificador para eliminar posibles burbujas presentes en la fase móvil, una bomba cuaternaria de pistones, un sistema de inyección automática a través de la cual se introducen 20 μ L de muestra en el seno de la fase móvil, una columna situada en el interior de un horno que permite controlar la temperatura a la cual ocurre la elución y un detector de índice de refracción (RID), el cual que responde casi a cualquier soluto, permitiendo la identificación simultánea de azúcares, aldehídos y ácidos.



Figura 3.13. Cromatógrafo de líquidos empleado para la cuantificación de productos y reactivos Agilent 1200

El detector, consta de dos compartimentos de 5 a 10 mL, a través de uno pasa disolvente puro y a través del otro la muestra. Para eliminar la radiación infrarroja (que calentaría la muestra), se hace pasar luz visible colimada (paralela) a través de la celda, con disolvente puro en los dos compartimentos, y se dirige a la fotocélula mediante una placa de deflexión. Cuando a la celda entra un soluto de diferente índice de refracción, el haz se desvía y la señal dada por la fotocélula varía. Los detectores de índice de refracción no sirven para llevar a cabo una elución con gradientes, porque es imposible ajustar exactamente la muestra y la referencia mientras varía la composición del disolvente. Además, consta de un detector adicional de absorción a diferentes longitudes de onda (DAD), este tipo de detector utiliza una rejilla para dispersar la luz en una matriz de fotodiodos después de que la luz ha pasado a través de la celda de flujo. Por lo tanto, la absorción se produce simultáneamente en todas las longitudes de onda, proporcionando un espectro de absorción completo del analito.

El método analítico empleado es análogo al de numerosos estudios que analizan derivados de biomasa, FFL o HMF [20]. En concreto, se emplea una disolución acuosa 0.005 M de H_2SO_4 como fase móvil. Se inyectan 20 μL de muestra en la columna Hipler-H (7.7 x 300 mm, 8 μm) cuya temperatura se encuentra a 50 °C siendo ésta, la misma temperatura utilizada en el detector. Las muestras fueron filtradas mediante filtros de jeringa de 0.22 μm y se les aplica un factor de dilución 1:2 o 1:4 en función de la reacción estudiada. Una vez que se han obtenido los cromatogramas con las áreas correspondientes, es necesario realizar los calibrados correspondientes para calcular la concentración tanto de los reactivos como de los productos. Cuando los datos de concentración son conocidos, se pueden calcular distintos parámetros como selectividades, conversiones, rendimientos y balances al carbono, entre otros. El procedimiento de cálculo de cada uno de estos parámetros depende en gran medida de la reacción estudiada por lo que se detalla en cada uno de los capítulos de resultados que componen esta Tesis Doctoral.

3.6. MODELIZACIÓN CINÉTICA

Para garantizar que las reacciones estudiadas se desarrollaran bajo un control cinético intrínseco, se seleccionaron cuidadosamente las condiciones de reacción. En primer lugar, se utilizó una distribución de tamaño de partícula del catalizador muy pequeña, en el rango de 50–80 μm . Este tamaño reducido de las partículas asegura que las limitaciones difusionales internas sean mínimas, permitiendo que la reacción esté dominada por la cinética de la superficie activa del catalizador.

Además, se empleó una alta velocidad de agitación de 700 rpm durante los experimentos. Esta velocidad fue seleccionada después de realizar pruebas comparativas empleando un modelo de ensayo catalítico para cada reacción a diferentes velocidades de agitación (600 y 1400 rpm). No se observaron diferencias significativas en la conversión ni en la selectividad de los productos al variar la velocidad de agitación, con diferencias menores al 3%. Esto sugiere que, a 700 rpm, se logra una agitación suficientemente vigorosa para evitar limitaciones difusionales externas y asegurar que la reacción se desarrolle bajo un control cinético intrínseco. Con estas consideraciones se asegura que los datos experimentales

obtenidos reflejan de manera precisa la cinética intrínseca del proceso catalítico, permitiendo una modelización matemática confiable.

Para llevar a cabo la modelización cinética del proceso, se empleó MATLAB, una plataforma de programación y cálculo numérico ampliamente utilizada en diversas disciplinas científicas e ingenieriles. MATLAB, acrónimo de "MATrix LABoratory", es un entorno de programación de alto nivel que facilita la manipulación de matrices, la visualización de datos, la implementación de algoritmos y la creación de modelos matemáticos complejos. Su versatilidad y capacidad para resolver ecuaciones diferenciales y optimizar parámetros lo hacen especialmente adecuado para estos estudios.

Los modelos cinéticos se presentan como un sistema de ecuaciones diferenciales ordinarias (ODEs) que describen matemáticamente los diferentes mecanismos propuestos. Para este propósito, se empleó la función "ode45", que es un integrador basado en el método de Runge-Kutta de orden variable, ideal para la resolución de ODEs de primer orden no lineales. Todos los datos experimentales obtenidos fueron considerados en estos cálculos para garantizar que los resultados obtenidos reflejen fielmente el comportamiento de todos los catalizadores evaluados en los experimentos. Este enfoque permitió una representación precisa y global de los fenómenos cinéticos, obteniéndose en todos los casos coeficientes de regresión superiores a 0.9.

El ajuste de los parámetros desconocidos del modelo se realizó utilizando el método de mínimos cuadrados. Para ello, se empleó la función "lsqcurvefit" de MATLAB, que facilita el ajuste de curvas no lineales a los datos experimentales. Este ajuste se realizó utilizando el algoritmo de Levenberg-Marquardt, lo que permitió obtener una descripción matemática detallada y ajustada del mecanismo de reacción propuesto.

3.7. REFERENCIAS

- [1] R.E. Patet, M. Koehle, R.F. Lobo, S. Caratzoulas, D.G. Vlachos, General Acid-Type Catalysis in the Dehydrative Aromatization of Furans to Aromatics in H-[Al]-BEA, H-[Fe]-BEA, H-[Ga]-BEA, and H-[B]-BEA Zeolites, *The Journal of Physical Chemistry C* **2017** (121) 13666-13679. <https://doi.org/10.1021/acs.jpcc.7b02344>

- [2] T. Xie, S. Yue, T. Su, M. Song, W. Xu, Y. Xiao, Z. Yang, C. Len, D. Zhao, High selective oxidation of 5-hydroxymethyl furfural to 5-hydroxymethyl-2-furan carboxylic acid using Ag-TiO₂, *Molecular Catalysis* **2022** (525) 112353. <https://doi.org/10.1016/j.mcat.2022.112353>
- [3] A. Lolli, R. Amadori, C. Lucarelli, M.G. Cutrufello, E. Rombi, F. Cavani, S. Albonetti, Hard-template preparation of Au/CeO₂ mesostructured catalysts and their activity for the selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, *Microporous and Mesoporous Materials* **2016** (226) 466-475. <https://doi.org/10.1016/j.micromeso.2016.02.014>
- [4] R. López-Asensio, J.A. Cecilia-Buenestado, C. Herrera-Delgado, M.Á. Larrubia-Vargas, C. García-Sancho, P.J. Maireles-Torres, R. Moreno-Tost, Mixed Oxides Derived from Hydrotalcites Mg/Al Active in the Catalytic Transfer Hydrogenation of Furfural to Furfuryl Alcohol, *Catalysts* **2023** (13) 45. <https://doi.org/10.3390/catal13010045>
- [5] C.M. Pichler, M.G. Al-Shaal, D. Gu, H. Joshi, W. Ciptonugroho, F. Schüth, Ruthenium Supported on High-Surface-Area Zirconia as an Efficient Catalyst for the Base-Free Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid, *ChemSusChem* **2018** (11) 2083-2090. <https://doi.org/10.1002/cssc.201800448>
- [6] C. Ampelli, G. Centi, C. Genovese, G. Papanikolaou, R. Pizzi, S. Perathoner, R.J. van Putten, K.J.P. Schouten, A.C. Gluhoi, J.C. van der Waal, A Comparative Catalyst Evaluation for the Selective Oxidative Esterification of Furfural, *Topics in Catalysis* **2016** (59) 1659-1667. <https://doi.org/10.1007/s11244-016-0675-y>
- [7] T. Pirmohamed, J.M. Dowding, S. Singh, B. Wasserman, E. Heckert, A.S. Karakoti, J.E.S. King, S. Seal, W.T. Self, Nanoceria exhibit redox state-dependent catalase mimetic activity, *Chemical Communications* **2010** (46) 2736-2738. <http://doi.org/10.1039/B922024K>
- [8] J. Quesada, R. Arreola-Sánchez, L. Faba, E. Díaz, V.M. Rentería-Tapia, S. Ordóñez, Effect of Au nanoparticles on the activity of TiO₂ for ethanol upgrading reactions, *Applied Catalysis A: General* **2018** (551) 23-33. <https://doi.org/10.1016/j.apcata.2017.12.004>
- [9] S. Eaimsumang, S. Wongkasemjit, S. Pongstabodee, S.M. Smith, S. Ratanawilai, N. Chollacoop, A. Luengnaruemitchai, Effect of synthesis time on morphology of CeO₂ nanoparticles and Au/CeO₂ and their activity in oxidative steam reforming of methanol, *Journal of Rare Earths* **2019** (37) 819-828. <https://doi.org/10.1016/j.jre.2018.11.010>
- [10] O.V. Larina, K.V. Valihura, P.I. Kyriienko, N.V. Vlasenko, D.Y. Balakin, I. Khalakhan, T. Čendak, S.O. Soloviev, S.M. Orlyk, Successive vapour phase Guerbet condensation of ethanol and 1-butanol over Mg-Al oxide catalysts in a flow reactor, *Applied Catalysis A: General* **2019** (588) 117265. <https://doi.org/10.1016/j.apcata.2019.117265>
- [11] M.A. Aramendía, V. Borau, C. Jiménez, A. Marinas, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Magnesium-containing mixed oxides as basic catalysts: base characterization by carbon dioxide TPD-MS and test reactions, *Journal of Molecular Catalysis A: Chemical* **2004** (218) 81-90. <https://doi.org/10.1016/j.molcata.2004.04.006>
- [12] R. Zanella, S. Giorgio, C.-H. Shin, C.R. Henry, C. Louis, Characterization and reactivity in CO oxidation of gold nanoparticles supported on TiO₂ prepared by deposition-precipitation with NaOH and urea, *Journal of Catalysis* **2004** (222) 357-367. <https://doi.org/10.1016/j.jcat.2003.11.005>

- [13] K.S.W. Sing, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984), *Pure and Applied Chemistry* **1985** (57) 603-619. <https://doi.org/10.1351/pac198557040603>
- [14] M. Králik, Adsorption, chemisorption, and catalysis. *Chemical Papers* 2014 (68) 1625-1638. <https://doi.org/10.2478/s11696-014-0624-9>
- [15] L.O. Paz-Borbon, R.L. Johnston, G. Barcaro, A. Fortunelli, Chemisorption of CO and H on Pd, Pt and Au nanoclusters: a DFT approach. *The European Physical Journal D* 2009 (52) 131-134. <https://doi.org/10.1140/epjd/e2009-00041-9>
- [16] S. Van de Vyver, J. Geboers, P.A. Jacobs, B.F. Sels, Recent Advances in the Catalytic Conversion of Cellulose, *ChemCatChem* **2011** (3) 82-94. <https://doi.org/10.1002/cctc.201000302>
- [17] S.J.S. JingJing, Z.H.Z. HongXiang, W.L.W. LiJun, L.X.L. XinLiang, N.S.N. ShuangXi, X.J.X. JianHua, Optimization of microwave-hydrogen peroxide pretreatment of cellulose, *BioResources* **2016** (11) 7416–7430. <https://doi.org/10.15376/biores.11.3.7416-7430>
- [18] Z. Yu, H. Jameel, H.-m. Chang, S. Park, The effect of delignification of forest biomass on enzymatic hydrolysis, *Bioresource Technology* **2011** (102) 9083-9089. <https://doi.org/10.1016/j.biortech.2011.07.001>
- [19] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S.F. Koelewijn, T. Renders, B. De Meester, W.J.J. Huijgen, W. Dehaen, C.M. Courtin, B. Lagrain, W. Boerjan, B.F. Sels, Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps, *Energy & Environmental Science* **2015** (8) 1748-1763. <http://doi.org/10.1039/C5EE00204D>
- [20] A. Toftgaard Pedersen, R. Ringborg, T. Grotkjær, S. Pedersen, J.M. Woodley, Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose–fructose mixtures, *Chemical Engineering Journal* **2015** (273) 455-464. <https://doi.org/10.1016/j.cej.2015.03.094>



4. RESULTS AND DISCUSSION



This PhD is focused on developing the full process to obtain FDCA from lignocellulosic biomass, according to the different steps outlined in **Figure 4.1**.

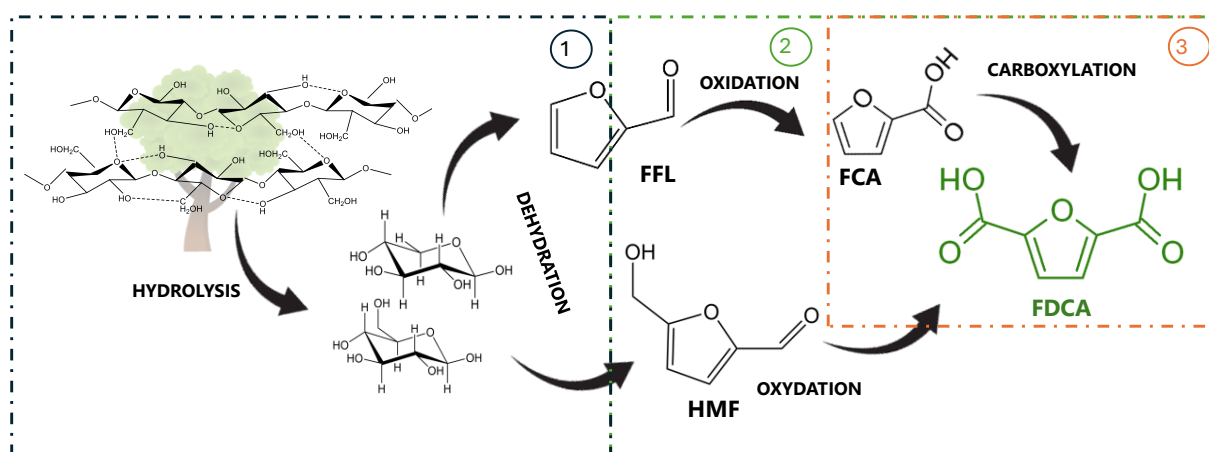
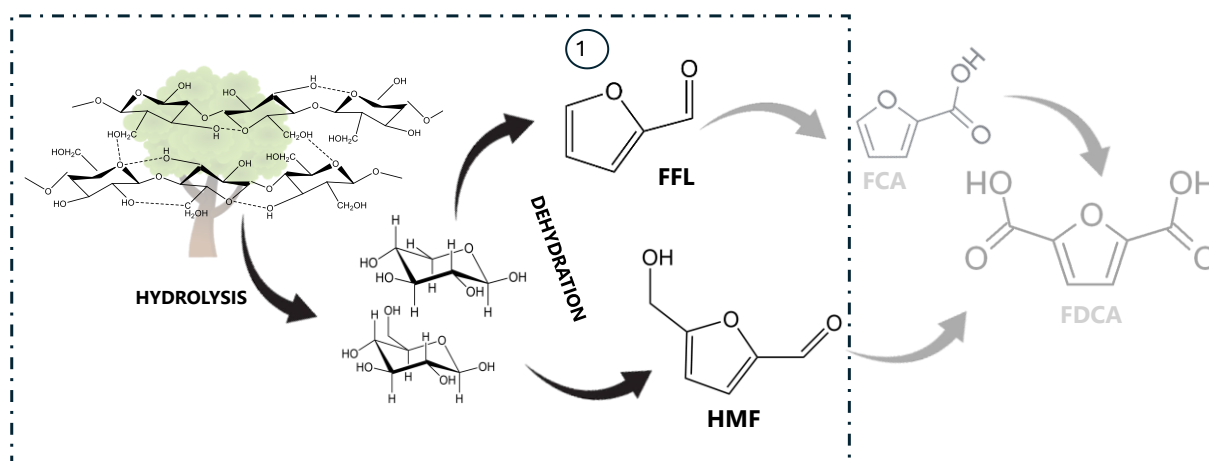


Figure 4.1. Pathway for the transformation of biomass into FDCA numbering the stages studied in the present PhD

The conversion of lignocellulosic biomass into FDCA requires a first step of hydrolysis to obtain carbohydrates by breaking the complex structure of this natural polymer. Previous pretreatments of this raw material to remove the lignin fraction is crucial to increase the efficiency of this step. The sugars are subsequently dehydrated to produce furfural (FFL) and 5-hydroxymethylfurfural (HMF). Using acid catalysts, both hydrolysis and dehydration are performed simultaneously. The oxidation of these intermediates leads to the formation of furoic acid (FCA) and FDCA, respectively. The conversion of FCA to FDCA requires an additional carboxylation step to introduce the necessary carboxyl groups.



4.1. PRODUCTION OF 5-HYDROXYMETHYLFURFURAL BY PRETREATED CELLULOSES HYDROLYSIS

Based on the conclusions of the previous literature, this work evaluates the cellulose hydrolysis using a bi-catalytic system, HCl and β -zeolite, to guarantee the Lewis and Bronsted acidity required to maximize the 5-hydroxymethylfurfural (HMF) productivity reducing the severity of the process. This zeolite has been chosen based on a previous work where the activity of different zeolites for glucose dehydration has been studied [1]. Three chemical pretreatments are considered: HCl, which introduces acidity; H_2O_2 , with oxidizing activity; and HNO_3 , which combines both effects. The influence on conversion and product distribution was studied as a function of the chemical dosage.

Results were described in terms of conversion, carbon balance closure and selectivity. The cellulose conversion is calculated in terms of liquid-phase carbon yield, i.e., the theoretical cellulose required to obtain all compounds detected in the liquid phase (cellobiose and maltose, glucose, HMF, formic and levulinic acid), according to Equation (4.1):

$$x_c = \frac{[V \cdot \sum (n_i \cdot C_i)]_{aq}}{0.4421 \cdot \frac{m_{cellulose}}{M_{cellulose}}} \quad [4.1]$$

where x_c is the liquid-phase carbon conversion, V is the total reaction volume, C_i the molar concentration of each compound detected in liquid phase, n_i the number of carbons in the

molecule of compound i , $m_{cellulose}$ the mass of cellulose introduced in the reactor (5.83 g), $M_{cellulose}$ the molar mass of cellulose (162 g/mol), and 0.4421 corresponds to the atomic percentage of carbon in this cellulose, according to results obtained by ICP analysis of the raw material (44.21% C, 6.2% H, 49.59% O).

Carbon balance closure (C.B.) and selectivity were calculated as follows:

$$C.B. (\%) = \frac{\sum_{i=1}^n m_{C_i} + m_{C_t}}{m_{C_{t=0}}} \cdot 100 \quad [4.2]$$

where $\sum_{i=1}^n m_{C_i}$ is the sum of the carbon mass present in all the reaction products; $m_{C_{t=0}}$ is the mass of carbon present in the cellulose initially introduced into the reactor; and m_{C_t} is the carbon mass of the cellulose collected by filtering and drying after the reaction.

$$S_i (\%) = \frac{n_i}{\sum_{j=1 \dots i}^n n_i} \cdot 100 \quad [4.3]$$

where n_i is the moles of carbon that contains the reaction product i and $\sum_{j=1 \dots i}^n n_i$ is the sum of the moles of carbon corresponding to reaction products.

4.1.1. Hydrolysis of the non-pretreated cellulose

The initial experiments evaluate the influence of HCl on cellulose hydrolysis in the presence of β -zeolite to identify the optimum concentration of this homogeneous catalyst considering the equilibrium between activity, selectivity, and process sustainability. By sustainability criteria, a maximum value of 0.4% w/w (400 mg/L) was established to prevent corrosive effects in the equipment and to guarantee that the wastewater produced could be assimilated to a municipal wastewater stream, being far from the maximum allowed by the normative (2000 mg/L in the Spanish laws). It is expected that these low concentrations also minimize levulinic acid production (promoted by strong acidity). All reactions were performed in the presence of β zeolite to promote the HMF formation by the glucose isomerization route. This study is the first one reporting the co-utilization of homogeneous and heterogeneous acids for treating polymeric biomaterials. Results are analyzed in **Figure 4.2**.

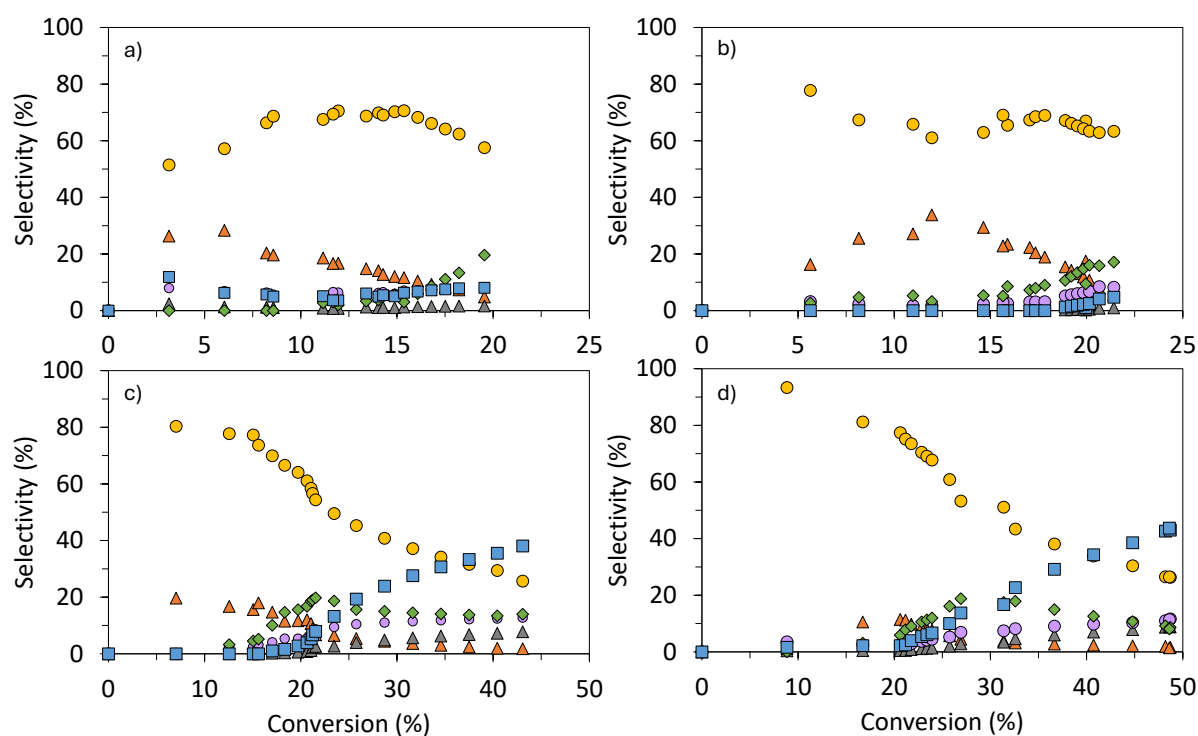


Figure 4.2. Selectivity vs. conversion plots obtained for the cellulose hydrolysis at 140 °C using 8% β -zeolite as a function of the HCl concentration: (a) absence of HCl; (b) 0.005%; (c) 0.02%; (d) 0.04%.

Symbols: (●) dimers; (▲) glucose; (◆) HMF; (●) AHG; (■) levulinic acid

The results shown in Fig. 4.2 are in good agreement with the general hydrolytic mechanism. Thus, dimers (mainly cellobiose but traces of maltose are also detected) are the first products obtained in the reaction, with very high selectivities at low cellulose conversion. The presence of heavier oligomers cannot be discarded but they cannot be analyzed because of their insoluble character (only the liquid phase is analyzed). For those reactions with low acidity, the initial selectivity of dimers is not 100% (close to 80%) because of the presence of glucose, even at very low conversions. This fact suggests the existence of terminal anhydroglucose units weakly linked to the general polymeric structure. These terminal units are easily hydrolyzed, resulting in an initial mixture containing oligomers but also glucose, as previously reported in the literature [2]. When using 0.02 and, mainly, 0.04%w/w, the high acidity increases the hydrolytic rate, and the relative weight of this glucose decreases because of the higher concentration of cellobiose.

As the reaction progresses, the decreasing selectivity of these dimers observed (more pronounced at higher acidity) is compatible with their hydrolysis into monomeric units. This behavior suggests that the hydrolysis at these diluted acidic conditions is limited, making

total conversion not possible to reach. In fact, cellulose conversion never exceeds 50%, although results with 0.04% demonstrate the advance of the reaction to subsequent steps once reached this threshold. According to the literature, glucose suffers dimerization in an acidic medium, establishing an equilibrium with cellobiose [3, 4]. Analyzing the results in concentration units (see **Figure 4.3**), this contribution cannot be discarded.

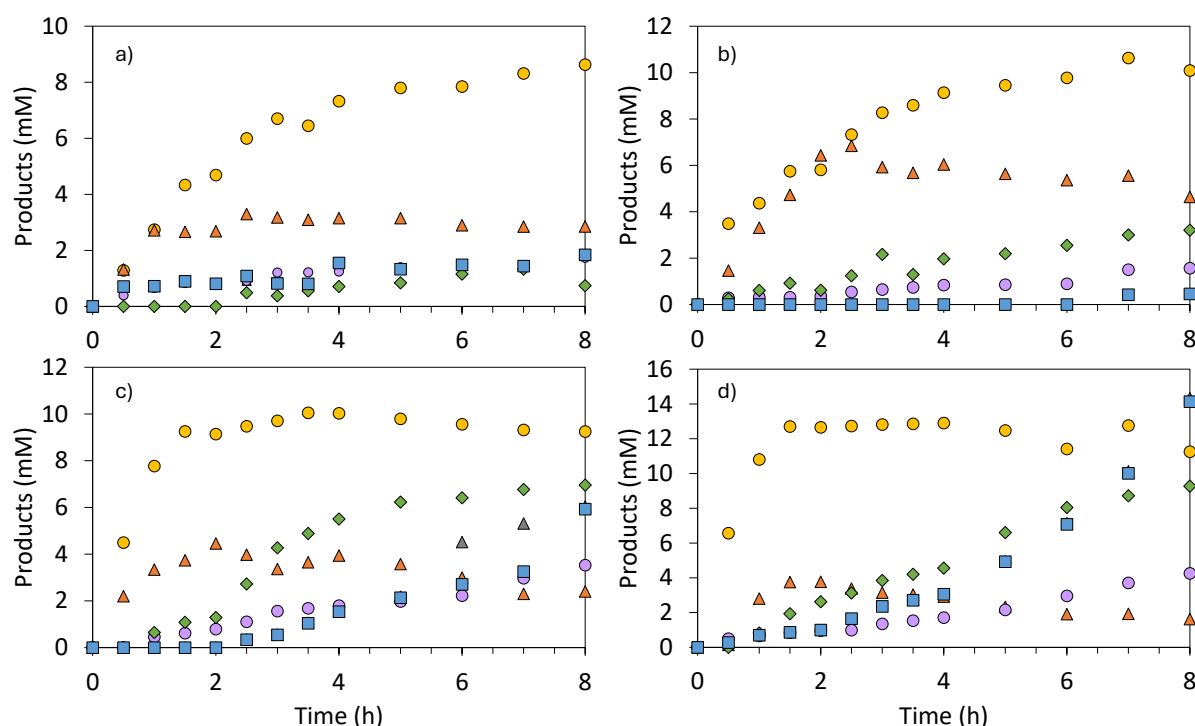


Figure 4.3. Products evolution obtained for the cellulose hydrolysis at 140 °C using 8% β -zeolite as a function of the HCl concentration: (a) absence of HCl; (b) 0.005 %; (c) 0.02 %; and (d) 0.04 %.

Symbols: (●) dimers; (▲) glucose; (◆) HMF; (●) AHG; (■) levulinic acid

Glucose selectivity decreases with the advance of the reaction because of the simultaneous appearance of two different compounds: HMF and anhydroglucose (AHG). Both compounds are obtained by glucose dehydration, being catalyzed by the same acidic sites. In the presence of β zeolite, HMF prevails over AHG because the Lewis acidity of the zeolite promotes the previous glucose isomerization into fructose, a requirement to promote the pathway to HMF, according to the literature [5, 6]. However, fructose is not included in Fig. 4.2 since its selectivity is always lower than 1% (it dehydrates rapidly).

AHG is a final product, with a soft but continuous increasing trend. On the other hand, HMF can suffer rehydration, mainly under strong acidity, obtaining levulinic and formic acids.

Both compounds are equimolar produced, their differences in selectivity being explained by the equation used (in carbon basis). These compounds are very relevant when cellulose conversion exceeds 30%.

This analysis was done considering theoretical cellulose conversion since its solid character makes its sampling impossible with the actual reaction system. To evaluate the carbon balance and determine the representativeness of these results, the reactions were repeated, reducing the time to 8 h (time that is expected to be the optimum one to maximize the HMF selectivity). The temporal profiles show (Fig 4.3) a discrepancy lower than 5% between both repetitions. **Figure 4.4** compares the results obtained after 8 h, in this case considering the conversion as the difference in weight between the initially introduced solid and the one recovered after the reaction. The recovered solids maintain their white color, discarding the presence of adsorbed humins, polymers obtained from glucose derivatives under high temperature and/or acidity [7, 8].

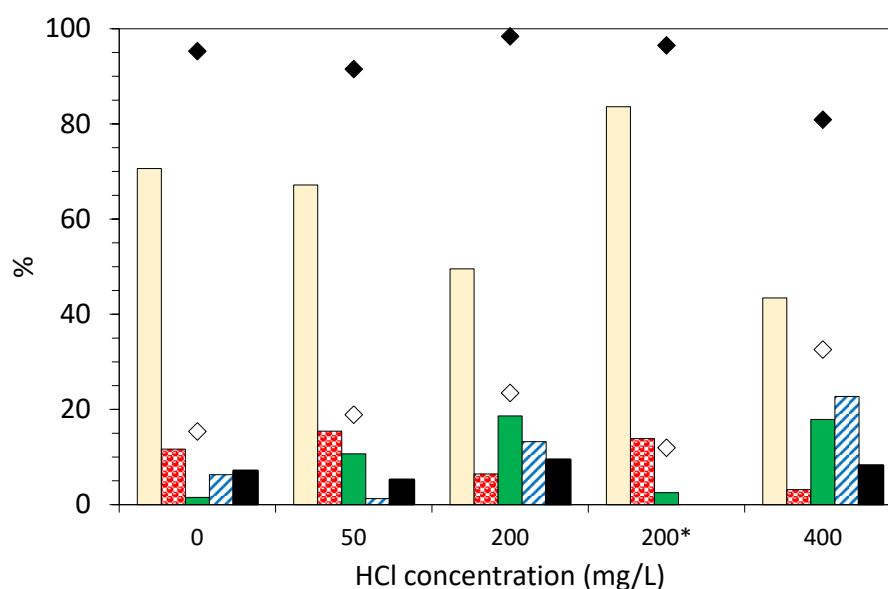


Figure 4.4. Cellulose conversion (◇), carbon balance (◆) and products selectivity obtained in the cellulose hydrolysis at 140 °C using 8% of zeolite as a function of the amount of HCl. Bars corresponding to dimer (yellow), glucose (red bubbles), HMF (green), levulinic acid (blue lines) and anhydroglucose (black). (*) Experiment in the absence of zeolite

The reaction performed in the absence of HCl mainly produces the dimer (9 mM), the compound that represents 70.6% of the products detected. Glucose is also obtained, being 11.7% selectivity. In the absence of any catalyst, the dehydration is almost negligible, HMF

being less than 3% of the total products. The high carbon balance (95.3%) indicates the representativeness of these data, suggesting that the production of soluble humins or other undetected liquid compounds is not very relevant.

The positive action of HCl is observed, leading to a linear dependence of cellulose conversion on acid concentration, from 15.4% in the absence of HCl to 32.6% when working with 0.04% of this acid (results after 8 h). The concentration of glucose dimer (cellobiose) remains almost constant despite the amount of HCl present, reaching final values (9-10 mM). These values are far from the maximum solubility of this compound (1g/mL) discarding the saturation of the sample. Acidity also promotes the HMF formation and the selectivity toward this compound rises to 10.7, 16.4, and 17.9%, with 0.005, 0.02, and 0.04% of HCl, respectively. At 0.02, and 0.04% of HCl, the rehydration of this compound is significantly promoted, levulinic and formic acid being the majority compounds detected (31.3 and 40.6 mM, selectivities of 13.6 and 22.7%, respectively). The good carbon balances obtained when working at 0.005 and 0.02% of HCl (91.5 and 98.4%) demonstrate a high control of the reaction. On the contrary, the significant depletion observed at 0.04% (80.9%) suggests that a relevant amount of cellulose is transformed into soluble humins. In global terms, 0.02% of HCl (pH 2.03) is suggested as the optimum acidity to enhance the HMF production.

As introduced before, fructose is only detected in traces. To identify if this fact is due to a null activity of the zeolite (i.e., all the HMF is produced directly by glucose dehydration) or if the fructose dehydration is so fast that fructose instantaneously disappears, a particular experiment with 0.02% of HCl but in the absence of zeolite is performed (see Fig. 4.4). Results after 8h demonstrate the relevance of these Lewis sites. When no zeolite is included, the HMF selectivity decreases by more than 84% (from 16.4 to 2.5%). Moreover, conversion is reduced by half in absence of zeolite, and the final mixture is enriched in dimers (83.6%), indicating the greater difficulty of breaking these structures and allowing the reaction to progress toward the final products. These effects are assumed to be due to the presence of Bronsted sites in the zeolite (proton form). Thus, solid cellulose particles migrate to the surface of the zeolite, which donates protons. The solid protonated cellulose on the surface of cellulose particles can degrade since part of it can dissolve and react with water. The corresponding chemisorption of oligomers justifies the improvement in glucose production, whereas the increase in HMF is justified by the previously mentioned role of Lewis sites. This experiment

also corroborates the dimerization equilibrium between glucose and cellobiose since comparing the results at the same cellulose conversion, the total yield to products obtained without the zeolite is significantly lower than with it. As dehydration steps consume glucose, this equilibrium is shifted.

To sum up, both catalysts (HCl and zeolite) contribute to all the steps of the hydrolysis of cellulose. Increasing the acidity is discarded as a valid option to promote HMF production since the impact on the levulinic acid formation is more relevant, with the subsequent decrease in the HMF selectivity. Thus, increasing the HMF concentration and selectivity requires evaluating other options, such as modifying the temperature, considering cellulose pretreatments to increase the hydrolysis capacity, or working with biphasic systems that could selectively extract the HMF to prevent its decomposition into levulinic and formic acid.

4.1.2. Influence of the severity of the reaction conditions

According to the literature, temperatures lower than 200-220 °C limit the depolymerization of cellulose only to its amorphous content [9]. However, the presence of levulinic acid is relevant at 140 °C and higher temperatures are assumed to increase its production. Thus, higher temperatures are not considered in this work, trying to balance the thermal activation by the co-presence of two catalysts (HCl and β zeolite). Two lower temperatures were studied (120 and 130 °C) considering that these conditions could minimize the HMF rehydration [3], increasing the selectivity by reducing its degradation into levulinic and formic acid. The main results after 8h are summarized in **Figure 4.5**.

As expected, cellulose conversion decreases when reducing the temperature (from 23.1 to 14.9%, from 140 to 120 °C). Higher temperatures promote all the steps, decreasing the dimer selectivity (from 60.4 to 50.9) and increasing the final products, levulinic and formic acids (from 6.6 to 13.6%). As to HMF, its selectivity is maximum at 130 °C (19.6%) but differences are not relevant enough to balance the differences in conversion. Thus, the maximum amount of HMF (18.6% of selectivity) is obtained at 140 °C.

The temporal evolution of all the compounds (see Fig. 4.6) is congruent with the intermediate character of the target compound (HMF). Thus, larger reaction times increase the cellulose conversion (20.5, 28.3 and 43.1% of cellulose conversion after 24h with 200 mg/L

of HCl at 120, 130 and 140 °C, respectively) but the HMF concentration slightly increases (from 4.5 to 5.0 mM, from 5.3 to 6.8 mM, and from 6mM to 9.6 mM, after 8 and 24 h at the temperatures considered in this study) because of the promotion of further steps.

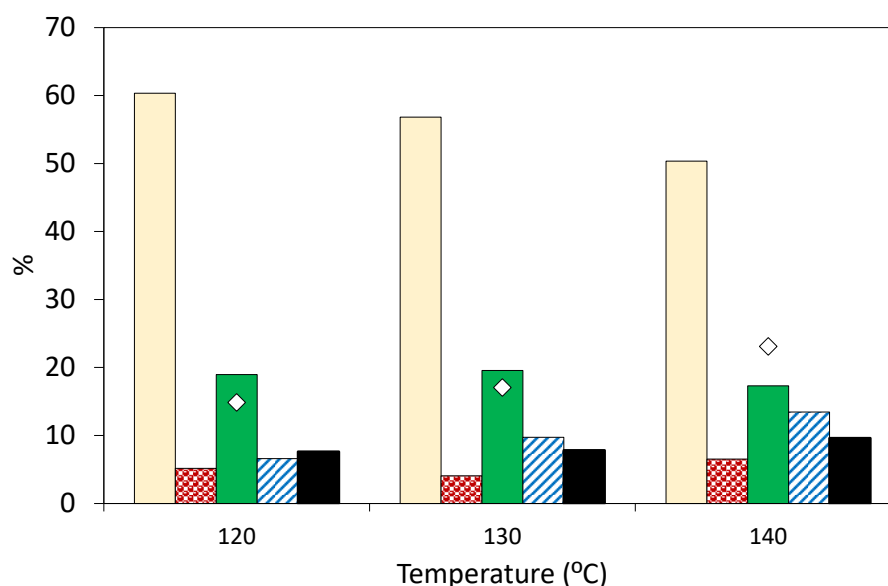


Figure 4.5. Cellulose conversion (◇) and products selectivity obtained in the cellulose hydrolysis using 8% of β -zeolite and 0.02% of HCl as a function of the temperature. Bars corresponding to dimer (yellow), glucose (red bubbles), HMF (green), levulinic acid (blue lines) and anhydroglucose (black)

Consequently, maximizing the HMF selectivity requires an equilibrium between temperature, acidity, and time. The combined severity factor (CSF) concept was used to integrate the effects of these three conditions [10]:

$$CSF = \log \left(t \cdot \exp \left(\frac{T}{14.75} \right) \right) - pH \quad [4.4]$$

where t is the reaction time of hydrolysis in minutes, T is the reaction temperature in Celsius, and pH is the acidity of the aqueous solution measures before the reaction (4.92, 2.76, 2.03 and 1.76, for 0, 0.005, 0.02, and 0.04% of HCl, respectively).

Figure 4.6 displays the effect of variations in conditions (CSF) on the HMF and levulinic acid concentration. In the case of HMF, the results show a cloud of data points where the results with 0.005 and 0.02% of HCl overlap. In other words, the concentration of HMF

increases as the severity of the process increases, regardless of whether this increase was achieved by increasing reaction time, temperature, or HCl concentration.

The results obtained with the highest HCl concentration (0.04%) show a different profile, characterized by lower concentrations at low CSF values and a very narrow area of higher concentrations (never exceeding those obtained with 0.02%). This instability rules out the use of these conditions.

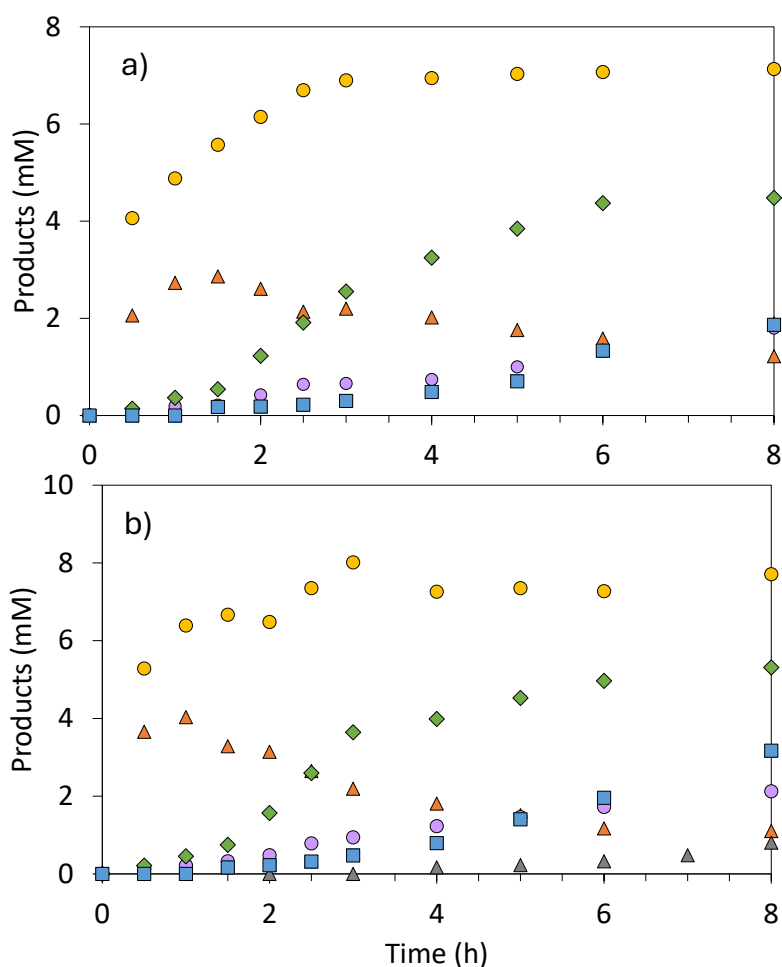


Figure 4.6. Products evolution obtained for the cellulose hydrolysis using 8% β -zeolite and 0.02 % of HCl as a function of the temperature: (a) 120 °C; (b) 130 °C. Symbols: (●) dimers; (▲) glucose; (◆) HMF; (●) AHG; (■) levulinic acid

The evolution of levulinic acid demonstrates increasing trends with CSF, requiring a minimum CSF of 4 to start observing it, and an exponential increase for values greater than this value. However, unlike what was observed with HMF, the results are scattered depending on the acid concentration. Thus, when working with 0.04%, higher levulinic acid values are obtained at lower CSF values.

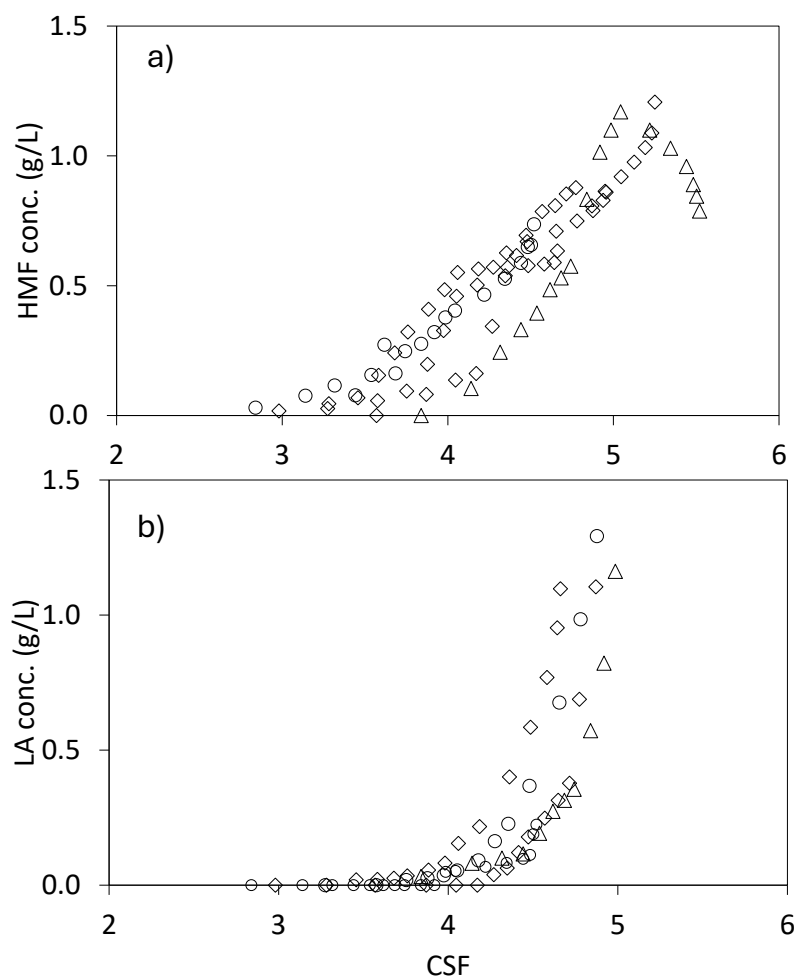


Figure 4.7. Effects of CSF on concentration of (a) HMF, and (b) levulinic acid. Data obtained with 0.005% of HCl (○); 0.02% of HCl (◇); 0.04% of HCl (△)

In conclusion, the maximum HMF selectivity (18.6%) obtained in this parametric study is higher than most of the typical values proposed in the literature for similar systems (10% at 150 °C [11], 15.5% at 220 °C [12]), suggesting a good activity of the catalytic system considered. Higher selectivities (up to 33%) have recently been proposed for a similar aqueous-phase system, using modified zeolites as heterogeneous catalysts [13]. Although this result is very relevant, a direct comparison with this work is not possible because of the different crystallinity degree of the raw material used, from 33-55% in the case of the bibliography, >82% in this case.

On the other hand, this study also demonstrates an HMF final yield (4.3%) conditioned by the low cellulose reactivity (23% conversion). This yield is congruent with previous literature, with values in the range of 2-7% [11, 12], suggesting the need for other strategies to increase the reactivity of cellulose.

4.1.3. Improving hydrolysis behavior by chemical liquid-phase pre-treatments.

The production of HMF by cellulose hydrolysis under dilute acid conditions is limited by the refractory character of the cellulose. Its almost complete crystallinity restricts the access of the catalyst to surface irregularities. A previous pretreatment could reduce the crystallinity of this biomass, increasing the number of potential active sites in the cellulose fiber for starting hydrolysis reactions and, subsequently, increasing the HMF production.

Three different chemical pretreatments were considered in this work, using a mineral acid (HCl), an oxidant (H_2O_2), and a chemical with both properties (HNO_3). In the three cases, the influence of the dosage in the pretreatment was studied. All the pretreatments were carried out at room temperature (20-25 °C) to limit the activity of these acids to reduce the crystallinity of the cellulose, making its surface more accessible during the reaction but without promoting its hydrolysis or any degradation of the bulk structure that could produce liquid compounds during the pretreatment. Thus, pretreated cellulose could be recovered by filtration and the acid solution could be reused, minimizing the environmental and economic impact of using these chemicals. **Figure 4.8** shows the results obtained after 24 h hydrolysis.

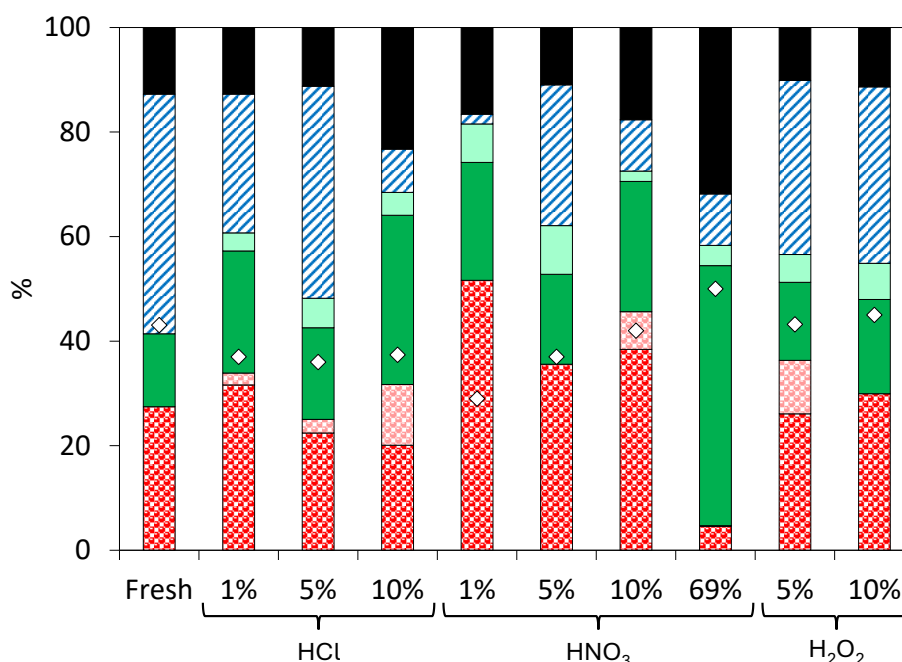


Figure 4.8. Results after 24h of cellulose hydrolysis at 140 °C using 8% of β -zeolite and 0.02% of HCl as a function of the cellulose pretreatment used. Diamonds correspond to cellulose conversion, selectivities are shown in bars: C6 sugars (red bubbles), C5 sugar (pink bubbles), HMF (green), furfural (light green), acids (blue bars), AHG (black)

Despite the intermediate character of HMF, this reaction time corresponds to the maximum selectivity towards this compound of all the pretreated samples. The complete temporal profiles are included in **Figures 4.9-11**.

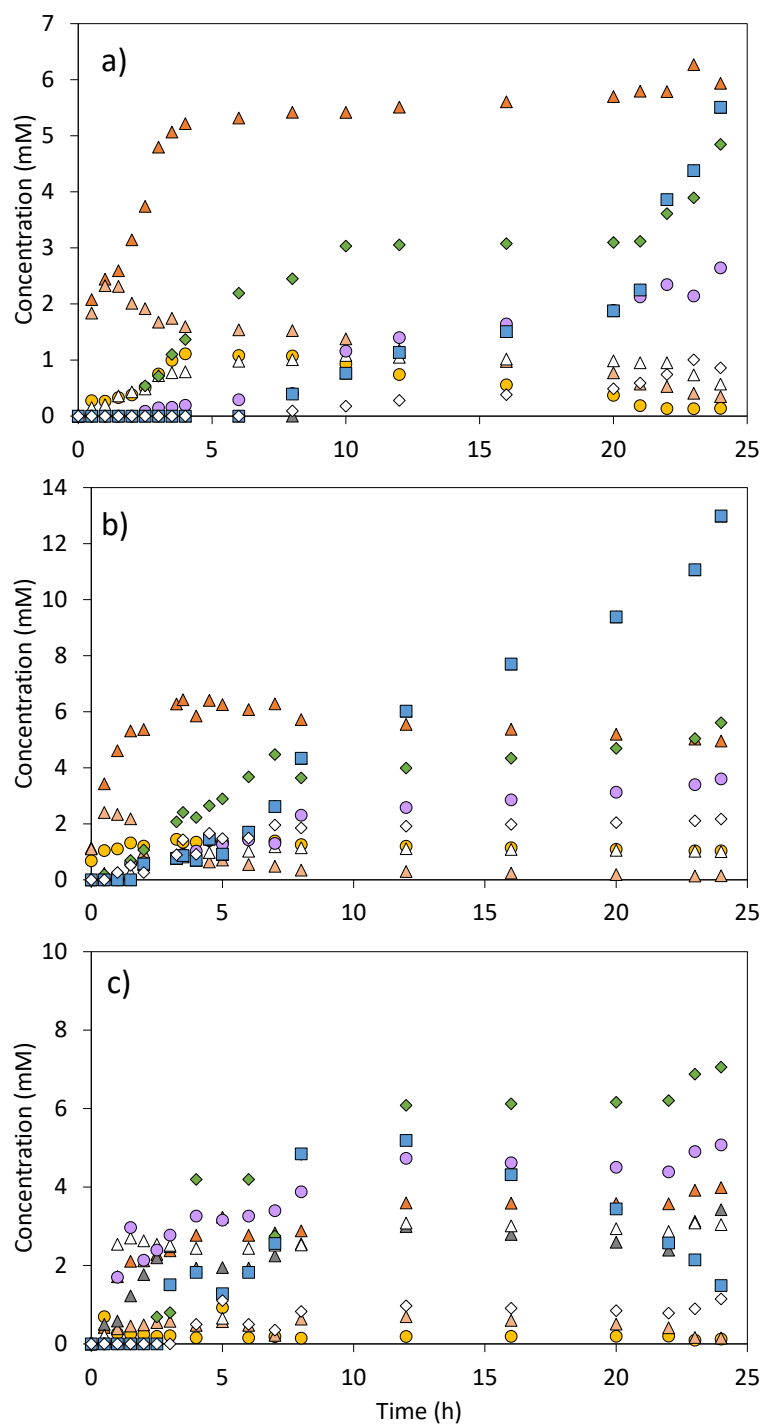


Figure 4.9. Products evolution obtained for the cellulose hydrolysis at 140 °C using 8% β -zeolite and 0.02 % of HCl using acidic pretreatment: (a) 1% HCl; (b) 5% HCl, and (c) 10% HCl. Symbols: (●) dimers; (▲) glucose; (△) fructose; (▽) arabinose; (◆) HMF; (◇) furfural; (●) AHG; (■) levulinic acid

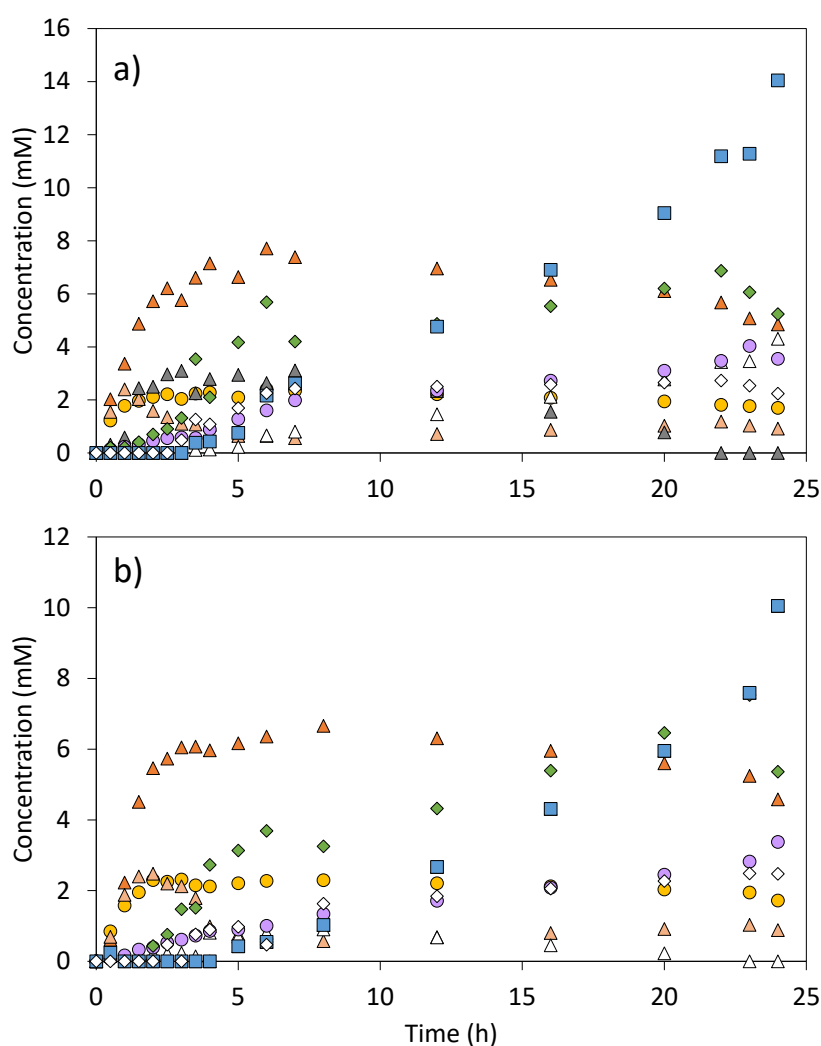


Figure 4.10. Products evolution obtained for the cellulose hydrolysis at 140 °C using 8% β -zeolite and 0.02 % of HCl using oxidizing pretreatment: (a) 5% H_2O_2 ; (b) 10% H_2O_2 . Symbols: (●) dimers; (▲) glucose; (▲) fructose; (△) arabinose; (◆) HMF; (◇) furfural; (●) AHG; (■) levulinic acid

In terms of conversion, pretreatments with HCl do not offer any improvement, obtaining very similar values in the three case studies (36-37.5%). These conversions are lower than the one obtained with the fresh cellulose (43%). This fact suggests that the potential surface degradation produced by this pretreatment does not lead to more accessible terminal glucose, but rather, a portion of the original terminal glucose (amorphous region) is dissolved during the pretreatment, removing the active sites of the fiber for starting hydrolysis reaction.

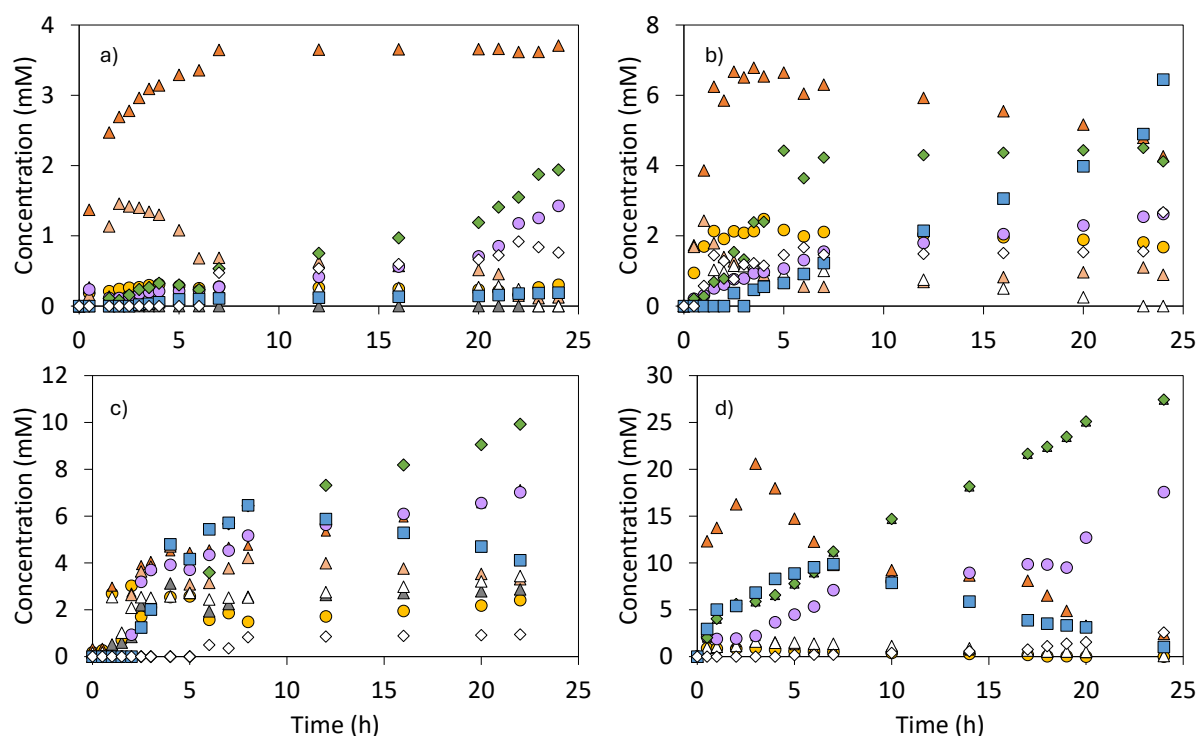


Figure 4.11. Products evolution obtained for the cellulose hydrolysis at 140 °C using 8% β -zeolite and 0.02 % of HCl using acidic-oxidizing pretreatment: (a) 1% HNO_3 ; (b) 5% HNO_3 ; (c) 10% HNO_3 ; (d) 69% HNO_3 . Symbols: (●) dimers; (▲) glucose; (▲) fructose; (△) arabinose; (◆) HMF; (◇) furfural; (●) AHG; (■) levulinic acid

To support this hypothesis, fresh and pretreated celluloses were characterized by different techniques, trying to identify the main effect of each pretreatment on the cellulose structure. **Figure 4.12** shows the diffractograms of all the samples, including the theoretical main diffraction peaks of the three polymorphs of cellulose, according to the molecular orientation and hydrogen-bonding network: cellulose I, cellulose II, and cellulose III. The analysis of these XRD results is shown in **Table 4.1**.

Native cellulose shows the typical XRD patterns of cellulose I (the expected polymorph of cotton cellulose), with diffraction peaks at $2\theta = 14.5^\circ$, 16.5° , and 22.5° attributed to the planes of $(1\ 1\ \bar{0})$, $(1\ 1\ 0)$ y $(2\ 0\ 0)$, respectively [14]. This cellulose has a crystallinity index of 82.5% and, according to Scherrer's equation, a crystallite size of 7.3 nm. The region around $2\theta=21^\circ$ could be initially attributed to the plane $(2\ 0\ 0)$ of cellulose type III. However, the lack of signals at 11.7° and 17° (planes $(1\ 1\ \bar{0})$ and $(1\ 1\ 0)$ of this polymorph) discards this hypothesis suggesting a contribution of a no well-ordered polymeric region. The typical rod-like structure of crystalline cellulose is observed by SEM (**Figure 4.13**). The purity

of this material is corroborated by the results after treating this sample with NaOH; the sample has a non-cellulosic material percentage of less than 2%.

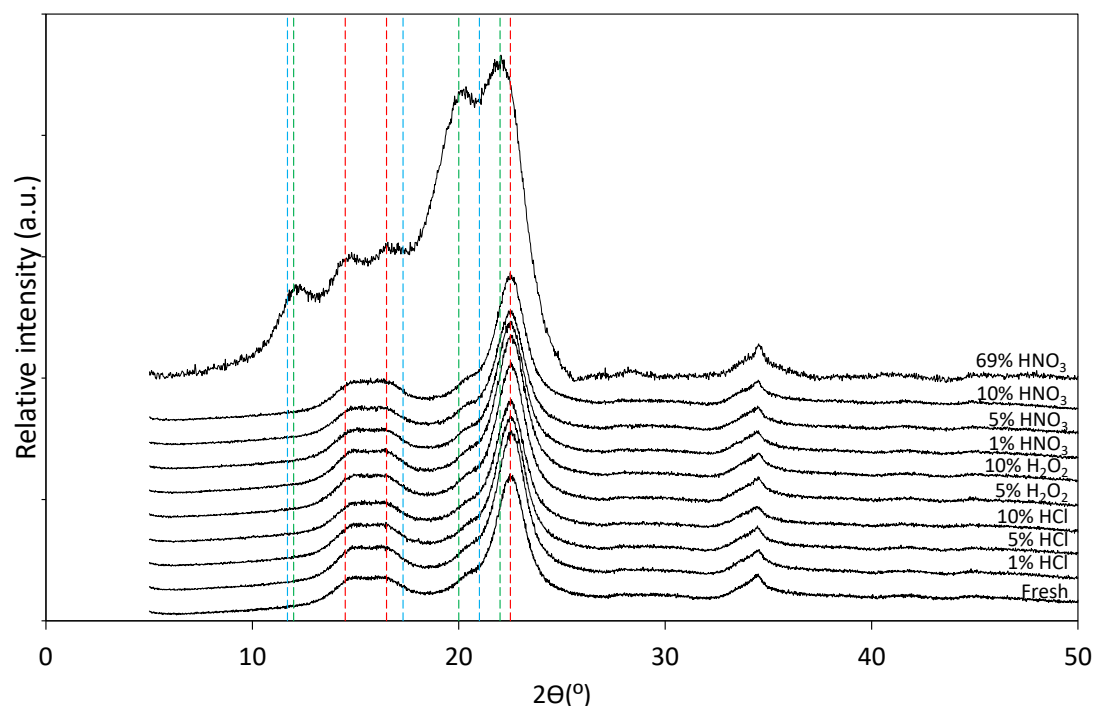


Figure 4.12. XRD patterns for different pretreated celluloses. XRD peaks of cellulose type I being identified by red lines; type II in green; type III in blue

Table 4.1. Crystallinity index (Crl), average crystallite size and non-cellulosic phase concentration of fresh and pretreated celluloses

Sample	Crl	Crystallite size (nm)	Non-cellulosic phase (%)
Fresh cellulose	82.1	7.3	1.8
1% HCl	82.4	9.2	3.6
5% HCl	82.4	9.5	13.4
10% HCl	82.5	9.9	24.2
5% H ₂ O ₂	82.9	7.9	48.6
10% H ₂ O ₂	83.2	9.2	49.1
1% HNO ₃	82.8	9.3	38.3
5% HNO ₃	83.1	9.5	38.8
10% HNO ₃	83.2	10.0	39.9
69% HNO ₃	37.8	7.8	41.9

Cellulose type I remains the predominant polymorph in samples pretreated with HCl, with no significant differences observed in comparison to the untreated cellulose. In fact, SEM micrographs do not reveal any significant difference (see Figure. 4.13). The effects of the pretreatments become evident through an increase in the crystallite size (from 7 to 9-10 nm) with a minimal rise in the crystallinity index. Both effects are congruent with the solubilization of the weakest parts of the surface (amorphous regions). The limited amount of weak β -glucosidic bonds on the parent surface (those susceptible to attack at these soft conditions) explains the low sensitivity of these results to the amount of HCl used.

The progressive increase in the percentage of non-cellulosic material, from 1.8 to 24.2%, explains the product distribution obtained, with an increasing selectivity in C₅ derivatives, both sugars (arabinose) and aldehyde (furfural), as the HCl concentration increases. It is suggested that the acidic pretreatment interacts with the terminal glucose of cellulose, altering their structure in such a way that, under reaction conditions (140 °C, copresence of a heterogeneous catalyst), these terminal units suffer not only hydrolysis but also decarbonylation, leading to arabinose and its aldehyde (total selectivity of 16% with 10% HCl). The presence of these molecules, although not the most common situation, has already been referenced in the literature under oxidative conditions [15]. The hydrolysis and dehydration rates of C₅ sugars are slower than the corresponding ones of glucose [16], justifying the lower conversions obtained. Moreover, furfural is significantly more stable than HMF, also explaining the lower relevance of acids in the reaction mixture. As to the target compound, the selectivity to HMF increases as the HCl concentration does, reaching a maximum of 32.3%, a value almost three times higher than the one obtained in the absence of any pretreatment.

Regarding the oxidizing pretreatment (H₂O₂), the conversion obtained with 5% of H₂O₂ is the same as with the fresh sample (43%). A slight increase is obtained when using 10% of H₂O₂, reaching a final conversion of 45%. Analyzing the products, the presence of C₅ sugars and aldehydes is also relevant (similar selectivities than when using HCl), but the percentage of HMF only increases from 14 to 18%.

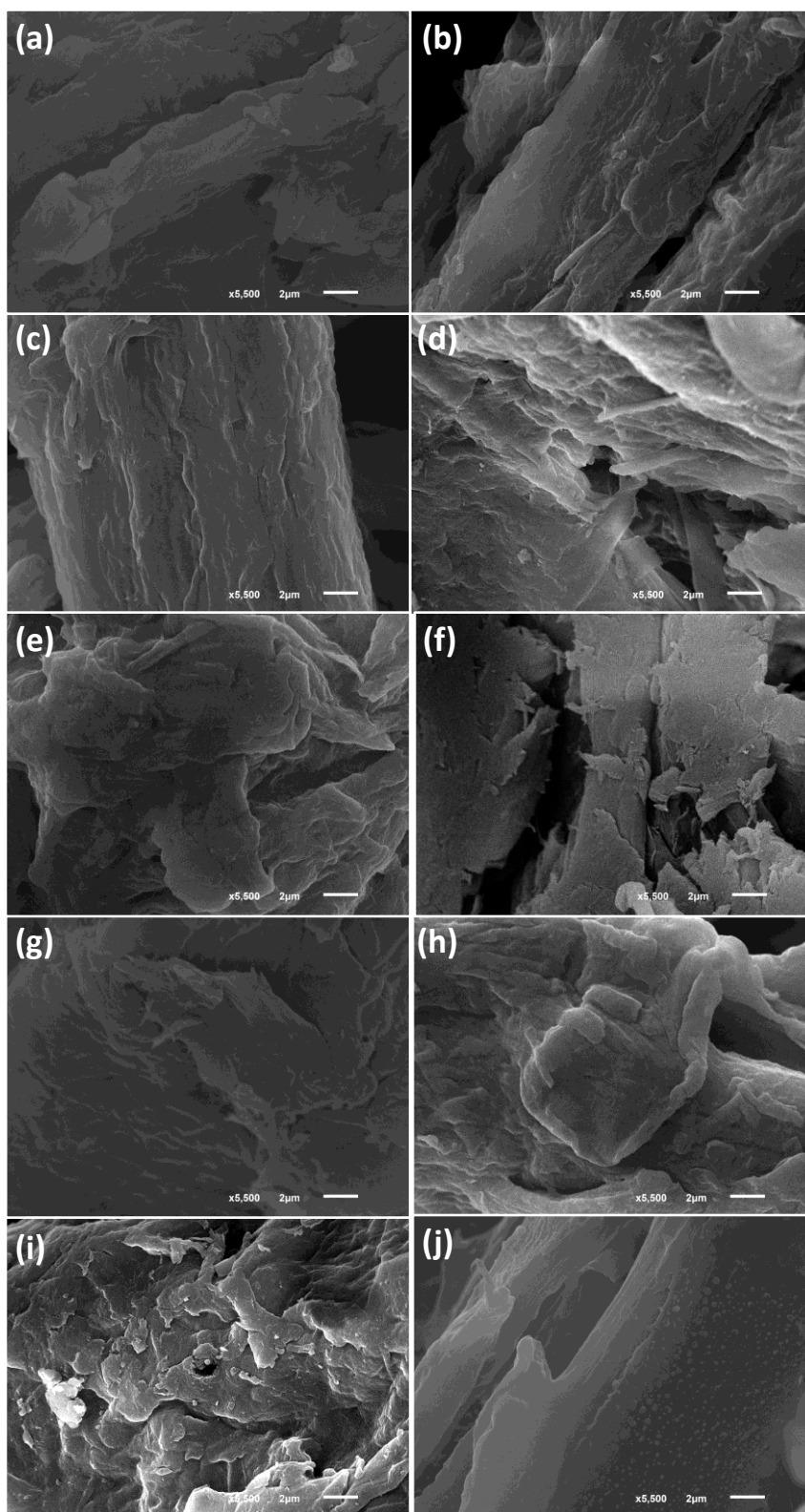


Figure 4.13. SEM micrographs of (a) raw microcrystalline cellulose; (b) 1% HCl; (c) 5% HCl; (d) 10% HCl; (e) 5% H₂O₂; (f) 10% H₂O₂; (g) 1% HNO₃; (h) 5% HNO₃; (i) 10% HNO₃; (j) 69% HNO₃

XRD diffractograms of these samples discard a deep change in the surface crystallography (Figure 4.12), cellulose type I being the main polymorph observed. With this chemical, the effects on the crystallinity index and the crystallite size are more evident than with HCl. The high percentage of “amorphous phase” (>45% in both cases) is not congruent with the conversion reached or the product distribution, suggesting that this pretreatment partially damages the cellulose surface, obtaining a solid that cannot lead sugars by acidic hydrolysis. Based on this fact, higher H₂O₂ concentrations were not tested.

Results with HNO₃ (acidic and oxidizing activity) demonstrate a high influence of concentration, obtaining lower conversions when using 1% (29%) and higher conversions (50%) when using a high-concentrated acid. This evolution is the result of two opposite effects: the acidic behavior of HNO₃ promotes the hydrolysis and solubilization of terminal oligomers during the pretreatment, limiting the potential conversion, whereas its oxidation activity (stronger than in the case of H₂O₂) partially degrades the cellulose surface increasing the terminal units available for the reaction. Increasing concentration remarks this positive effect because the number of sugars available for solubilization during pretreatment is limited, while the capacity to degrade the surface through the oxidative action increases. Based on this analysis, oxidative pretreatment is more effective than the acidic one.

The morphology and crystalline structure of samples treated with 1, 5, and 10% of HNO₃ are very similar and the cellulose I polymorph is the predominant one in the three cases. 1% of nitric acid is enough to produce the main differences, both in the crystallinity index and the crystalline size, whereas almost null differences were observed when increasing the nitric acid concentration. In agreement with XRD results, a continuous but soft increase in the amount of non-cellulosic percentage is observed, highlighting that more than 95% is obtained with only 1% of HNO₃. This analysis does not allow us to determine the specific amorphous character of this fraction. Conversion results suggest that this fraction is easier to hydrolyze after being treated with high HNO₃ concentration.

Pretreatment with 69% of HNO₃ demonstrates to be significantly more effective in deeply modifying the cellulose surface. Diffraction peaks of cellulose type I and type II ($2\theta=12^\circ$, 20° , and 22° [14]) coexist in this sample. The probable explanation for this result is that the crystalline regions swelled during the attack with HNO₃, leading to a rearrangement of the cellulose crystalline structure. This effect has been previously observed when cellulose

is treated with strong mineral acids [17]. Cellulose type II is more stable than cellulose type I, justifying the low effect on conversion of this relevant change.

The degradation produced by this pretreatment is very effective in terms of selectivity, reaching 50% of HMF. Furfural is also obtained, reaching a final selectivity of 4%. The low sugar selectivity (<5%) demonstrates that, despite this pretreatment having limited effectiveness in increasing the availability of hydrolysable sugars, it does reduce the stability of glucosidic bonds, favoring the progression of the reaction toward the dehydration stage.

Selectivity results are comparable to those proposed in the literature, even when using more severe pretreatment conditions [18]. The selective extraction of HMF in an organic solvent could be an interesting option for increasing its selectivity. The purification of the stream is out of the scope of this work, but we have deeply studied this approach in a previous study using glucose as a reactant and the main conclusions could be extrapolated to this system [2]. On the contrary, the maximum yield obtained in this study (18%) is slightly lower than the optimum values reported in the literature (up to 60% for aqueous reactions), as discussed in the review previously indicated. However, the direct comparison is unrealistic due to the different conditions under which they are conducted. Those employed in this study, both for pretreatment and reaction, including temperatures, acid concentrations, and catalyst amounts, are significantly milder than those suggested in previous studies, resulting in a more sustainable process.

4.1.4. Reusability tests

The solid after 24 h of reaction time (using cellulose pretreated with 69% of HNO_3) was recovered by filtration and resuspended in a fresh HCl solution for a new hydrolytic batch. This solid includes zeolite as well as non-reacted cellulose, and the lack of any reaction (conversion lower than 1%) and, more relevant, the absence of glucose is congruent with the recalcitrant character of cellulose since the first step of hydrolysis does not need the catalytic activity of the zeolite. Thus, extending the reaction over 24 h is not a good approach to increase HMF productivity.

This result does not give clear information about possible zeolite deactivation since the role of this catalyst is mainly relevant for glucose isomerization. To study the zeolite

stability, a new cycle feeding the recovered solid (mixture of used zeolite and recalcitrant cellulose) into a new cellulose suspension (using pretreated cellulose as fresh reactant) was performed. In this batch, the recalcitrant cellulose is considered as an inert solid and new pretreated-cellulose (69% HNO_3) and HCl is introduced to guarantee the initial conditions. Results after 24 h are plotted in **Figure 4.14**. As observed, the final mixture is enriched in reductive sugars, with a total selectivity of 76.3% (28.6% of arabinose, 23.6% of fructose and 24.1% glucose). A quite relevant HMF selectivity is also observed (14.2%). The presence of fructose indicates that the zeolite is still partially active (glucose isomerization is catalyzed by Lewis acidity). The lower conversion reached in this second cycle (22.8 % vs. 50%) as well as the lack of total fructose dehydration corroborates the initial hypothesis that Bronsted acid sites of the zeolite collaborate with HCl catalyzing the cellulose hydrolysis and the dehydration steps and these sites are at least partially deactivated after the first cycle. A possible reason for this deactivation could be the adsorption of cellulose oligomers or humins precursors, both aspects being discarded according to the good carbon balance obtained at these mild conditions (98.4%, see Fig. 4.4).

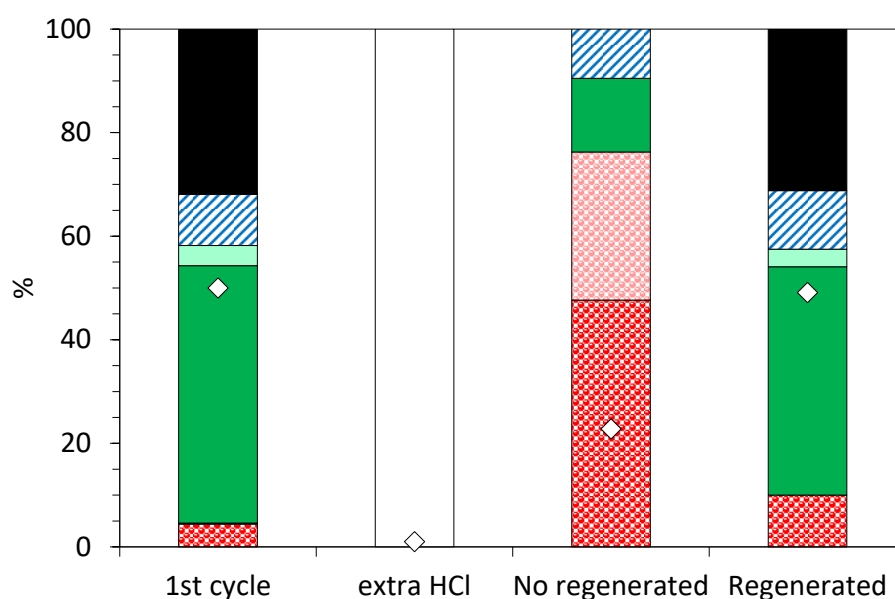
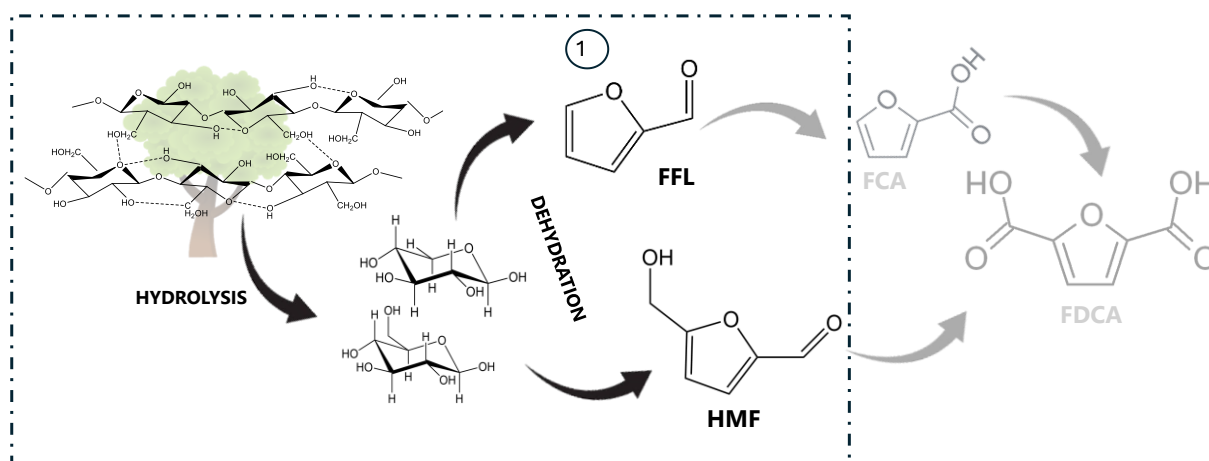


Figure 4.14. Stability tests of pretreated cellulose (69% HNO_3) hydrolysis at 140 °C using 8% of β -zeolite and 0.02% of HCl. Results obtained after 24 h. Diamonds correspond to cellulose conversion, selectivities are shown in bars: C6 sugars (red bubbles), C5 sugar (pink bubbles), HMF (green), furfural (light green), acids (blue bars), AHG (black)

An alternative explanation of these results is related to the method used to get the catalyst after the first reaction, suggesting that the remaining cellulose could be stuck on the zeolite surface, blocking the access to the active sites. To check this hypothesis, the solid recovered after the first cycle was calcined in furnace (550 °C, 8h) to remove the cellulose. The zeolite after the thermal treatment was introduced in a new cycle with pretreated cellulose, the results after 24 h being summarized in Fig. 4.14. As observed, zeolite recovers its initial activity, obtaining very similar conversion (49.1%) and a product distribution enriched in HMF (44.1%) and AHG (32.2%). These results reinforce the interesting results obtained in the cellulose hydrolysis at soft conditions using a pretreatment based on HNO_3 .



4.2. PRODUCTION OF 5-HYDROXYMETHYLFURFURAL AND FURFURAL BY PINE SAWDUST HYDROLYSIS

This work analyses the effects of the oxidative and reductive delignification pretreatments in the subsequent hydrolysis of pine sawdust, considered as a model biomass. The hydrolysis is studied using HCl as catalyst, considering the influence of temperature and acid concentration. The aim of this work is to identify the optimum conditions to enhance the production of different platform molecules, levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) being the most relevant ones. Despite the HMF is faster produced after the isomerization of glucose into fructose by the presence of a Lewis acid [3, 19], a mineral acid is proposed as catalyst considering that temperature and time could balance the kinetic without introducing a solid catalyst that could significantly reduce the kinetic of the first step of the reaction, due to the low efficiency of the solid-solid interactions [20].

The sawdust conversion is calculated in terms of liquid-phase carbon yield, a concept involving the theoretical sawdust required to obtain all compounds detected in the liquid phase, extensively used in biomass conversion [1, 21, 22]. The direct use of the conversion calculated from solid weight measurement before and after the reaction is discarded since the temporal evolution cannot be analyzed based on this parameter, and the accurateness is limited by the presence of humins or other insoluble products (mainly the trimers). The liquid-phase carbon yield is calculated according to Equation (4.5):

$$\varphi_s = \frac{V \cdot \sum(n_i \cdot C_i) \cdot MW_C}{\%C \cdot m_{sawdust}} \cdot 100 \quad [4.5]$$

where “V” is the volume of the solution; “C_i”, the molar concentration of each compound detected in each liquid phase; “n_i”, the number of carbon atoms in the molecule of “i” compound; “m_{sawdust}” is the mass of cellulose introduced in the reactor at the initial point; “MW_C” is the molar mass of carbon; and “%C” corresponds to the mass percentage of carbon in this sawdust, according to the elemental analysis.

The selectivity to any individual product quantified in the liquid phase is indicated in carbon basis, according to Equation [4.6]:

$$S_i (\%) = \frac{n_i \cdot C_i}{\sum_{j=1 \dots i}^n n_i \cdot C_i} \cdot 100 \quad [4.6]$$

being $n_i \cdot C_i$ the moles of carbon that contains the reaction product i and $\sum_{j=1 \dots i}^n n_i \cdot C_i$ the sum of the moles of carbon corresponding to reaction products.

With the aim of guaranteeing the reproducibility of these analyses, each reaction was carried out at least twice. Considering the heterogeneity and complexity of this raw material, results were validated if the standard deviation between two experiments is lower than 7 %. In case of a higher discrepancy, a third experiment allowed defining the good results. As consequence, all the values shown in this work correspond to the average of two experiments.

4.2.1. Sawdust characterization before and after delignification

The amount of cellulose, hemicellulose and lignin was determined before and after the delignification pretreatments, the results being summarized in **Table 4.2**. Each analysis was carried out twice obtaining deviations lower than 3%. Results shown in Table 4.2 are the average values obtained with both analyses.

Data obtained for natural sawdust are in good agreement with typical composition of softwood, with percentages from 25 to 35 % of the three main polymers and less cellulose than hardwood [23]. From a macroscopic point of view, the oxidative pretreatment seems to be quite efficient, since the original brown color of the pine sawdust disappears, obtaining a

white material. This evolution is a clear consequence of the lignin removal [24], and it is not totally observed in the case of the reductive pretreatment. However, the use of carbonaceous support could alter this appreciation.

Table 4.2. Sawdust characterization, in terms of fractionation and elemental analysis, before and after delignification pretreatment. Result expressed in dry basis.

	Natural Sawdust	Oxidative delignification	Reductive delignification
Extractives (%)	6.9	-	-
Cellulose (%)	24.9	58.1	38.5
Hemicellulose (%)	31.5	35.2	57.1
Lignin (%)	36.6	6.7	4.4
C (%)	46.9	40.7	42.6
O (%)	43.6	52.0	49.1
H (%)	6.2	6.3	5.5
N (%)	2.2	0.4	0.7
S (%)	1.1	0.6	2.1

Considering the quantitative analysis, the lignin content decreases considerably after both pretreatments, with the subsequent increase in the relative percentage of cellulose or hemicellulose. Thus, 81.5 % of lignin is removed in case of the oxidative delignification, whereas this value increases up to more than 88 % with the reductive method. These values are in good agreement with previous literature applied to other raw materials, suggesting that the reductive pretreatment is more effective than the oxidative one [25, 26]. Despite the similar delignification efficiency, significant differences between both methods related to the effects on the hydrocarbon structure are observed. It can be concluded that the reductive method mainly affects the lignin fraction, since the decrease in the proportion of this fraction directly correlates with the increase in the cellulose and hemicellulose ones (theoretical values corresponding to this delignification ratio: 42.2 % of cellulose and 53.4 % of hemicellulose), with slight differences (less than 4 %) in favor of hemicellulose. This fact indicates that only a small fraction of cellulose is partially degraded, obtaining a less crystalline structure with similar behavior as the hemicellulose. On the other hand, when the oxidative method is used, the expected percentages of cellulose and hemicellulose if only

lignin was removed would be 41 and 52 %, respectively. Considering the high discrepancy with respect to the values obtained, a partial degradation of hemicellulose is produced. It removes a relevant fraction of external functional groups, obtaining a high ordered polymer, with a structure closer to cellulose than to the initial hemicellulose one. This conformation evolution could affect sawdust behavior in hydrolysis conditions, making it not possible to determine if this is a positive or a negative effect before being tested in the reaction. According to these results, the reductive pretreatment is less aggressive with the hemicellulosic structure of the sawdust, obtaining a more selective delignification than with the oxidative one.

This hypothesis is corroborated by elemental analysis, whose results are also summarized in Table 4.2. Regarding to the fresh material, values are similar to those proposed in the literature for other softwoods [27]. Results related to delignified samples are congruent with the removal of lignin, with a decrease in N and C, and a slight increase in the oxygen percentage (present in high amount in sugar structures). The decrease in the C/H ratio is also congruent with the removal of aromatic rings, typical structures of lignin fractions, and the prevalence of saturated compounds. The more marked changes observed with the oxidative method are in good agreement with its more aggressive character. This fact suggests that samples after reductive pretreatment have lost the lignin fixed structure, but the total decomposition is not achieved, with some S and N remaining in the solid sample.

4.2.2. Hydrolysis of fresh sawdust

The acidic hydrolysis of fresh sawdust (without any pretreatment) was carried out using HCl as catalyst, in the range 200 – 1000 ppm, to identify the optimum conditions, and to determine the effect the pH in these reactions. The mineral acid has been reported as an active catalyst for the hydrolysis of biomass polymers [28-30], but it could also enhance the subsequent steps of sugar dehydrations and degradations, obtaining acids and humins [1, 4, 31]. Thus, a balance between positive and negative effects requires a well-defined concentration, different for each type of wood, trying to enhance the production of desired platform molecules. A blank experiment was done to discard hydrothermal hydrolysis, despite being not expected considering the temperatures of the non-catalytic hydrolysis reported in the literature [32, 33]. The evolution of the liquid-phase carbon yield with time is

analyzed in **Figure 4.15a**. Values plotted in this figure correspond to the average ones after two repetitions, obtaining standard deviations lower than 7 % in all cases, as observed by the small error bars. Then, in some cases, it cannot be appreciated.

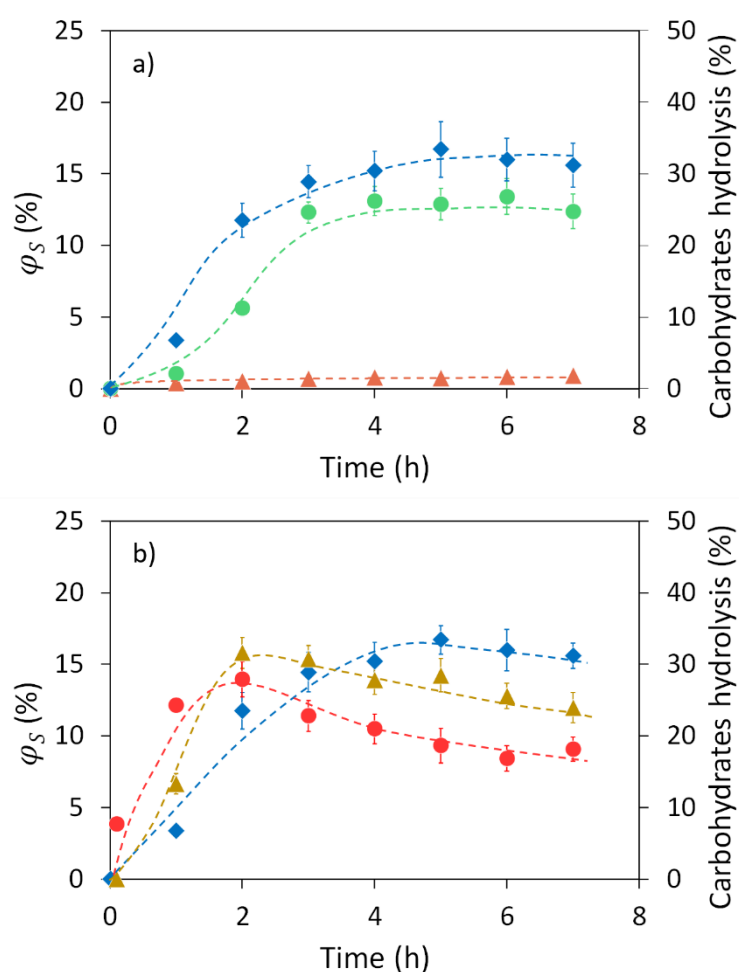


Figure 4.15. Temporal evolution of the liquid-phase carbon yield obtained in the hydrolysis of fresh sawdust as function of: (a) the acid concentration and (b) the reaction temperature. Data analyzed considering the total amount of sawdust (left axes) and only the potential sugars, cellulose, and hemicellulose (right axes). Results corresponding to (▲) 200 ppm of HCl, 140 °C; (●) 600 ppm of HCl, 140 °C; (◆) 1000 ppm of HCl, 140 °C; (▲) 1000 ppm of HCl, 180 °C, (●) 1000 ppm of HCl, 220 °C

Results obtained with 200 ppm indicate an almost negligible degradation activity at these conditions, reaching constant yield in less than two hours (0.9 %). Considering the total amount of carbohydrates present in sawdust (cellulose and hemicellulose), this liquid-phase carbon yield represents 1.8 % of the maximum theoretical grade of hydrolysis. A clear evolution is observed when increasing the acidity up to 600 ppm, with a maximum carbon

yield obtained after 4 h of reaction (12.5 %). This value corresponds to the hydrolysis of 24.6 % of the total sugar fractions in this sawdust. Once the maximum is reached, it keeps constant with the time, without observing any evolution when the reaction is extended up to 24 h. This result suggests that conditions are not severe enough to degrade the recalcitrant structure of biomass polymers. This hypothesis is congruent with results obtained with 1000 ppm of HCl, observing a faster hydrolysis that only reaches a maximum of 15.6 % (equivalent to 31.4 % of the sugar polymers). This value, obtained after 5 h, is not stable, followed by a continuous decrease for products detected, up to 9.8 % after 24 h. Considering the irreversible character of this reaction, the decreasing trend suggests that, at these conditions, different side reactions involving solid products (humins production) take place. According to the literature, humins are formed by cross-polymerization reactions between HMF, furfural (FFL) and sugars during the acid catalyzed hydrothermal hydrolysis [34, 35]. The fact that this is only observed in the most severe conditions suggests a different product distribution, which is analyzed in **Figure 4.16**.

This figure analyses the results in terms of carbon selectivities. The compounds considered for this analysis represent a carbon balance closure higher than 60 % in all cases, the value being higher as the acidity decreases (70.4, 75.4 and 60.5 %, for 200, 600 and 1000 ppm of HCl, respectively). Seven compounds derived from the typical route of acid-catalyzed biomass hydrolysis are detected: dimers (corresponding mainly, but not only, to cellobiose), three reduced sugars (glucose, arabinose and xylose), HMF (cyclic aldehyde derived from hexose), FFL (cyclic aldehyde derived from pentoses), levulinic and formic acids. These last two products are obtained by the rehydration of HMF in equimolar amounts. Considering that there is not any other reaction that consumes any of these acids, the same concentrations of both acids are obtained, so only levulinic acid is shown in the graphs (to prevent repeated information). An almost perfect carbon balance closure is obtained (higher than 90 % in all cases) if this analysis is completed with light alcohols detected at significant extent. These alcohols are identified as terminal units of sugar polymers, this location justifying the high amount obtained. However, as these compounds do not interfere in the main reaction scheme, they are not included in the following analyses.

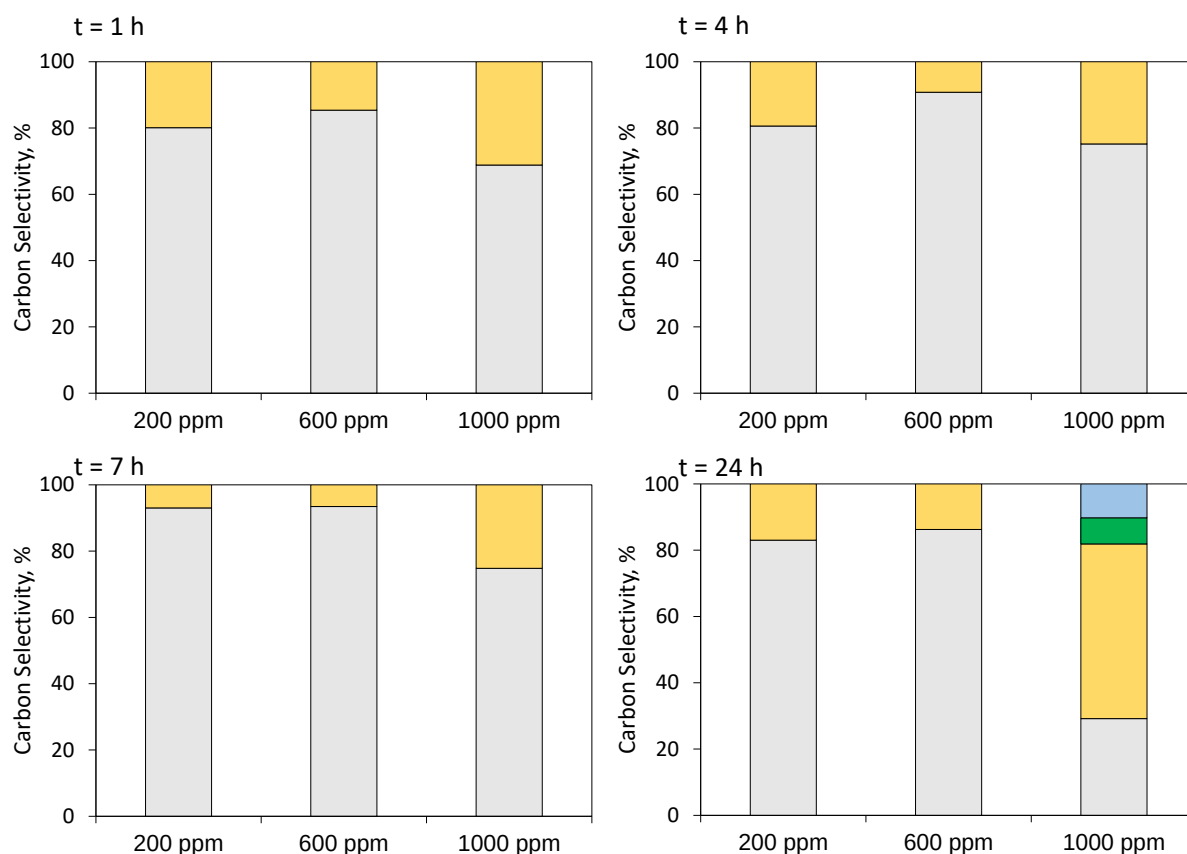


Figure 4.16. Comparative distribution of products selectivities obtained with fresh sawdust as function of the acidity. Data corresponding to dimers (grey); TRS (yellow); HMF (green); FFL (blue)

As anticipated by the soft conditions (low temperature and low acidity), dimers are the main product obtained during the first 7 h, despite the HCl concentration used. The absence of glucose and the detection of arabinose and xylose during the first 2 h is congruent with the recalcitrant structure of cellulose and the presence of pentoses in the external structure of hemicellulose (weakest bonds, the most easily hydrolyzed ones). With 200 and 600 ppm of HCl, the relative relevance of these pentoses decreases as the incomplete hydrolysis of cellulose increases, observing low amount of glucose and suggesting that most of the dimers correspond to cellobiose (experimentally tested). Thus, stable selectivities around 7 % of total reduced sugars (TRS) are obtained during the first 7 h. A slight improvement with the time is observed, with an increase up to 17 and 13.7 % of TRS, with 200 and 600 ppm. However, considering the low hydrolysis degree, these values only correspond to 68 and 277 ppm of TRS, respectively. As anticipated, no aldehydes or acids are observed under these conditions. The evolution with 1000 ppm is considerably different, with a relevant formation of TRS (24 % after 7 h, 52.8 % after 24 h, corresponding with 686 and

1020 ppm, respectively). Aldehydes formation is clearly observed after 24 h, with 8 % of HMF and 10.2 % of FFL, whereas levulinic acid is not detected in these experiments. The presence of aldehydes in the liquid phase is congruent with the promotion of humins and the decrease in the carbon balance.

According to these results, increasing the reaction temperature working with 1000 ppm of HCl is suggested as the following approach, trying to balance the promotion of the desired steps with the avoidance of side reactions. The influence of temperature was studied in the range 140-220 °C, obtaining the evolution of the liquid-phase carbon yield observed in **Figure 4.15b**.

Experimental results follow the anticipated trend considering the positive effect of temperature in the kinetics and the relevance of side reactions obtained when working at 140 °C. Thus, there is a first increase in the liquid-phase carbon yield, reaching a maximum value of around 16 %, despite the temperature. This result indicates the maximum hydrolysis efficiency at these conditions, corresponding with 34 % of the potential amount of sugars. This result suggests that temperature is not the key parameter for this variable. However, it is worth noticing that this first step requires less time as the temperature increases, i.e., 4-5 h, 2 h and around 1.5-2 h at 140, 180 and 220 °C, respectively. After these maximums, the relevance of side reactions is clearly observed, being promoted by the temperature. In good agreement, final carbon balance closures after 24 h decrease from 59 % to 54 and 33 %, as the temperature increases.

These results only consider the solubilization of sugar fractions, the analysis of selectivities being required to determine the optimum conditions for recovering each platform molecule. The simultaneous comparison after different reaction times is plotted in **Figure 4.17**.

A clear influence of reaction temperature is observed, being all the products observed from the first hour when the temperature is higher than 140 °C. Xylose is the main product detected at intermediate temperatures and short times, whereas a fast dehydration is observed at 220 °C, aldehydes and acids prevailing over the TRS. A similar amount of arabinose obtained at 180 and 220 °C, not only in selectivity but also in concentration. This result suggests that FFL is mainly produced by the dehydration of xylose, pentose for which

the differences are more marked. The glucose dehydration to produce HMF is observed at 180 and 220 °C, with selectivities of 5.6 and 14.5 %, respectively, in less than 1 h. According to the previous literature, Lewis acidity is defined as a key factor to promote the HMF via glucose isomerization, since the fructose dehydration is thermodynamically favored [28]. The role of temperature in this step is more relevant when the catalyst is a Brønsted acid (such as the HCl), because of the higher activation energy of the direct glucose dehydration [29].

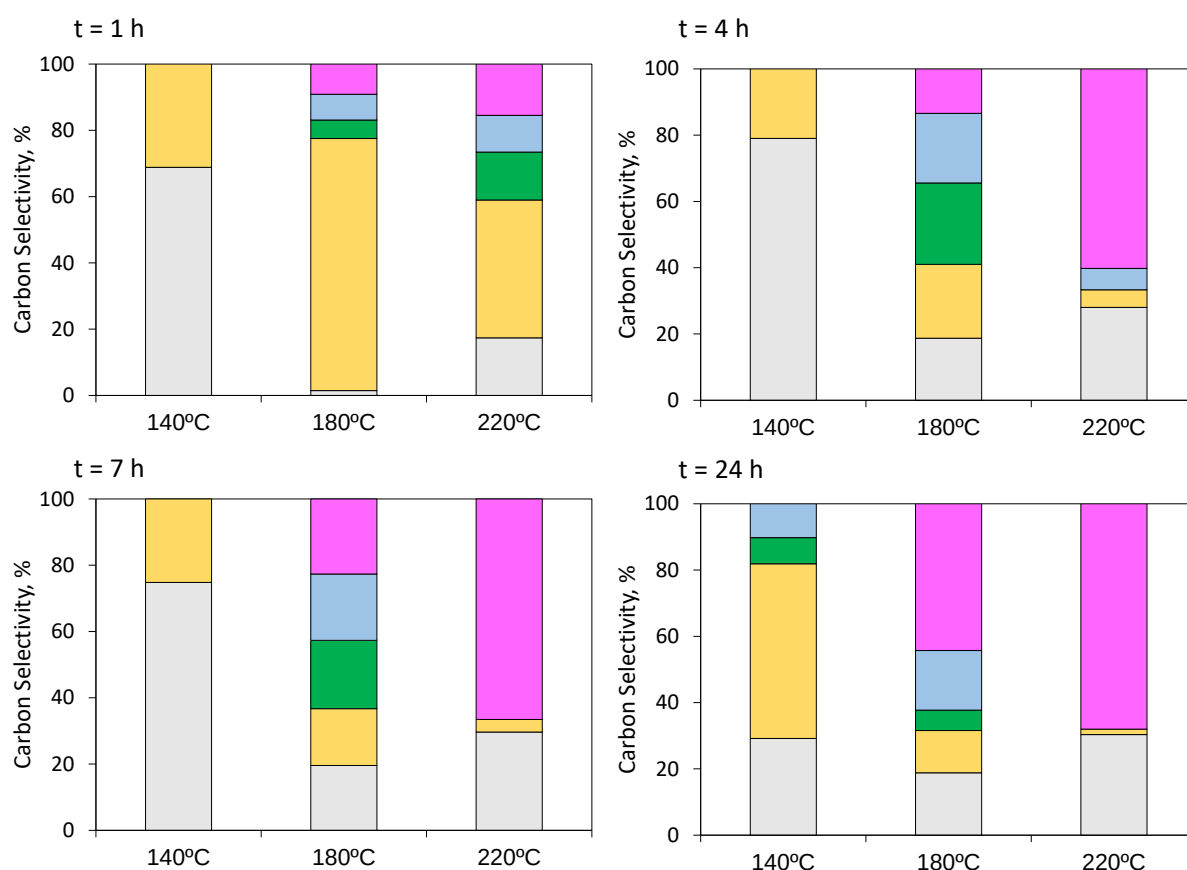


Figure 4.17. Comparative distribution of products selectivities obtained with the fresh sawdust as function of the reaction temperature. Data corresponding to dimers (grey); TRS (yellow); HMF (green); FFL (blue); and levulinic acid (purple)

At larger reaction times, side reactions determine the observed product distribution. On the one hand, the almost total rehydration of HMF into levulinic and formic acid is clearly observed at 220 °C, with the disappearance of this aldehyde and a relevant increase of levulinic acid selectivity (60, 66 and 68 % after 4, 7 and 24 h). This effect is less marked at 180 °C. On the other hand, the FFL total amount reaches a maximum of 330 ppm at 180 °C

after 4 h (selectivity of 21 %), with a soft decrease to 250 ppm after 24 h (equivalent to 18 % of selectivity). However, this effect is much more relevant at 220 °C, reaching the maximum FFL concentration (270 ppm) after only 2 h, with a total disappearance of this compound in less than 5 h, due to the promotion of humins.

According to these results, there is not a clear range of conditions to maximize the productivity and selectivity of almost any compound. This fact seems to be determined by the low rate of the first step of the process: the sugar solubilization to produce TRS. Thus, all the concentrations are quite low, and the reaction conditions required to promote this step are so strong that the subsequent steps occur too fast. In this context, the lignin pretreatment could play a relevant role since a feasible degradation of the recalcitrant structure of sugar polymers could reduce the severity requirements to enhance the hydrolysis. Then, the temperature and reaction time would have a key role in maximizing the productivity and selectivity of the platform molecules.

4.2.3. Influence of the oxidative and reductive pretreatments

To identify the effect of both pretreatments, the comparative analysis of liquid-phase carbon yield obtained is shown in **Figure 4.18** (Fig. 4.18a and 4.18b). In these plots, values over and below the diagonal line indicate higher or lower values once the pretreatments are applied with respect to the reaction with fresh sawdust, always comparing data at same conditions (temperature and acidity) and time on reaction. The discrepancies between results of each pair of experiments were lower than 8 % in all the cases, 2-3 % being the typical errors obtained. The error bars are included in the temporal profiles of concentration evolutions.

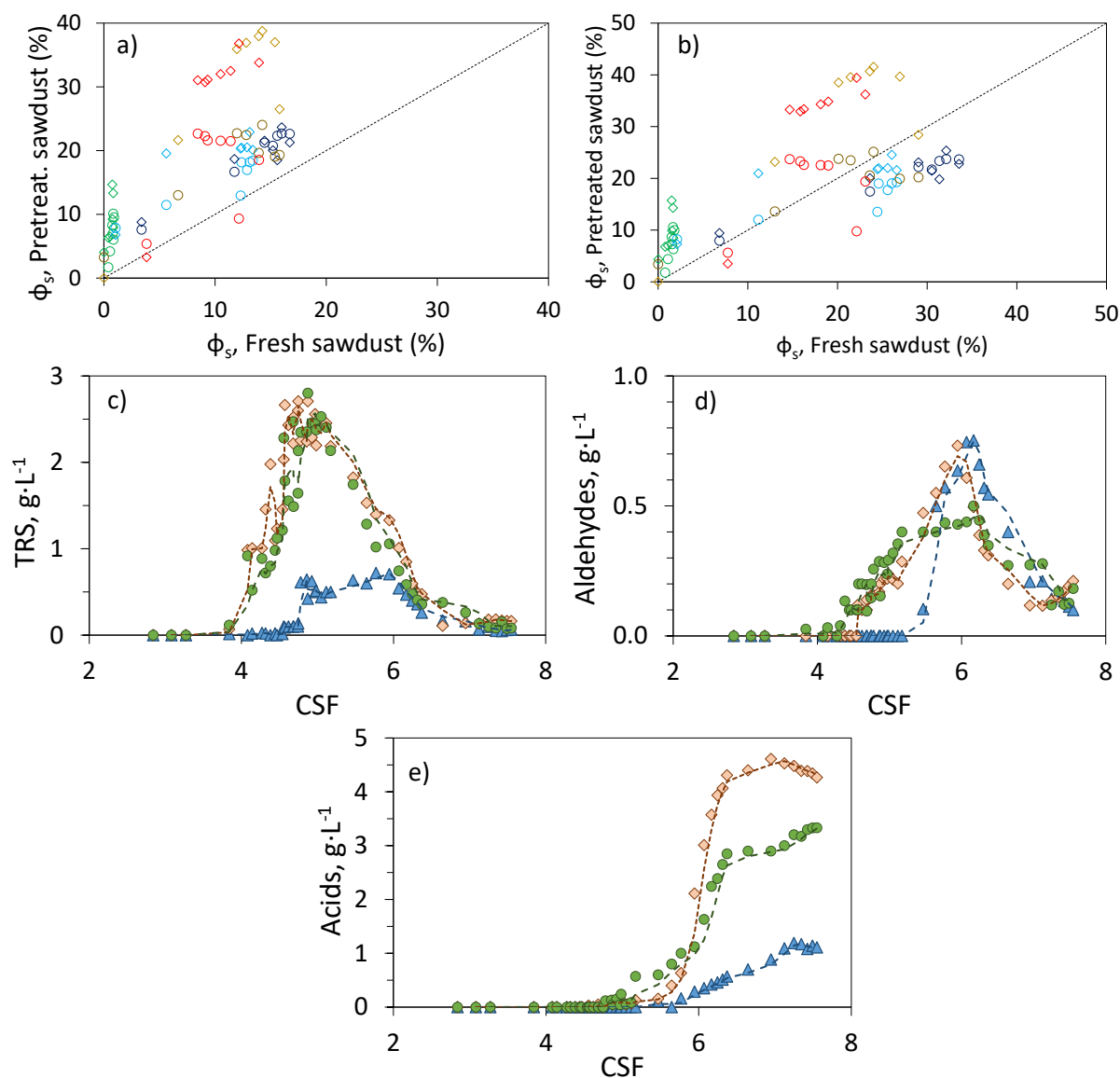


Figure 4.18. Comparative analysis of liquid-phase carbon yields obtained with the pretreated (circles for the reductive delignification, diamonds for the oxidative one) and fresh sawdust considering (a) the total amount of sawdust; and (b) cellulose and hemicellulose. Results corresponding to: 200 ppm of HCl and 140 °C (green), 600 ppm of HCl and 140 °C (light blue), 1000 ppm of HCl and 140 °C (dark blue), 1000 ppm of HCl and 180 °C (gold), 1000 ppm of HCl and 220 °C (red). Evolution of (c) TRS, (d) aldehydes, and (e) acids as function of the CSF factor. Data correspond to (▲) fresh sawdust; delignified sawdust using (◆) oxidative and (●) reductive pretreatments

The comparison considering the total amount of sawdust treated (Fig. 4.18a) indicates that both pretreatments have a positive effect in the liquid-phase carbon yield, duplicating the values at almost all the conditions, reaching maxima close to 40 % when the oxidative pretreatment is applied, at 180 and 220 °C. In addition, the humins production slows down, in good agreement with the increase of the carbon yield increases observed for the

pretreated samples. For example, at 220 °C, a decreasing trend is observed after 2 h of reaction, this time being increased up to 5 and 7 h, after the reductive and oxidative pretreatment, respectively. However, if same values are analyzed considering only the potential maximum amount of sugars (Fig. 4.18b), these values are quite different, since they are strongly affected by the almost total absence of lignin in the pretreated samples. In this case, the differences between reductive and oxidative pretreatments are more evident, with a clear prevalence of the oxidative one, when working at with 1000 ppm of HCl and 180 or 220 °C. Softer conditions (600 ppm and 140 °C) do not imply any improvement with respect to the hydrolysis of fresh sawdust. Despite the low values obtained when working with 200 ppm of HCl, around 10 % of liquid-phase carbon yield is reached with both pretreatments whereas no reaction is observed with the fresh material. Two main conclusions of these results can be drawn: i) pretreatments do not modify the potential amount of sugar polymers (increase or reduction) that can be hydrolyzed at these conditions; ii) these pretreatments seem to debilitate the glycosidic bonds, reducing the severity to obtain a similar hydrolytic efficiency. A deeper study of these pretreatments requires the analysis of the products distribution, these data being shown in **Figure 4.19**.

Reactions carried out with 200 ppm of HCl mainly produce dimers and TRS, the dimer concentration being always higher with the oxidative pretreatment than with the reductive one. Thus, in the case of the oxidative pretreatment, dimers correspond to 90 % of the total liquid products during the first 4 h of reaction, decreasing only to 75 % after 7 h. On the contrary, an initial 41 % of dimer is obtained with the reductive pretreatment, with less than 6 % observed after 7 h, when more than 89 % of the total selectivity corresponds to TRS and small traces of aldehydes can be observed (1.5 of HMF and 3.7 % of FFL). Thus, these conditions are identified as the optimum ones to selectively obtain these sugar monomers, the mixture being always enriched in xylose (75 and 80 % when working with the oxidative and reductive treated sawdust). In concentration values, working with 200 ppm, 1.55 g/L of TRS is obtained when working with the treated sample (reductive pretreatment), this value being more than 3 times higher than the value obtained with the oxidative pretreated sample, and 140 times higher than the corresponding one obtained with the fresh sample.

A logical evolution with the acidity, temperature and reaction time is obtained, despite the samples analyzed, with an increase in the degradation process as all these

parameters increase. In general, reactions with the oxidized samples suggest a more sensitivity to the reaction parameters, making it difficult to control the reaction in the intermediate steps. Thus, levulinic and formic acid are the main compounds identified in the samples at 220 °C after only 1 h of reaction, 79 % of selectivity, whereas the corresponding value obtained with the samples pretreated with Ru/C is lower than 10 %.

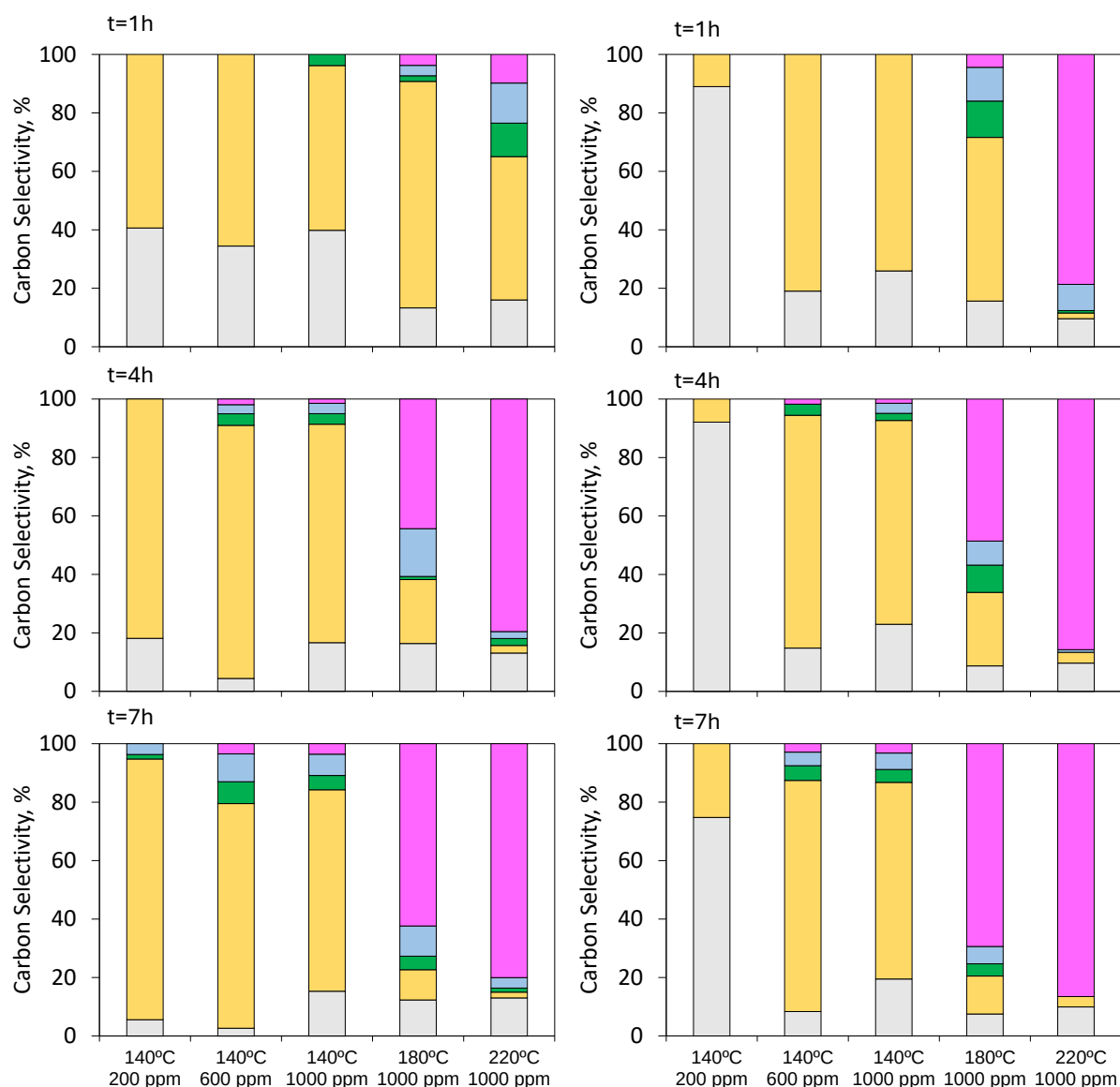


Figure 4.19. Comparative distribution of products selectivities obtained with the hydrolysis of pretreated sawdust as function of the reaction time. Left graphs related to reductive pretreatment; right graphs related to the oxidative one. Data corresponding to dimers (grey); TRS (yellow); HMF (green); FFL (blue); and levulinic acid (purple)

These results conclude that the oxidative pretreatment is the optimum one to maximize the production of these platform molecules, obtaining almost a total degradation

of all the sugars in less than 7 h (selectivity to levulinic acid higher than 86 %). This selectivity cannot be reached without a previous pretreatment, even increasing the reaction time up to 24 h. In concentration terms, this selectivity corresponds to 3.2 g/L of levulinic acid produced with the oxidative pretreatment. With the reductive pretreatment, this amount is limited to 2.4 g/L, these two values being significantly higher than the one obtained during the hydrolysis of the fresh sample (0.8 g/L).

Concerning the aldehydes (HMF and FFL), a selective production of these intermediates is not possible, since HMF is faster degraded to levulinic acid, and a high selectivity of FFL is limited by the undesired oligomerization. In any case, the pretreatments also imply an improvement at this point, the reductive process being the optimum to enhance the selectivity of FFL (19 % after 3 h of reaction at 180 °C with 1000 ppm of HCl, this selectivity being reduced to 16 % at 4 h). The maximum value obtained with sawdust after the oxidative process is limited to 11 %. Seeing both aldehydes together, 35.4 % of both compounds are obtained in less than 1 h of reaction at 220 °C with the reductive pretreatment. This selectivity corresponds with the maximum concentration observed for these compounds (1.2 g/L). This concentration is 1.8 times higher than the maximum one obtained with the fresh sawdust, 0.68 g/L after 4 h at 180 °C with 1000 ppm of HCl. A similar selectivity than with the reductive process (34 %) is obtained with oxidative pretreatment, even at softer conditions (180 °C, 4 h). However, considering the total conversion, this selectivity only corresponds with 0.75 g/L, this value being only half of the concentration reached after the oxidative pretreatment.

To globally identify the impacts of delignification processes in sawdust hydrolysis, and considering the simultaneous effect of acidity, temperature and reaction time, the evolutions of different intermediates and final products are compared considering the combined severity factor (CSF). This parameter has been previously proposed in the literature to unify the role of all the variables involved in one coefficient, according to Eq. 4.4 [36, 37].

In this case, " t " is the reaction time of hydrolysis in minutes, " T " is the reaction temperature in Celsius, " T_{Ref} " is the reference temperature, most often 0 °C, and pH is the acidity of the aqueous solution measured before reaction. These values correspond to 2.1, 1.8 and 1.6, for reactions with 200, 600 and 1000 ppm of HCl, respectively. The concentrations of

total reduced sugars (TRS), aldehydes and acids as function of the CSF values are plotted in **Figure 4.18** (parts c to e).

The soft trends obtained for all the compounds studied corroborate the utility of this parameter, showing distributions with clear maxima, which indicates a common evolution as function of the acidity, temperature, and reaction time for all the platform molecules. A similar effect of both pretreatments in the TRS productivity is observed (Fig. 4.18c), with a maximum clearly concentrated in CSF values 4.5 – 5 and a fast decrease in the concentration at both, lower and higher CSF values. In these two cases, the maximum concentration is close to $3 \text{ g}\cdot\text{L}^{-1}$. More severe conditions are required in the hydrolysis of fresh sawdust, with and more extensive optimum CSF range from 5 to 6. Even at the optimum conditions, the total amount of sugars obtained is significantly lower than with the pretreated sawdust (maximum $0.75 \text{ g}\cdot\text{L}^{-1}$).

As to the aldehydes (HMF and FFL), the maximum obtained with the fresh sawdust is concentrated in a very narrow range (5.8 -6.4), without observing HMF nor FFL with CSF values under 5. The concentration at these optimum conditions, $0.8 \text{ g}\cdot\text{L}^{-1}$, is also the optimum obtained with the oxidative pretreatment, the most relevant difference being the presence of aldehydes even at CSF values lower than 5. The most extended range is observed for sawdust after the reductive pretreatment, obtaining aldehydes almost at all the conditions tested. However, this sawdust follows a flat evolution in the range 5 – 6.5, being not possible to identify clear optimum conditions, and with a maximum concentration lower than $0.5 \text{ g}\cdot\text{L}^{-1}$.

In concentration terms, acids (levulinic and formic acid considered together) are the compounds most affected by the pretreatment used. However, the general trends are the same, and CSF values higher than 6.5 are required in all the cases to obtain these compounds in significant amounts. The clearest difference is then the slope of this increasing trend, the oxidative pretreatment being the most efficient one to increase acid yields.

According to this analysis, the oxidative delignification method is considered the best one to clearly identify different optimum conditions, in terms of productivity and selectivity, for each platform molecule. On the contrary, these optimum values partially overlapping with the reductive pretreated and fresh sawdust.

4.2.4. Kinetic study

To sum up, relevant influences are observed as a function of the pretreatment carried out. These higher reaction progresses can be analyzed in kinetic terms, proposing a kinetic model to describe the solubilization of hexoses and pentoses present in sawdust as well as their degradation to HMF, FFL and levulinic and formic acids. For this model, the quantity of sugar polymers is obtained as the difference between the initial amount (experimentally determined) and the sum of all compounds detected in liquid phase. The evolution of all the compounds (grouped by families) with the time could be assimilated to a sequence of irreversible first-order steps in series configuration, see Eq. [4.7]:



where: C_P is the sum of hemicellulose and cellulose in the sawdust; C_D and C_M are the dimer and monomer (hexoses and pentoses) concentrations detected in the liquid phase, respectively; $C_{ald.}$ the sum of HMF and FFL; and $C_{ac.}$ the amount of formic and levulinic acid. All concentrations are expressed in g/L.

To guarantee the absence of any limitation because of the amount of HCl, only the set of reactions obtained with 1000 ppm of this catalyst were considered for the adjustment. This decision is justified by the negligible pH evolution observed in these experiments during the 8 h analyzed. Considering the possible humins formation, as well as the subsequent alteration in the theoretical amount of polymers, a fifth rate was evaluated, being responsible for aldehyde oligomerization to obtain these solid deposits. Experimental data were fitted to this kinetic model using MATLAB code ("ode45"). The fitting of the unknown parameters was accomplished by the least-square method using the "lsqcurvefit" function and the Levenberg-Marquardt algorithm, obtaining the kinetic rates summarized in **Table 4.3**.

The comparison of these data requires corroborating the reliability of these values. An ANOVA analysis confirms that temperature is a significant model terms that influences the kinetic of the hydrolysis, for fresh and pretreated samples, with p-values lower than 0.5 in all the cases (0.028, 0.022 and 0.016 for fresh samples and sawdust after oxidative and reductive pretreatments, respectively). The sawdust pretreatments also produce a relevant influence in the kinetic, mainly at 220 °C, when the p value is 0.036. This influence is not so significant

at lower temperatures, with p-values a bit higher: 0.17 and 0.11, for 140 and 180 °C, respectively. These values are too high to conclude a clear influence of these pretreatments at low temperatures at this level of confidence (95 %). The p-values decrease up to less than 0.07 if only the first steps of the reaction are considered (sugar solubilization), in good agreement with the suggested hypothesis of a main effect of these pretreatments making easier the cellulose and hemicellulose hydrolysis, whereas the subsequent steps of the process are mainly conditioned by the acidity of the medium.

Table 4.3. Kinetic model parameters for the hydrolysis of sawdust catalysed by 1000 ppm of HCl.

Raw Material	Temp. (°C)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	k_3 (s ⁻¹)	k_4 (s ⁻¹)	k_5 (s ⁻¹)
Fresh sawdust	140	$4.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$	$2.5 \cdot 10^{-7}$	$7.0 \cdot 10^{-5}$
	180	$7.7 \cdot 10^{-5}$	$8.5 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
	220	$2.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$
	Ea (kJ·mol ⁻¹)	33.7	54.1	120.0	193.3	31.9
	r ²	0.93	0.95	0.99	0.96	0.93
Delignified by oxidative method	140	$4.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$3.5 \cdot 10^{-5}$	0
	180	$8.6 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$	$6.4 \cdot 10^{-4}$	$3.7 \cdot 10^{-6}$
	220	$1.6 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$	$9.1 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$
	Ea (kJ·mol ⁻¹)	27.8	49.1	78.9	113.9	205.1
	r ²	0.999	0.95	0.83	0.999	0.999
Delignified by reductive method	140	$1.13 \cdot 10^{-5}$	$5.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$3.4 \cdot 10^{-5}$	$4.7 \cdot 10^{-8}$
	180	$2.9 \cdot 10^{-5}$	$7.6 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	$5.3 \cdot 10^{-4}$	$7.0 \cdot 10^{-5}$
	220	$3.9 \cdot 10^{-5}$	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$5.8 \cdot 10^{-4}$
	Ea (kJ·mol ⁻¹)	29.0	14.0	45.9	84.1	202.0
	r ²	0.93	0.997	0.95	0.97	0.94

The good fit of this model with experimental values is shown in **Figure 4.20**, including the reactions at 220 °C as examples. The good regression coefficients of kinetic rates as function of the temperature indicates an optimum adjustment of experimental data according to Arrhenius model. This model, previously proposed in the literature [31, 38, 39] represents a first approach to the kinetic since a deeper analysis would require individual steps for the hydrolysis of each sugar polymer, as well as particular steps of degradation of

each monomer. However, the common existence of glucose in both polymers, cellulose and hemicellulose, prevents this possibility.

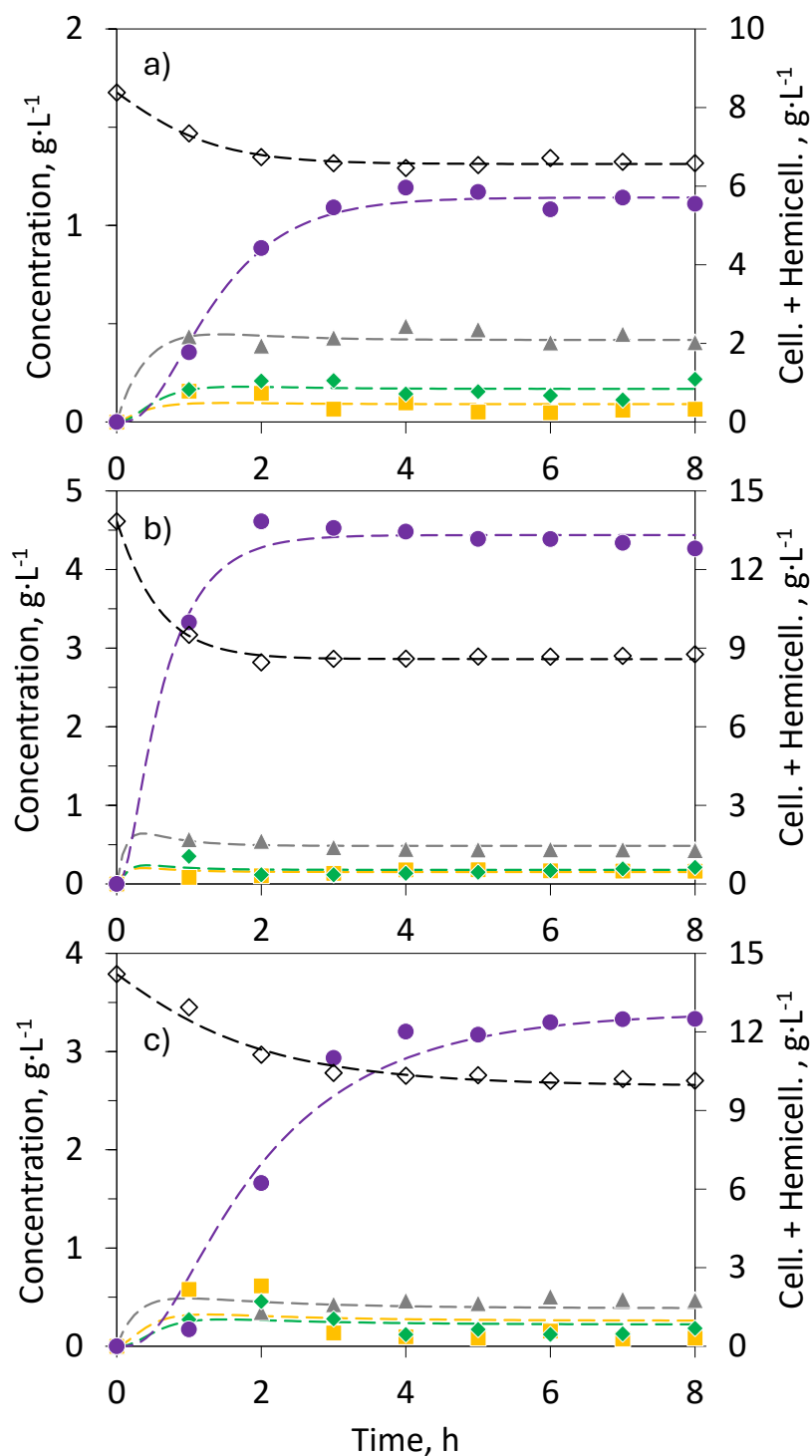
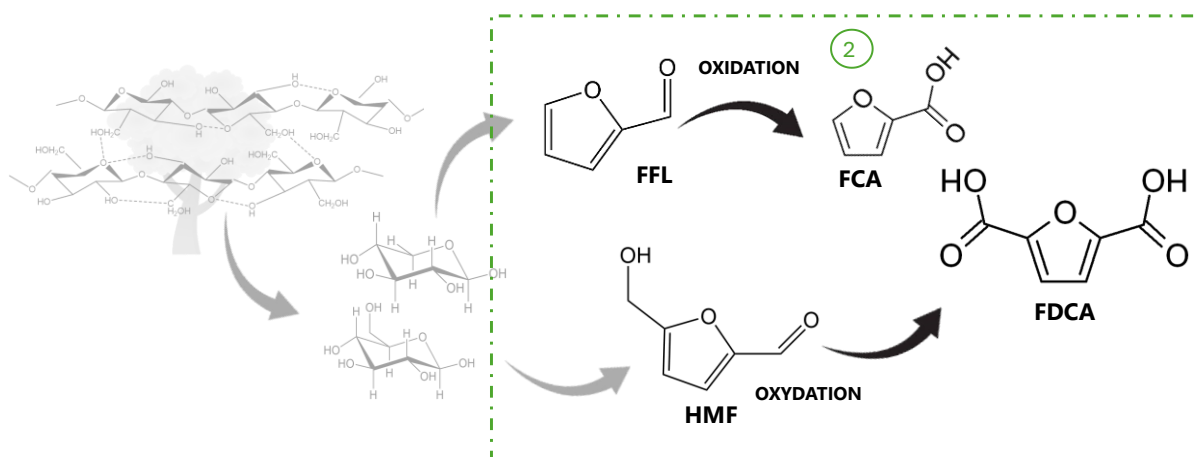


Figure 4.20. Kinetic adjustment of experimental data according to the kinetic model proposed.

Results corresponding to hydrolysis at 220 °C with 1000 ppm of HCl of the (a) fresh sawdust; (b) pretreated sawdust by oxidative method; and (c) pretreated sawdust by reductive method. Symbols:

(◇) sugar polymer; (■) dimers; (▲) TRS; (◆) aldehydes; (●) acids

Despite this general character, the influence of delignification pretreatments is clearly observed, with significant decreases in the activation energy of all the kinetic rates of the hydrolysis pathway. On the contrary, significant increases in the activation energy of undesired reaction is observed after both pretreatments, being more evident in the case of the oxidation one. All these results are congruent with the initial assumption, considering that removing lignin has a positive effect increasing the accessibility to the sugar polymers, promoting their solubility and the subsequent steps. In addition, removing lignin as well as the external functional groups of hemicellulose (more evident in the case of oxidative pretreatment) significantly decreases the humins formation, preventing the oligomerization of aldehydes involved in the reaction.



4.3. FUROIC ACID PRODUCTION BY CATALYTIC OXIDATION OF FURFURAL WITH H_2O_2

The partial oxidation of FFL using hydrogen peroxide is evaluated focusing on a catalyst screening and on the optimization of reaction parameters to increase FCA selectivity limiting other by-products formation such as maleic acid, and 2-hydroxyfuran. Experiments were conducted in a batch reactor using different catalytic supports like MgAl, MgZr, CeO_2 , and TiO_2 , with the incorporation of metals such as Au, Pd, and Pt. These materials have different redox, acidic, and basic properties, offering a range of behaviors in oxidation reactions. The evolution of the different involved compounds (organics and H_2O_2) is present in terms of conversion, selectivity, yield, and carbon balance closure, according to the following expressions:

$$x_{FFL} (\%) = \frac{C_{FFL,0} - C_{FFL,t}}{C_{FFL,0}} \cdot 100 \quad [4.8]$$

$$x_{H_2O_2} (\%) = \frac{C_{H_2O_2,0} - C_{H_2O_2,t}}{C_{H_2O_2,0}} \cdot 100 \quad [4.9]$$

$$Selectivity (\%) = \frac{n_i \cdot C_i}{\sum (n_i \cdot C_i)} \cdot 100 \quad [4.10]$$

$$Yield (\%) = \frac{n_i \cdot C_i}{5 \cdot C_{FFL,0}} \cdot 100 \quad [4.11]$$

$$C.B. (\%) = \frac{\sum (n_i \cdot C_i)}{5 \cdot C_{FFL}} \cdot 100 \quad [4.12]$$

4.3.1. Reaction pathway in absence of heterogeneous catalysts

According to literature [40], compounds with five but also four carbon atoms are expected to be obtained during the furfural oxidation, releasing formic acid that acts as a homogeneous catalyst. Considering the high oxidation capacity of H_2O_2 , a contribution of the autocatalytic process is not discarded, with the subsequent formic acid production that triggers the homogeneous catalytic mechanism. Thus, a correct study of the heterogeneous catalytic mechanism requires a preliminary analysis of these concomitant effects.

An initial experiment in the absence of heterogeneous catalysts was carried out at 50 °C, with a 3/1 H_2O_2 /furfural molar ratio, to study the influence of autocatalytic and homogeneous catalytic mechanisms. The evolution of reactants and products concentration is plotted in **Figure 4.21**. A continuous H_2O_2 conversion is observed, more markedly during the first 2h, reaching 55% of conversion after 8 h. A similar furfural conversion is observed (58%), but the temporal profile indicates a faster reaction rate after 2h. This profile is congruent with the presence of catalytic steps activated by an intermediate.

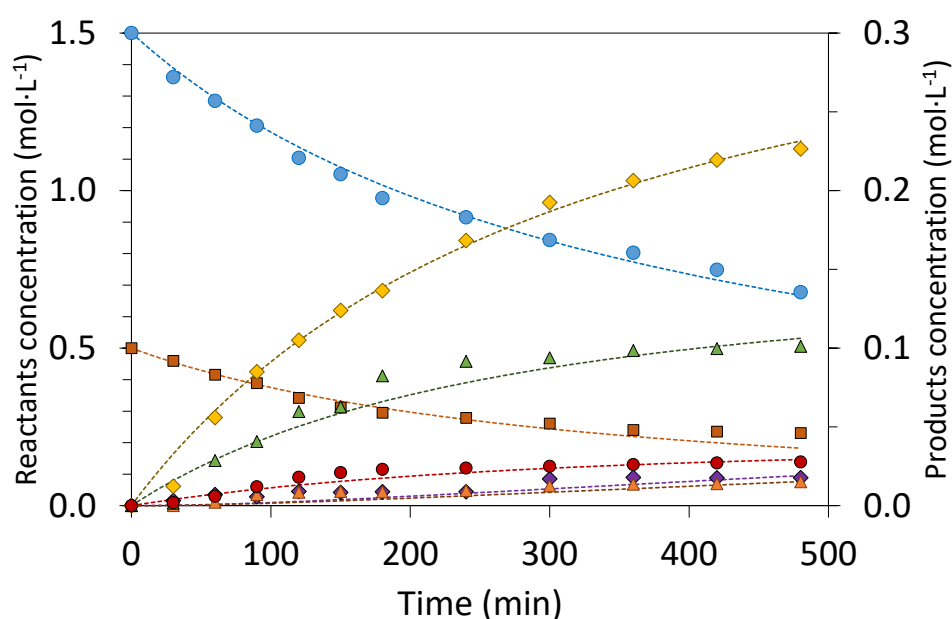


Figure 4.21. Furfural oxidation with H_2O_2 at 50 °C in absence of a catalyst. Symbols: H_2O_2 (●); furfural (■); formic acid (◆); 2-hydroxyfuran (▲); furoic acid (●); maleic acid (◆); and 2(5H) furanone (▲). Broken lines correspond to the kinetic model predictions

The product distribution is congruent with previous literature, despite the diverging values because of the different temperatures used [41]. Formic acid (FA) is the main reaction

product, with a clear increasing trend, yielding more than $0.2 \text{ mol}\cdot\text{L}^{-1}$ after 6 h. 2-Hydroxyfuran is also relevant (HF, $0.12 \text{ mol}\cdot\text{L}^{-1}$), showing a typical profile of a primary compound, with an almost flat concentration after 4 h justified by its decomposition. The same trend is detected for furoic acid (FCA), although FCA is obtained with significantly lower concentrations (max. value of $0.03 \text{ mol}\cdot\text{L}^{-1}$). The stable phase of HF and FCA corresponds with an increase in minority products, 2(5H)-furanone (FN) and maleic acid (MA), suggesting that these compounds are obtained by the oxidation of one or both precursors (HF and FCA). Consequently, their formation is equilibrated with their decomposition. The final concentrations of FN and MA, 0.018 and $0.015 \text{ mol}\cdot\text{L}^{-1}$, are too low to support a strong discussion about the mechanistic route to their formation.

The final carbon balance in the liquid phase is 85.4%, suggesting a significant carbon loss in the gas phase. The presence of any other condensate product in the liquid phase or humins was discarded considering the lack of any unknown signal on the HPLC chromatograms. Moreover, solids were not recovered after the reaction. This loss is then compatible with CO_2 released because of the total oxidation of the different compounds. A separate analysis of the gas phase by a mass-spectrometer identifies CO_2 as the only carbon-containing molecule of the gas sample.

These results suggest that formic acid (FA) is a common product obtained by all the routes that produce C_4 compounds from furfural (C_5). In fact, there is a good correspondence between FA concentration and the difference between the furfural converted and the furoic acid obtained (once the carbon balance closure is considered). Based on this premise, FA is excluded from the selectivity analysis (see Figure 4.22), only considering the C_4 - C_5 compounds. Thus, in carbon basis (Eq. 4.12), the reaction in absence of catalyst produces 60% of HF and similar selectivity of FCA (20.5%) and the mixture of FN and MA (9 and 10.5%). In global terms, these results indicate that the 2-hydroxyfuran route (Baeyer-Villiger mechanism, henceforth, B-V) prevails, the compounds of this pathway being 80% of the total mixture. It is expected that introducing a heterogeneous catalyst could modify the ratio between the two main routes of furfural partial oxidation and, subsequently, the relative distribution of products.

4.3.2. Influence of the catalytic support

Once the relevance of the homogeneous reaction pathways was determined, the activity of the bulk supports was compared. The main characterization results in terms of morphology, acidity, and basicity of the supports considered are summarized in **Table 4.4**. Data shown in this table are obtained by the analysis of N₂ physisorption isotherms, NH₃ and CO₂ spectra included in **Figures 4.22-24**).

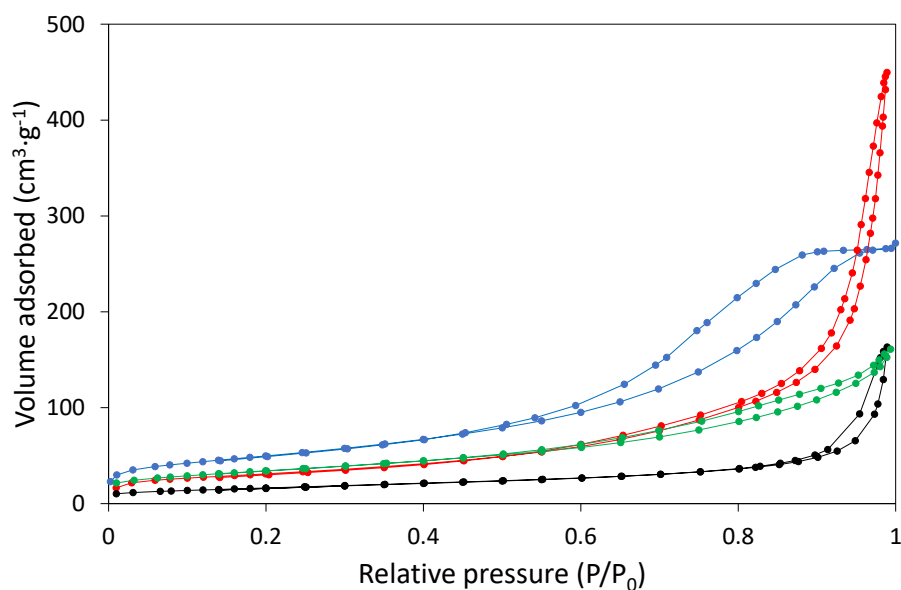


Figure 4.22. N₂ physisorption isotherms of MgAl (blue), MgZr (red), TiO₂ (black), and CeO₂ (green)

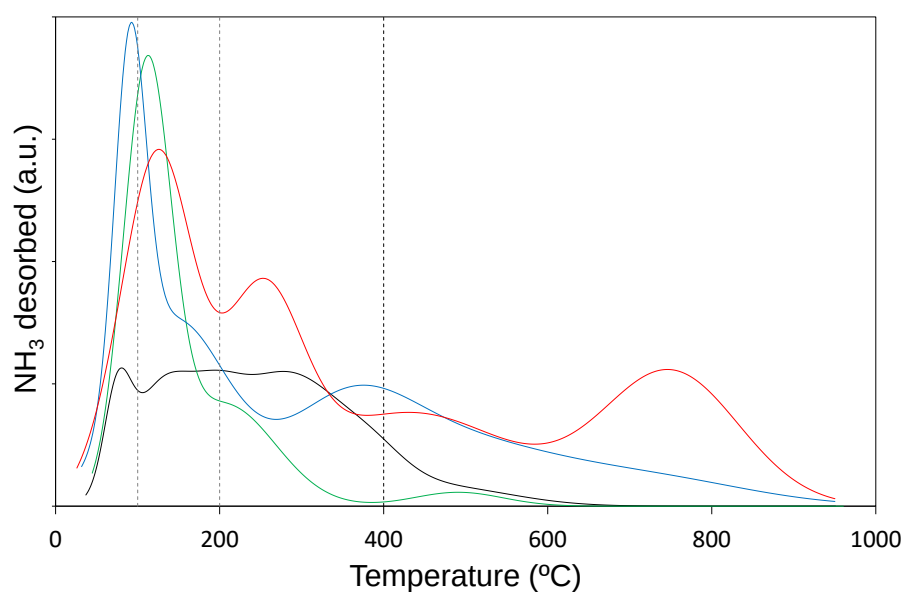


Figure 4.23. NH₃-TPD desorption profiles of MgAl (blue), MgZr (red), TiO₂ (black), and CeO₂ (green)

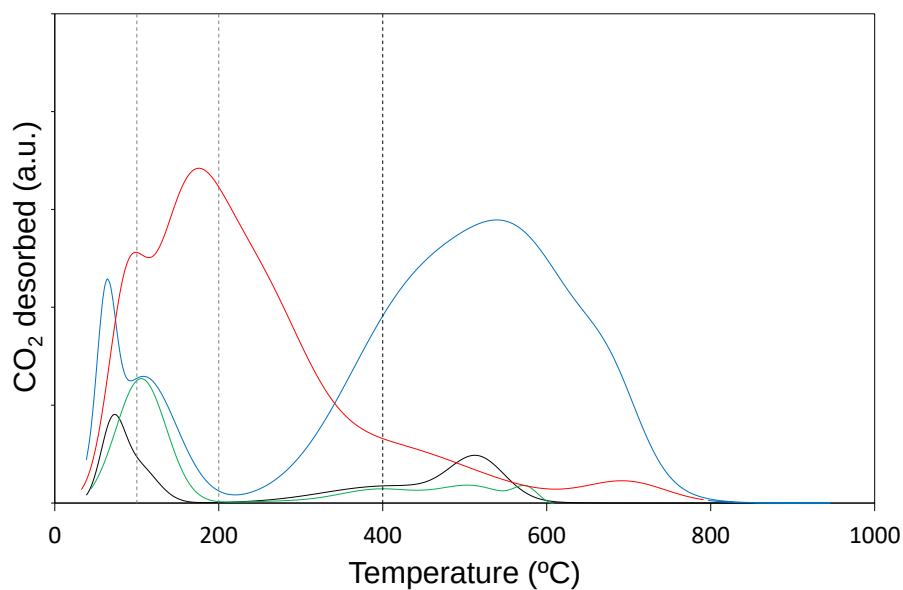


Figure 4.24 CO₂-TPD desorption profiles of MgAl (blue), MgZr (red), TiO₂ (black), and CeO₂ (green)

Table 4.4: Main morphological and chemical properties of the different supports used in this work.

	MgAl	MgZr	TiO ₂	CeO ₂
N₂ physisorption				
Surface area (m ² ·g ⁻¹)	179	111	59	123
Pore volume (cm ³ ·g ⁻¹)	0.4	0.7	0.3	0.3
Pore diameter (nm)	7	18	19	8
Acidity (μmol NH₃·g⁻¹)				
Physisorbed (<100 °C)	109.6	16.3	17.4	0
Weak (100 – 200 °C)	181.5	227.0	67.3	45.7
Medium (200 - 400 °C)	78.5	147.4	127.7	177.3
Strong (>400 °C)	161.2	183.7	18.6	9.2
Total	530.7	574.4	231.1	232.2
Basicity (μmol CO₂·g⁻¹)				
Physisorbed (<100 °C)	14.2	17.9	15.6	22.5
Weak (100 – 200 °C)	40.1	50.3	0	0
Medium (200 - 400 °C)	0	97.2	11.3	9.5
Strong (>400 °C)	268.5	0	11.0	6.1
Total	322.7	165.3	37.9	38.2

All the catalysts are mesoporous materials with surface areas from 60 (TiO_2) to $180 \text{ m}^2\cdot\text{g}^{-1}$ (MgAl) and pore diameters significantly higher than the kinetic diameter of all the molecules involved in the process.

Figure 4.25 illustrates, in terms of selectivity vs. conversion, the experimental data obtained with the four metal oxides tested, keeping the temperature (50°C) and the initial H_2O_2 /furfural ratio (3) of the homogeneous experiments described in the previous section. Results obtained with MgAl match those obtained in the absence of a catalyst, whereas the other three supports present relevant differences, including the formation of other intermediates, such as 5-hydroxy-2(5H)-furanone (HFN), β -formylacrylic acid (BFA), and malic acid (MAL). The presence of these compounds suggests that some steps of the global mechanism require a heterogeneous catalyst to be feasible.

Obtained results can be turned by the reactivity of the hydrogen peroxide. Relevant differences between materials were found, from a slight increase with MgAl and MgZr (64 and 70% at the final reaction time) to an almost total decomposition in the case of CeO_2 (93.7%), with an intermediate behaviour for the TiO_2 .

Furfural conversions are lower than the one reached without a catalyst, detecting values from 33% (MgZr) to 46.7% (MgAl), with an opposite trend than the one observed for H_2O_2 conversion. These results indicate that H_2O_2 is involved in all the steps where furfural is. Thus, the fast decrease of H_2O_2 concentration leads to a reduction in the rates of these reactions, with the subsequent reduction in the furfural conversion. This conclusion is supported by the literature. López Granados and co-workers demonstrate that the larger the H_2O_2 concentration, the faster the furfural conversion rate [42], and several authors propose using different oxides as catalysts for hydrogen peroxide decomposition [43, 44].

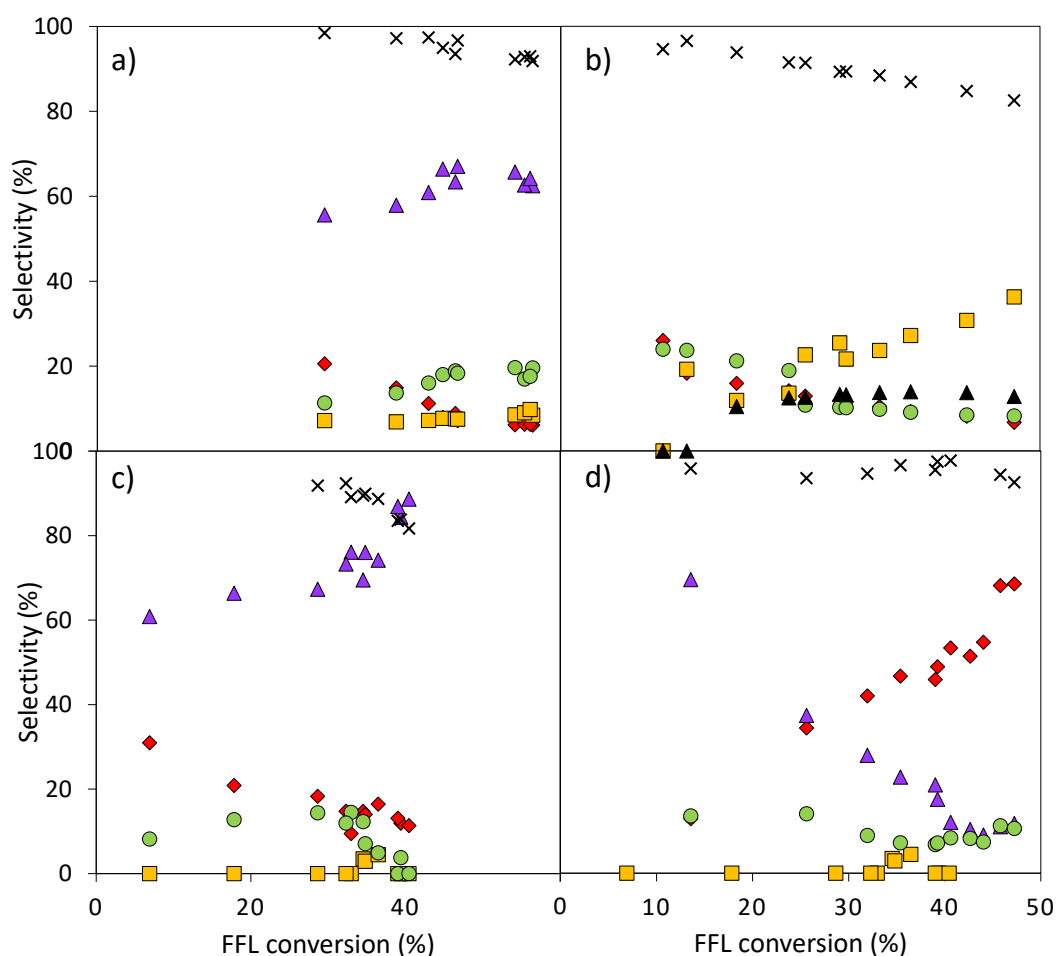


Figure 4.25. Conversion - selectivity plots for furfural oxidation using H_2O_2 at 50°C over (a) MgAl, (b) MgZr, (c) CeO_2 , and (d) TiO_2 . Data correspond to carbon balance (*), and selectivities to MA (♦), FN (■), HF (▲), FCA (●), and HFN (▲)

According to the previous discussion, the H_2O_2 conversion and, subsequently, the furfural one is improved by the redox properties of Ce [45], Ti [46], and Zr [47]. However, the comparison between the blank and experiments with MgZr suggests that the role of acidic/basic properties of the catalysts in the product distribution and the reaction control cannot be discarded.

With MgAl, the distribution of the main products is quite similar than in absence of any catalyst, obtaining a final sample enriched in HF (66.6%) with 18.3% of FCA and 17% of the sum of FN, MA and HFN (catalytic route not observed with the blank). The high carbon balance (93%) and the constant concentration of FCA suggests a positive role of strong basic sites preventing CO_2 formation and stabilizing the resulting organic acids.

In the case of MgZr, the higher strength of the acid sites promotes B-V oxidation pathways [48], observing a significant decrease in the furoic acid selectivity (10.1%), as well as an increase in the formation of acyclic compounds (selectivity of 33.7% of BFA), and their total decomposition to CO₂, fostered by the absence of strong basic sites that could stabilize the organic acids.

With CeO₂, furoic acid is only observed in traces at the beginning of the reaction and FN, HFN, BFA or MAL are not detected. This material presents the highest production of 2-hydroxyfuran (HF), with almost constant selectivity during all the reaction (~90%). In addition to the redox activity of this catalyst, its marked medium-strength acidity (see data in Table 1), with the subsequent total H₂O₂ decomposition (only observed with this material) explains the promotion of this route. The carbon balance (83.2%) suggests that the decomposition of organic compounds is relevant. The maleic acid selectivity is not negligible (11.3%). These results are explained by the easy Ce³⁺/Ce⁴⁺ redox transition, increasing the oxygen mobility and storage capacity, favoring total oxidations [49].

TiO₂ highlights by the fast decomposition of primary products, with maximum selectivities of 67.2% for HF (after 30 min), and 17.4% for FCA (after 1h). Due to their decomposition, maleic acid represents more than 66% of the total selectivity after 8 h, result that corresponds to 20.7% of the product yield. This material presents the best carbon balance (94.8%), discarding relevant decomposition to CO₂. The acidity and basicity properties of this material cannot explain these results, its redox capacity being proposed as the main responsible of it. In the case of TiO₂, oxidations are enhanced but not decompositions, suggesting a complex effect of support oxygen vacancies.

According to this support screening, the role of heterogeneous catalysts tuning the selectivity is very relevant, in such a way that CeO₂ is proposed for the selective production of hydroxyfuran (HF), whereas maleic acid (MA) formation is promoted with TiO₂. This analysis is not so conclusive concerning other reaction intermediates, such as furoic acid. For this compound, a maximum selectivity of 28% is obtained with MgZr, but this result corresponds to a low FFL conversion (9.2%, 1h) and the FCA yield is then almost negligible (1.2%). On the contrary, results with MgAl present a better balance between conversion and selectivity, reaching a maximum yield of 6.7% after 6 h. To sum up, the analysis of relevant

reaction intermediates requires a balance between the catalytic activity and the reaction time to prevent the advance of the reaction to more oxidized compounds.

4.3.3. Kinetic study

With the temporal evolution of reactants and products obtained with and without catalysts and considering the literature [50-52], the mechanism shown in **Figure 4.26** is proposed.

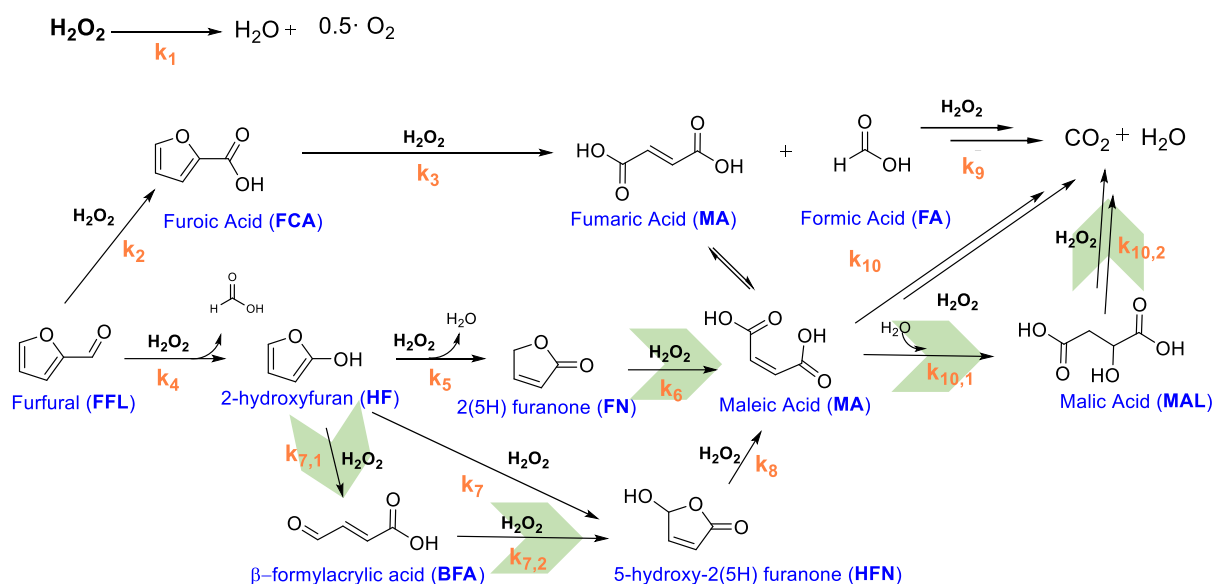


Figure 4.26. Scheme of reaction network of furfural oxidation using H_2O_2 as oxidizing agent. Steps highlighted in green require a heterogeneous catalyst

According to this mechanism, furfural is oxidized by two parallel pathways, obtaining furoic acid and 2-hydroxyfuran, respectively, as primary compounds. Through the second pathway (B-V), oxidation implies a partial decomposition, releasing formic acid. 2-hydroxyfuran is a reactive intermediate that undergoes dehydration, yielding 2(5H)-furanone. The co-presence of hydrogen peroxide and formic acid catalyzes the oxidation of furoic acid and 2(5H)-furanone into maleic and fumaric acid, two isomers in cis-trans rearrangement equilibrium. The low pH (2.8 after 8 h) and the oxidizing medium promotes the degradation of these compounds through consecutive oxidative decarboxylations, releasing CO_2 and water [53]. The absence of a direct correspondence between the products and the hydrogen peroxide conversion suggests an independent self-decomposition of this reactant.

Experimental results were fitted to the kinetic model obtained by applying the mass balances suggested by the reaction mechanism and considering the hypothesis of an ideal stirred batch reactor, according to Eq. (4.12) to (4.18). In these equations, fumaric and maleic acid are considered together. All the compounds are labeled as indicated in Figure 4.26 to simplify the mathematical expressions.

$$\frac{dC_H}{dt} = -k_1 \cdot H - k_2 \cdot FFL \cdot H - k_3 \cdot FCA \cdot H - k_4 \cdot FFL \cdot H - k_6 \cdot FN \cdot H - k_7 \cdot HF \cdot H - k_8 \cdot HFN \cdot H - k_9 \cdot MA \cdot H - k_{10} \cdot MA \cdot H \quad [4.12]$$

$$\frac{dC_{FFL}}{dt} = -k_2 \cdot FFL \cdot H - k_4 \cdot FFL \cdot H \quad [4.13]$$

$$\frac{dC_{FCA}}{dt} = k_2 \cdot FFL \cdot H - k_3 \cdot FCA \cdot H \quad [4.14]$$

$$\frac{dC_{FA}}{dt} = k_3 \cdot FCA \cdot H + k_4 \cdot FFL \cdot H - k_9 \cdot MA \cdot H \quad [4.15]$$

$$\frac{dC_{MA}}{dt} = k_3 \cdot FCA \cdot H + k_6 \cdot FN \cdot H + k_8 \cdot HFN \cdot H - k_{10} \cdot MA \cdot H \quad [4.16]$$

$$\frac{dC_{HF}}{dt} = k_4 \cdot FFL \cdot H - k_5 \cdot HF \cdot H - k_7 \cdot FN \cdot H \quad [4.17]$$

$$\frac{dC_{FN}}{dt} = k_5 \cdot HF \cdot H - k_6 \cdot FN \cdot H \quad [4.18]$$

The coexistence of homogeneous and heterogeneous reaction pathways is modeled considering each kinetic rate constant as the sum of two values: a constant one due to the homogeneous contribution (related to the activity of hydrogen peroxide and protons), and a variable one related to the solid catalyst. Due to the extended number of terms, this disaggregation ($k_i = k_{(i,hom)} + k_{(i,het)}$) is not specified in the equations. This methodology requires a previous analysis of the blank experiment to isolate the contribution of the homogeneous rates in those steps identified without a solid catalyst. This analysis also allows identifying those steps that require a solid catalyst to be promoted (identified with green shadow in Figure 4.26).

The low pH (<3) obtained in less than 2h allows considering the homogeneous catalysis is due to the presence of protons as constant. Based on these appreciations, the effect of the acidity is embedded in the common contribution (homogeneous terms) without including any extra term in the mass balances. Since no relevant differences between the

acids that could release these protons were observed, the main contribution is attributed to formic acid because of its significantly higher concentration (more than 90% in some cases).

In contrast, experimental results demonstrate a marked influence of the hydrogen peroxide concentration on the different steps, as well as a different evolution of its concentration as a function of the catalyst used. Therefore, it is a relevant parameter in the mass balances for the heterogeneous catalysis, leading to an apparent second order kinetics for most of the steps, as well as a decomposition rate (k_1) with a homogeneous and a heterogeneous contribution, in the same way as for the organic compounds.

The kinetic rates of the main steps (k_1 - k_4) are summarized in **Table 4.5**, whereas the values for secondary steps that could be affected by a higher inaccuracy (due to the lower concentrations to be fit) are included in **Table 4.6**. The kinetic rates reported for the different supports correspond only to the heterogeneous contribution. The real rates are obtained by the sum of both terms, but the discussion is more clearly based only on those terms affected by the solid catalysts.

The goodness of fit for the blank experiment is illustrated in Figure 4. 21, observing a great correspondence between experimental (dots) and fitted values (broken lines). These values represent a common homogeneous contribution for those experiments with a solid catalyst.

Table 4.5. Reaction rate constants based on the proposed reaction network. Units: k_1 (s^{-1}); $k_2 - k_4$ ($L \cdot mol^{-1} \cdot s^{-1}$). Except in the case of the blank experiment, values shown correspond to the heterogeneous contribution to each step, the total rate being obtained as the sum of the homogeneous rate (blank experiment) and each value.

	Blank	MgAl	MgZr	CeO ₂	TiO ₂
k_1	$1.8 \cdot 10^{-5}$	0	$3.2 \cdot 10^{-5}$	$2.2 \cdot 10^{-4}$	$9.3 \cdot 10^{-6}$
k_2	$1.0 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$
k_3	$5.2 \cdot 10^{-5}$	$3.9 \cdot 10^{-1}$	$3.9 \cdot 10^{-1}$	$6.4 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
k_4	$1.9 \cdot 10^{-5}$	$3.4 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$	$2.8 \cdot 10^{-5}$	$9.9 \cdot 10^{-6}$
r^2	0.914	0.909	0.903	0.919	0.931

Table 4.6. Reaction rate constants based on the proposed reaction network (k_1 indicated in s^{-1} , the other constants in $L \cdot mol^{-1} \cdot s^{-1}$)

	Blank	MgAl	MgZr	CeO ₂	TiO ₂
k_1	$1.8 \cdot 10^{-5}$	-	$3.2 \cdot 10^{-5}$	$2.2 \cdot 10^{-4}$	$9.3 \cdot 10^{-6}$
k_2	$1.0 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$
k_3	$5.2 \cdot 10^{-5}$	$3.9 \cdot 10^{-1}$	$3.9 \cdot 10^{-1}$	$6.4 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
k_4	$1.9 \cdot 10^{-5}$	$3.4 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$	$2.8 \cdot 10^{-5}$	$9.9 \cdot 10^{-6}$
k_5	$2.0 \cdot 10^{-5}$	-	$1.4 \cdot 10^{-4}$	-	$2.5 \cdot 10^{-5}$
k_6	-	-	-	$2.0 \cdot 10^{-9}$	-
k_7	$5.0 \cdot 10^{-6}$	-	$9.9 \cdot 10^{-5}$	-	$1.6 \cdot 10^{-8}$
$k_{7,1}$	-	$3.0 \cdot 10^{-6}$	$3.0 \cdot 10^{-4}$	-	$1.2 \cdot 10^{-4}$
$k_{7,2}$	-	$3.3 \cdot 10^{-4}$	$4.6 \cdot 10^{-5}$	$2.8 \cdot 10^{-4}$	$4.9 \cdot 10^{-5}$
k_8	$5.1 \cdot 10^{-6}$	-	-	$6.9 \cdot 10^{-3}$	-
k_9	-	$2.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	$1.3 \cdot 10^{-7}$	$2.1 \cdot 10^{-5}$
k_{10}	-	-	$5.2 \cdot 10^{-1}$	-	$1.1 \cdot 10^{-8}$
$k_{10,1}$	-	$6.4 \cdot 10^{-4}$	$6.6 \cdot 10^{-7}$	$6.0 \cdot 10^{-4}$	$7.4 \cdot 10^{-5}$
$k_{10,2}$	-	$1.0 \cdot 10^{-2}$	-	$1.7 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$

As illustrated in Figure 4.26 when a solid catalyst is involved, the quantification of all the intermediates suggests that steps 7 and 10 of the original mechanism must be decomposed into two intermediate ones, justifying the detection of β -formylacrylic (BFA) and malic acid (MAL), compounds not detected without a catalyst. The detailed temporal profiles comparing experimental and fitted data obtained with the most promising supports (TiO₂ and MgAl) are included in **Figure 4.27**, whereas the corresponding ones with MgZr and CeO₂ are incorporated **Figure 4.28**.

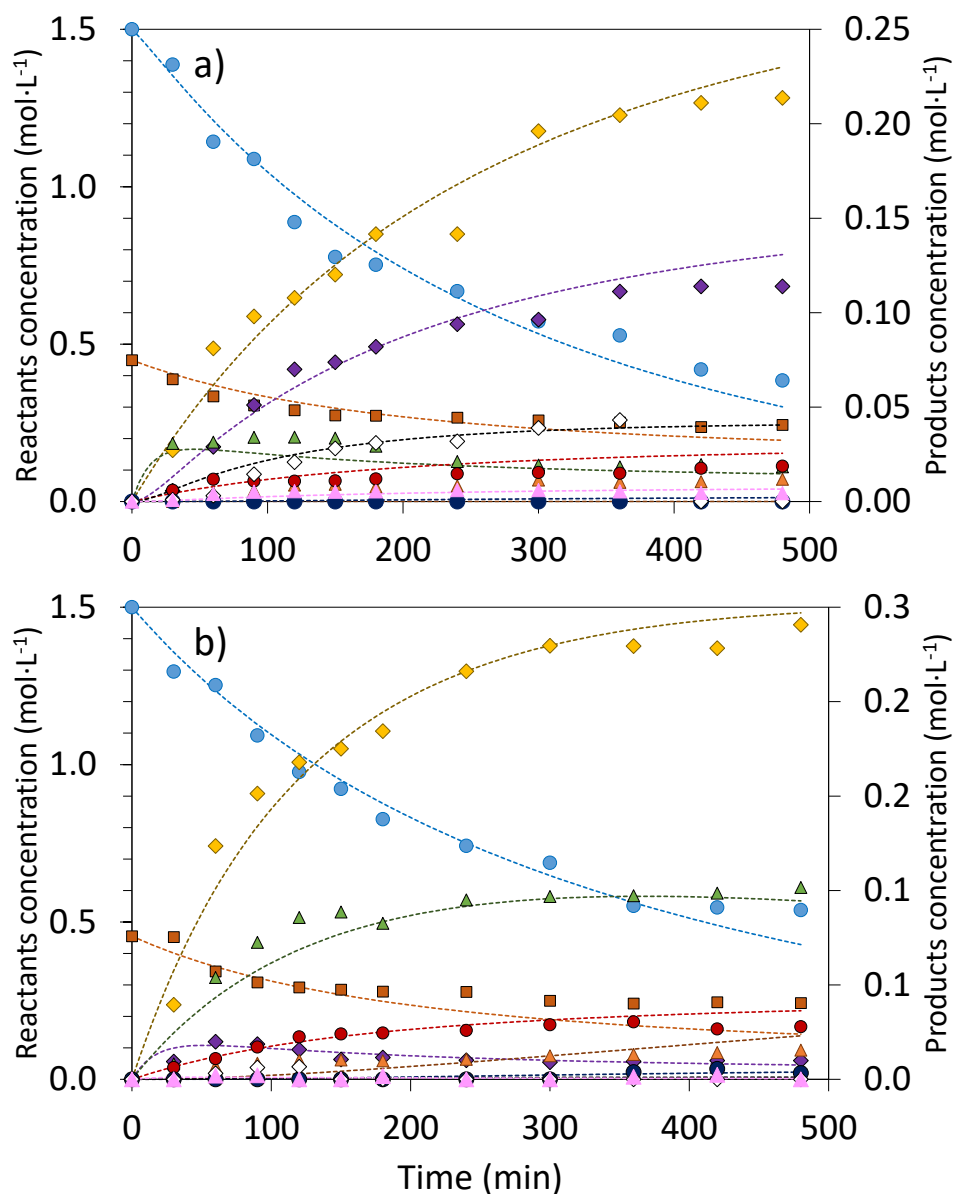


Figure 4.27. Furfural oxidation with H_2O_2 at 50 °C in presence of (a) TiO_2 and (b) MgAl . Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲). Broken lines correspond to the kinetic model predictions

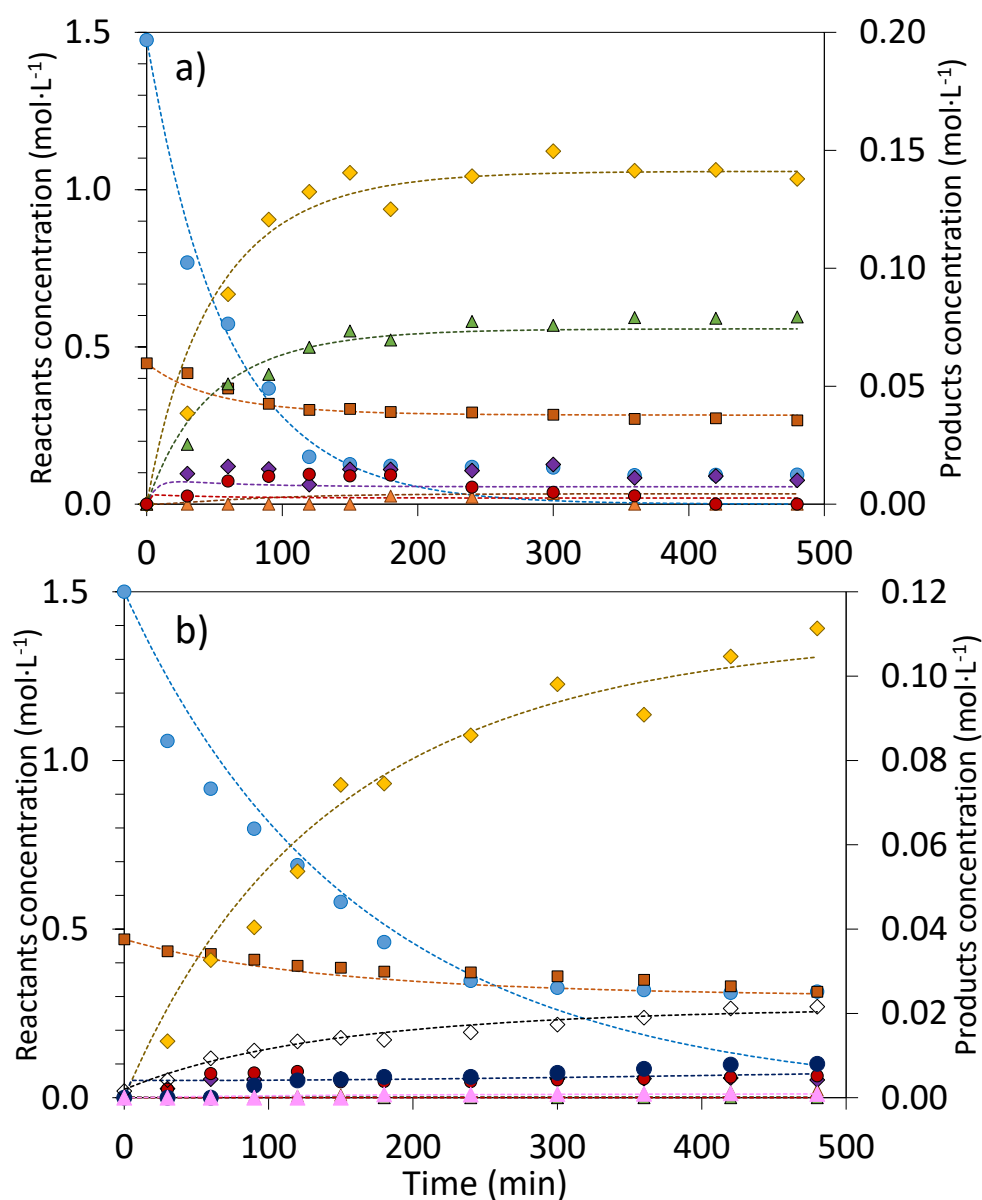


Figure 4.28. Furfural oxidation with H_2O_2 at 50 °C with (a) CeO_2 , and (b) MgZr . Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲). Broken lines correspond to the kinetic model adjustment

The complexity of the mechanism limits the analysis based on the characterization parameters. However, a clear correspondence between the main kinetic rates and the catalyst acidity is observed, as shown in **Figure 4.29**.

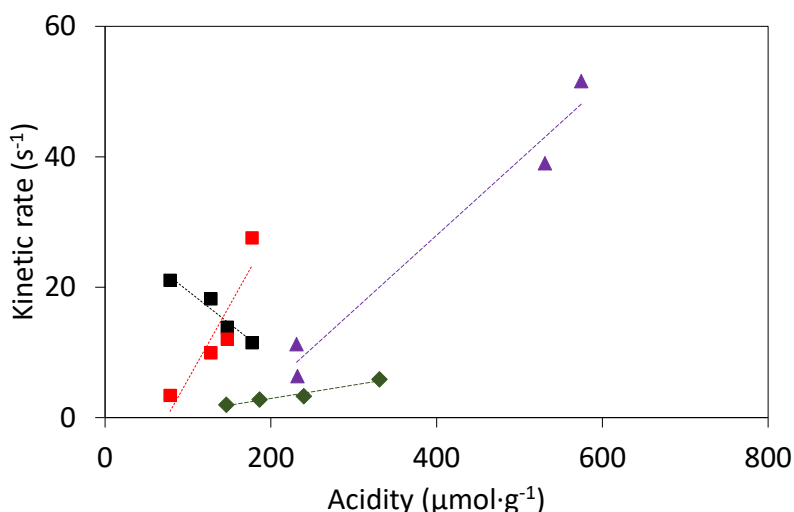


Figure 4.29. Evolution of the kinetic constants for furfural conversion considering both pathways, k_2 (■, $\times 10^{-5}$) and k_4 (■, $\times 10^{-6}$), as a function of the medium-strength acidity; HF oxidation, $k_5 + k_7 + k_{11}$ (◆, $\times 10^{-4}$) as a function of the medium-strength and strong acid sites, and the furoic acid oxidation, k_3 (▲, $\times 10^{-2}$) as a function of the total acidity of the oxides used as catalysts

As anticipated by the literature [54, 55] and corroborated with our experimental results, the lateral route of 2-hydroxyfuran formation (B-V mechanism) is promoted by the acidity (k_4), the medium-strength sites being the most relevant ones for this step. An opposite influence is observed for the furoic acid production, supporting the negative role of acidity to maximize its yield. In the same way, a positive effect of acidity is observed also for the following oxidizing steps, with a higher relevance of the strong acidic sites for the total decomposition of the two main products of the reaction, the 2-hydroxyfuran, and furoic acid, producing CO_2 as the final compound.

The parallel analysis considering the basicity of these materials is not conclusive. The lack of a clear correlation between oxidizing steps and basicity discards the prevalence of the Cannizzaro disproportionation mechanism also proposed in the literature [56, 57]. In good agreement, furfuryl alcohol is not observed. Although a positive role of basicity is suggested by the experiments (increasing the acids stability and preventing their total decomposition into CO_2), the redox properties of some of these catalysts alter the H_2O_2 available to produce the furfural conversion, this fact prevailing over the basicity. These effects are more relevant for first intermediates, such as the furoic acid (FCA), compounds whose production is more sensitive to the weak equilibrium between activity, selectivity and stability.

4.3.4. Activity of bifunctional catalysts

Bifunctional catalysts were prepared with a theoretical 1% of Pt, Pd, or Au. These metals were chosen considering their high oxidation capacity demonstrated for similar systems [49], to analyze their influence tuning the selectivity of the reaction. The low metal loading leads to good metal dispersions, maximizing the activity of these metal particles and enabling a direct comparison with the bulk material. In good agreement, there is a complete correspondence between the surface structure of the bulk and the metal-modified catalysts, as observed by XRD (**Figure 4.30-31**). **Table 4.7** shows the main characterization results, in terms of morphology, metal loading and dispersion, and surface chemistry.

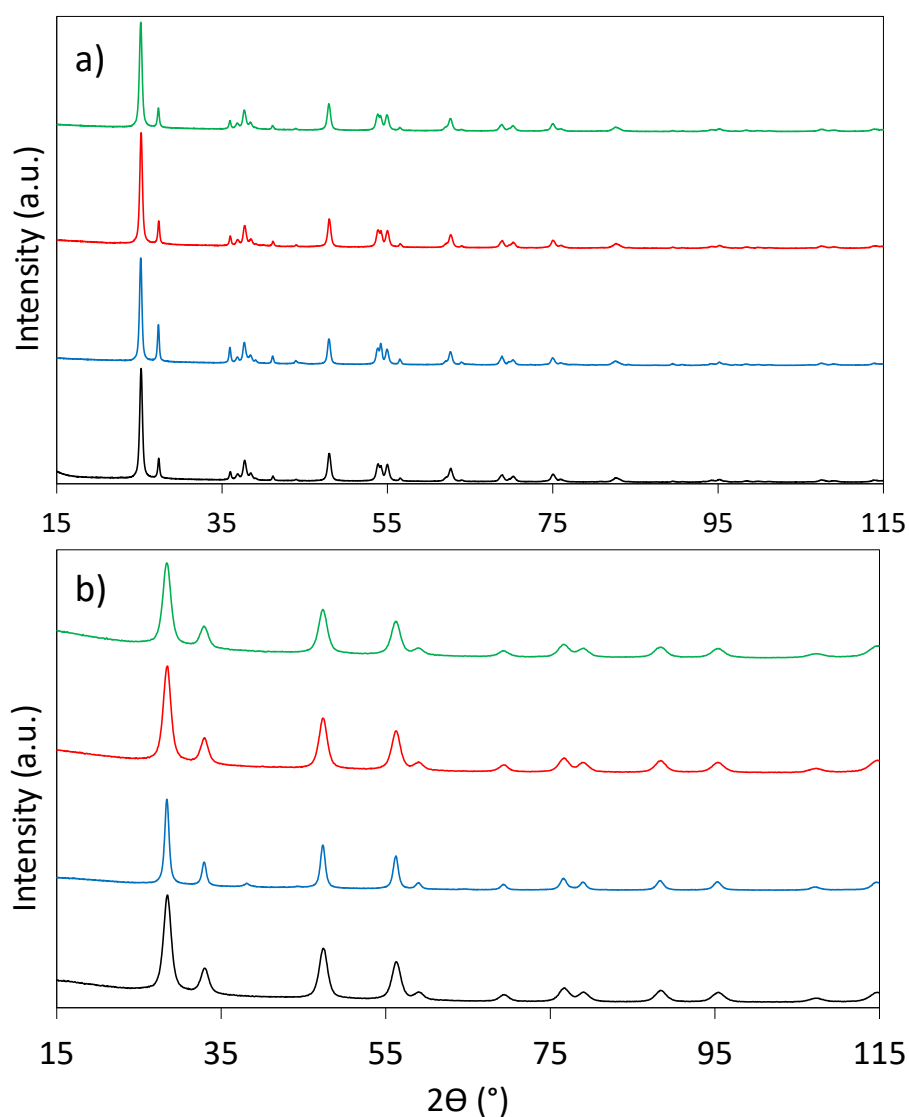


Figure 4.30. XRD diffractograms of (a) TiO₂ (black), Au/TiO₂ (blue), Pd/TiO₂ (red) and Pt/TiO₂ (green) and (b) CeO₂ (black), Au/CeO₂ (blue), Pd/CeO₂ (red) and Pt/CeO₂ (green)

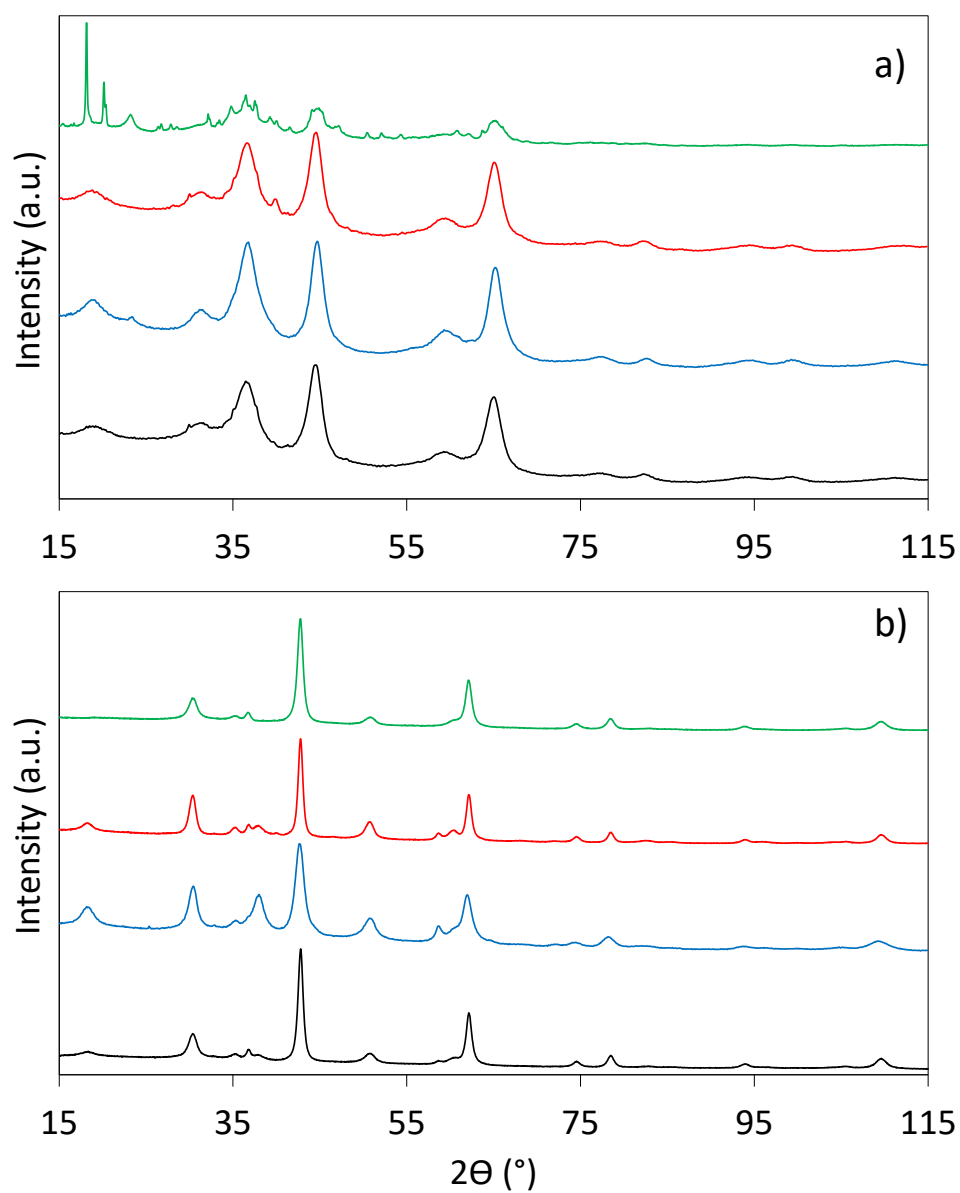


Figure 4.31. XRD diffractograms of (a) MgAl (black), Au/ MgAl (blue), Pd/ MgAl (red) and Pt/MgAl (green) and (b) MgZr (black), Au/ MgZr (blue), Pd/ MgZr (red) and Pt/MgZr (green).

Table 4.7. Main characterization properties of the different bifunctional oxides used in this work

	Au/TiO ₂	Pt/TiO ₂	Pd/TiO ₂	Au/CeO ₂	Pt/CeO ₂	Pd/CeO ₂	Au/MgZr	Pt/MgZr	Pd/MgZr	Au/MgAl	Pt/MgAl	Pd/MgAl
N₂ physisorption												
Surface area (m ² ·g ⁻¹)	151	165	196	82	128	78	118	114	115	66	54	63
Pore volume (cm ³ ·g ⁻¹)	0.4	0.3	0.4	0.7	0.6	0.3	0.2	0.2	0.2	0.4	0.4	0.7
Pore diameter (nm)	8	12.1	5.6	23.1	17.7	11.9	4.8	4.4	4.7	21	24.4	36
ICP, Metal loading (%)	0.87	0.87	1.05	0.97	0.88	0.89	0.8	0.79	1.06	0.85	0.82	1
TEM												
Particle size (nm)	8.3	7.7	9.9	7.8	11.9	8.6	1.5	4.6	9.3	8.5	10.8	6.5
Dispersion (%)	14.1	21.6	15.9	16.5	15.4	14.7	49.4	36.4	13.8	13.1	11	24
Acidity (μmol)												
Physisorbed (<100 °C)	0	19.7	116	0	52.4	75.5	0	0	35.5	22.9	25.4	22
Weak (100 – 200 °C)	0	58.9	158	120	117	192	201	231	36.2	81.4	78.3	53
Medium (200 - 400 °C)	315	36.5	64.1	109	148	130	0	22.9	124	0	50.3	55
Strong (>400 °C)	50.7	43.5	0	192	86.3	0	0	0	0	0	0	0
Total	366	159	338	422	403	397	201	254	196	104	154	130
Basicity (μmol)												
Physisorbed (<100 °C)	24.8	12.2	36.4	6.6	40.3	13.8	24.1	111	28.3	17.1	24.5	15
Weak (100 – 200 °C)	0	58	80.3	37.5	78.3	33.1	0	0	8.1	0	0	0
Medium (200 - 400 °C)	117	93.1	199	50.4	110	70.2	0.8	16.4	0	4.9	3.1	6.5
Strong (>400 °C)	157	56.5	0	25.9	20.9	0	4.5	37.8	14.1	46.7	38.8	3.8
Total	298	220	316	120	250	117	29.4	164	50.5	68.6	66.3	25

Bifunctional catalysts keep the surface properties of the bulk materials, observing slight decreases in the surface area due to the non-porous surface of metal nanoparticles. The N_2 isotherms are included in **Figure 4.32**

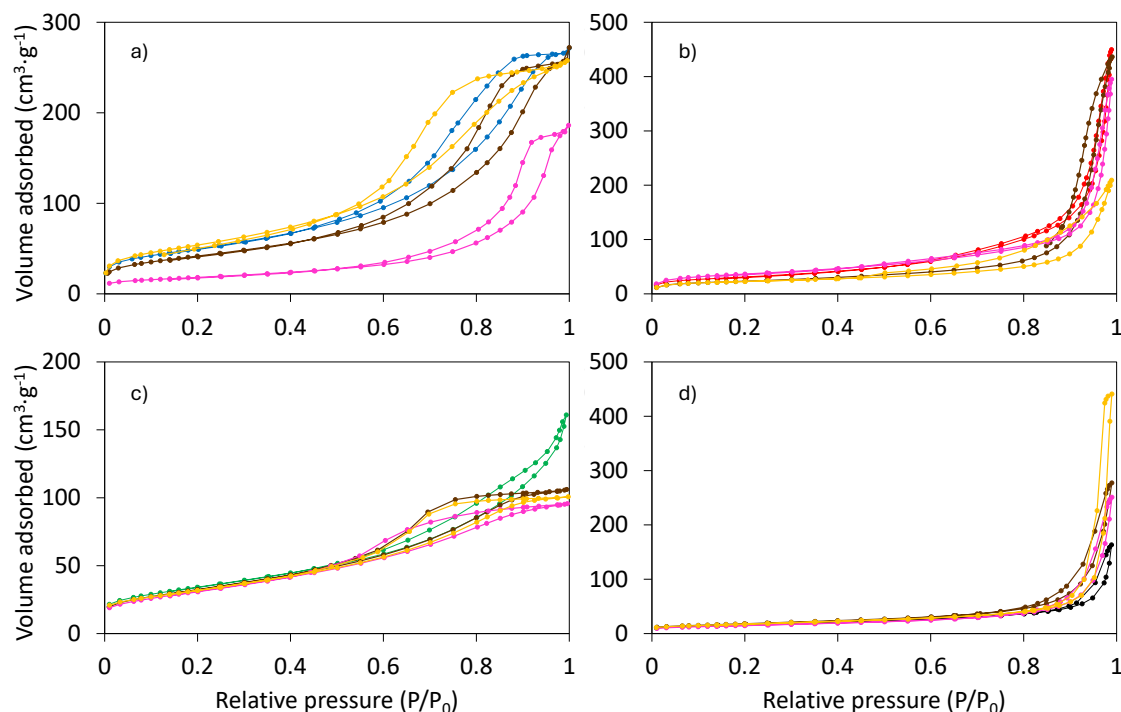


Figure 4.32. N_2 isotherms of catalysts based on (a) MgAl, (b) MgZr, (c) CeO_2 , and (d) TiO_2 . See Fig. 4.22 to codes for the supports. Au-based materials are indicated in yellow, Pd in brown, and Pt in pink

Considering the preparation methodology (dry impregnation except in the case of Au materials), these particles are located inside the pores. Consequently, there is a slight increase in the average size of the pores because the smallest ones can be completely blocked, increasing the relative weight of the biggest ones. This partial blockage is also congruent with the differences observed in surface chemistry. In most cases, the total concentration of the acid sites is lower than the one of the bulk materials, keeping the same relative weight in strength terms. The highest decrease is observed with Pt/MgAl (70.1% with respect to the total concentration of the parent material), being also very significative with Pd/ TiO_2 (33.4%), Pd/ TiO_2 (54.9%) and Au/ TiO_2 (43.7%). For the other materials, the decrease is less relevant, in general lower than 20%. The effect on the basicity is not so clear. There is a relevant decrease in basicity with Au/ TiO_2 and Pt/MgAl (~33%), whereas the basicity of other materials, such as Pt/ TiO_2 and Pd/ TiO_2 significantly increases. The TPD data are included in **Figure 4.33-34**.

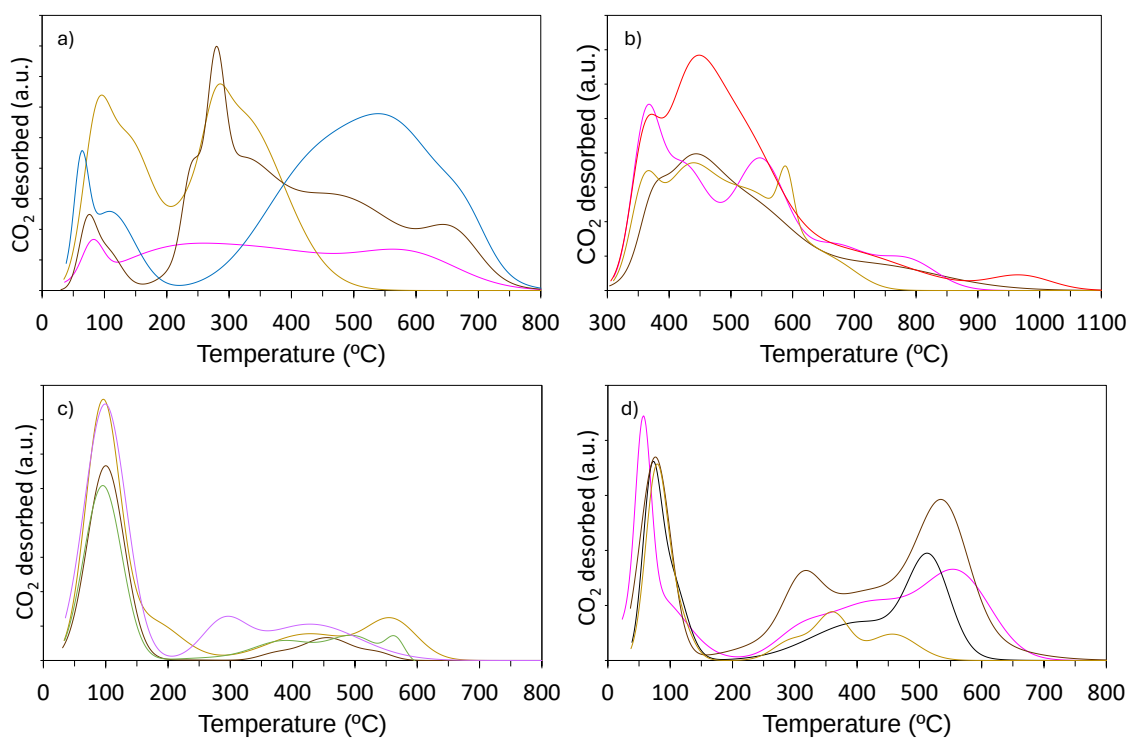


Figure 4.33. CO_2 desorbed during the TPD- CO_2 of catalysts based on (a) MgAl, (b) MgZr, (c) CeO_2 , and (d) TiO_2 . See Fig. 4.22 to codes for the supports. Au-based materials are indicated in yellow, Pd in brown, and Pt in pink.

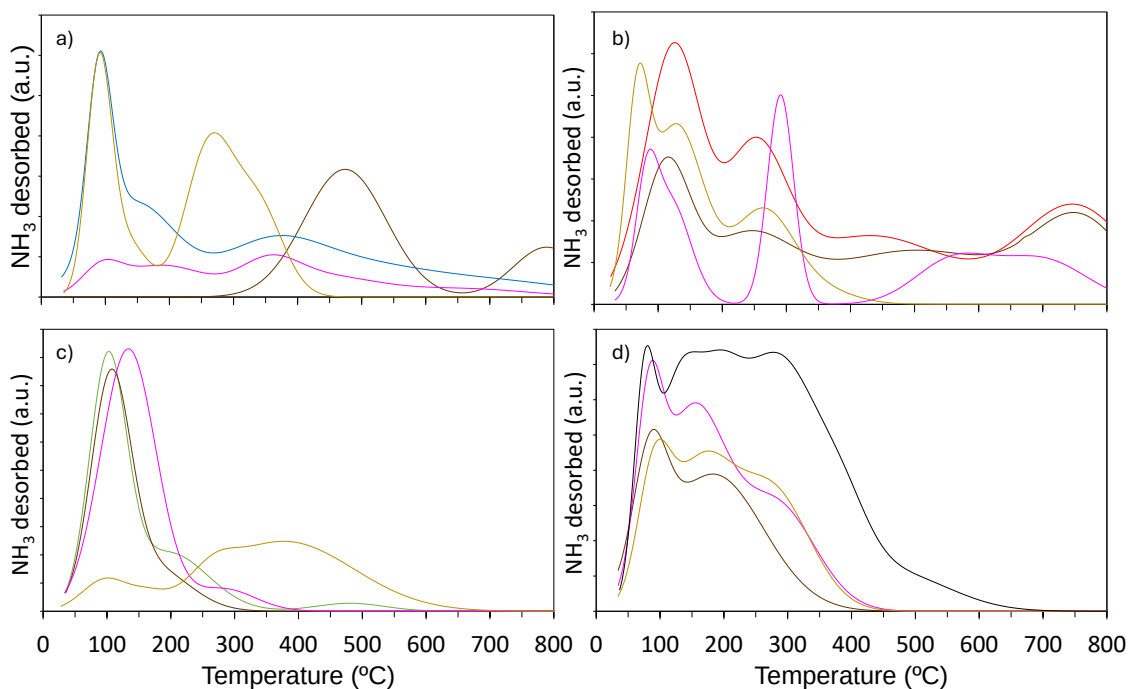


Figure 4.34. NH_3 desorbed during the TPD- NH_3 of catalysts based on (a) MgAl, (b) MgZr, (c) CeO_2 , and (d) TiO_2 . See Fig. 4.22 to codes for the supports. Au-based materials are indicated in yellow, Pd in brown, and Pt in pink.

The dispersion values indicated in Table 4.7 correspond to TEM results. The CO chemisorption analyses were also carried out, obtaining discrepancies lower than 5% in most cases (see **Table 4.8**). However, these results were not included in Table 4.7 since this technique could not be efficiently applied to Au-catalysts. TEM results demonstrate the presence of reduced metal particles in the range of 5.5-7.5 nm, with slightly lower values for Pt/CeO₂ and Pd/CeO₂ (4.6 and 1.5 nm). These values were obtained after measuring more than 300 particles from micrographs such as those shown in **Figure 4.35-38**. In agreement with these similar particle sizes, most of these materials have a similar metal dispersion, from 18 to 30 %, reaching values up to 45 % for those catalysts with the smallest particle size.

Table 4.8. CO chemisorption results of the different bifunctional oxides used in this work

	Pd/MgAl	Pt/MgAl	Au/MgAl	Pd/MgZr	Pt/MgZr	Au/MgZr	Pd/CeO ₂	Pt/CeO ₂	Au/CeO ₂	Pd/TiO ₂	Pt/TiO ₂	Au/TiO ₂
CO chemisorption												
Particle size (nm)	11	6.5	9.9	10	9.7	13	2.4	0.8	-	8.9	7.9	-
Dispersion (%)	15	21	16	11	17	8.9	46	49	-	13	14	-
Adsorbed CO (cm ³ /g SPT)	0.17	0.21	0.19	0.13	0.20	0.10	0.35	0.44	-	0.14	0.16	-

Table 4.9. Selectivities distribution and carbon balance obtained with the different bifunctional catalysts used in this work

	Pd/MgAl	Pt/MgAl	Au/MgAl	Pd/MgZr	Pt/MgZr	Au/MgZr	Pd/CeO ₂	Pt/CeO ₂	Au/CeO ₂	Pd/TiO ₂	Pt/TiO ₂	Au/TiO ₂
FCA	37	35	37	37	0	24	14	0	21	23	15	39.1
FN	0	4	2.2	0	100	4	0	0	0	0	6.8	0
MA	5.9	3.9	18	7.7	0	18	7.1	0	5.6	77	9.8	0
MAL	19	10	0.3	28	0	1.9	21	79	0	0	7.7	38.1
HF	7	0	25	7.5	0	25	46	22	37	0	0	16.5
HFN	0	47	0	0	0	0	0	0	0	0	61	0
BFA	28	0	18	20	0	28	12	0	37	0	0	6.3
Carbon Balance (%)	91	96	86	94	80	98	94	74	93	87	91	86.3

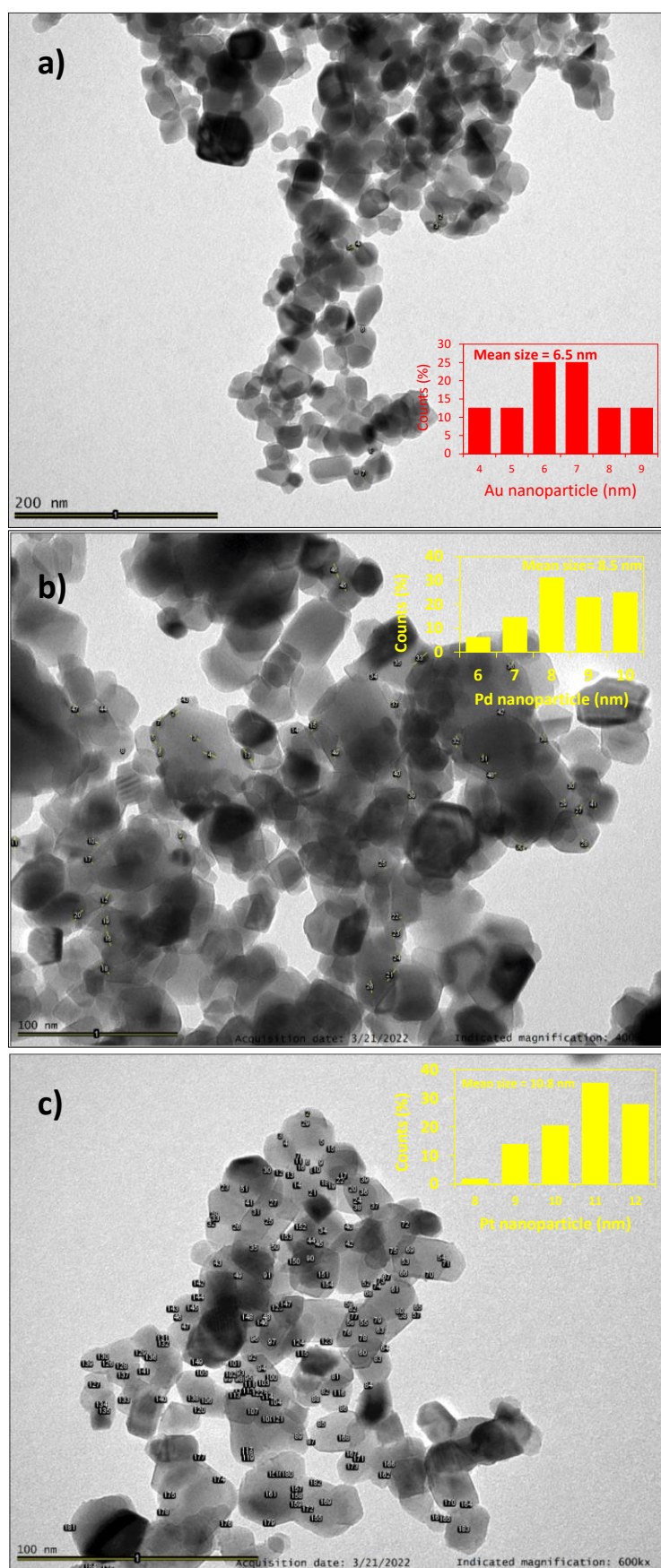


Figure 4.35. TEM micrographs and histograms of (a) Au/TiO₂, (b) Pd/TiO₂, and (c) Pt/TiO₂

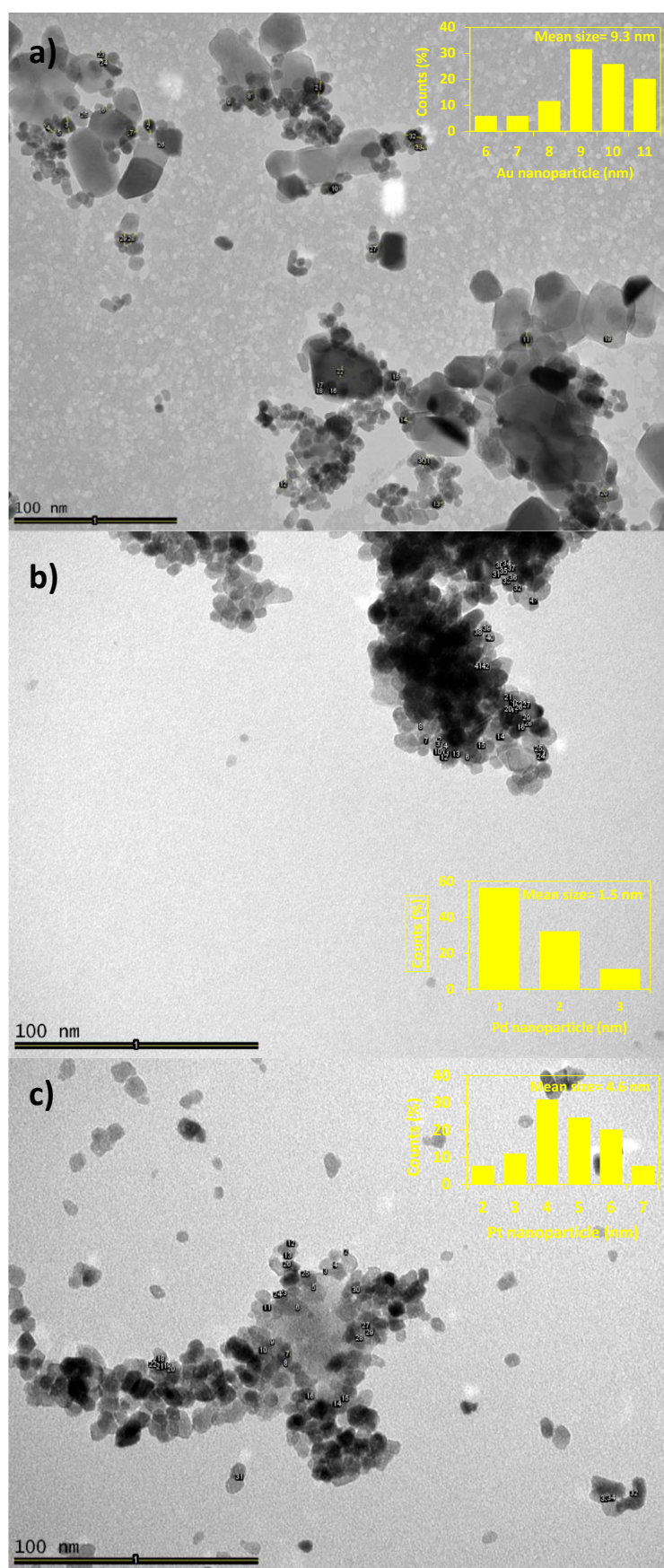


Figure 4.36. TEM micrographs and histograms of (a) Au/CeO₂, (b) Pd/CeO₂, and (c) Pt/CeO₂

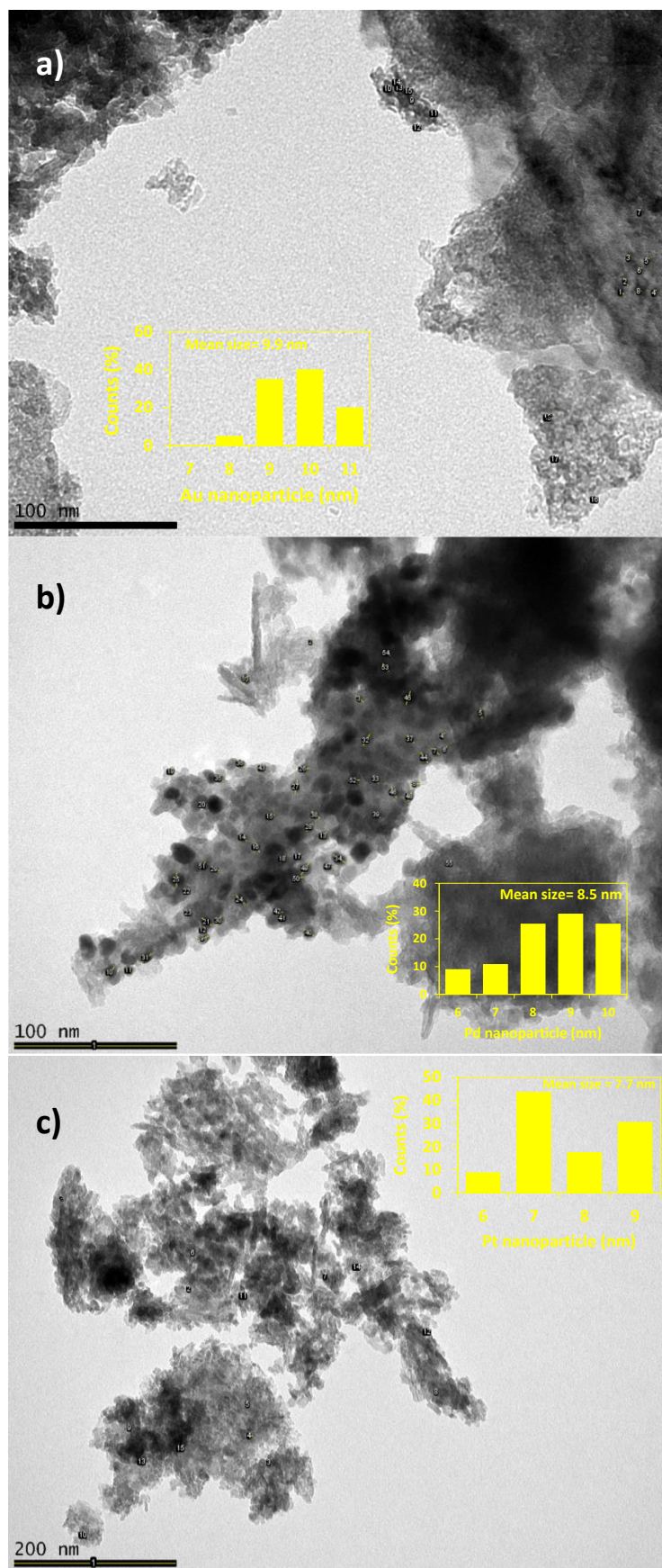


Figure 4.37. TEM micrographs and histograms of (a) Au/MgAl, (b) Pd/MgAl, and (c) Pt/MgAl

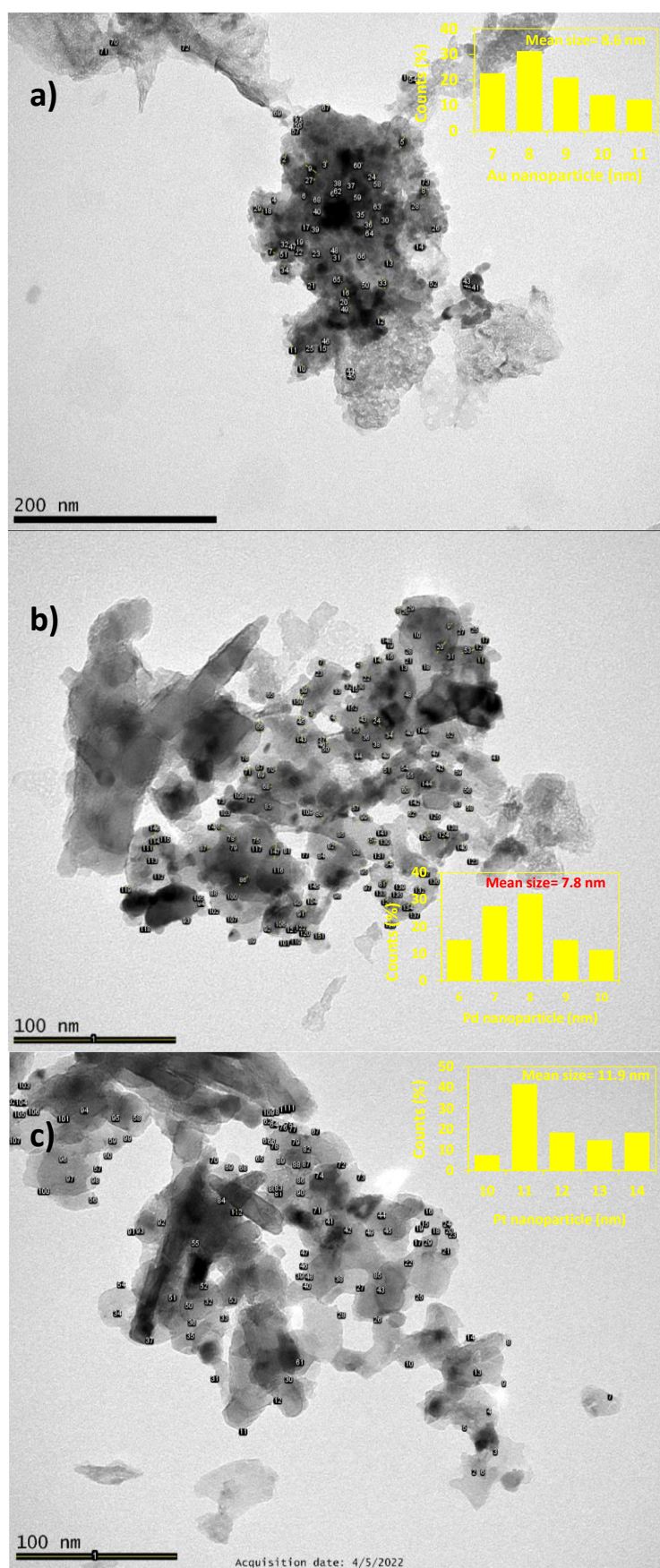


Figure 4.38. TEM micrographs and histograms of (a) Au/MgZr, (b) Pd/MgZr, and (c) Pt/MgZr

These dispersion results, as well as the own nature of these metals and their synergetic effect with the surface chemistry of the catalytic support, are assumed to be the most relevant parameters to discuss the catalytic activity of these bifunctional catalysts. TPR analyses of the spent catalysts discard that experimental results are affected by a total or partial oxidation of metal particles. As indicated in the introduction section, furoic acid (FCA), 2(5H)-furanone (FN), maleic and malic acids (MA and MAL, respectively) are the most interesting compounds obtained by furfural partial oxidation. 2(5H)-furanone (FN) is not significantly produced with almost none of the catalysts tested, except for Pt/MgZr, a catalyst that selectively produces this compound (100%).

Figure 4.39 shows the FCA selectivity-conversion plots for the different catalysts, whereas main results after 8h reaction time are summarized in **Table 4.10** (the detailed products distribution is included **Table 4.9**). As observed in Fig. 4.39, the presence of noble metals increases the maximum selectivity of FCA obtained with each support. Platinum is the only exception, its behaviour strongly depends on the support. Thus, using MgZr and CeO₂, FCA is not detected whereas, with the other two oxides (MgAl and TiO₂), the maximum selectivities (40.8 and 23.3%) are reached in less than 1h. In the case of Pt/MgAl, the corresponding FFL conversion is almost negligible (1.5%), whereas Pt/TiO₂ is significantly more active, with 18.9% of FFL conversion after this 0.5h.

Pt/MgAl shows the slowest kinetic (9.2% of FFL conversion after 8 h), but its selectivity and stability to FCA is quite high, with a remaining selectivity of 34.8%. Both results are congruent with the significant blockage of acidic sites produced by Pt nanoparticles, slowing down all the oxidizing reactions. On the contrary, Pt/TiO₂ is discarded because of the poor FCA stability observed.

Pd/MgAl is the catalyst that produces the maximum FCA selectivity (49.2% after 3 h of reaction, with a 11.2% of FFL conversion). The slow activity also observed with this material results in a quite stable FCA production (remaining selectivity after 8 h of 37.1%). Very similar results are reached with Pd/MgZr (37.1% of selectivity with 12% of FFL conversion). The FCA selectivities obtained when using supports with redox activity are significantly lower, both comparing the maximum values (22.3 and 23.3% with Pd/CeO₂ and Pt/TiO₂, respectively), and results after 8h.

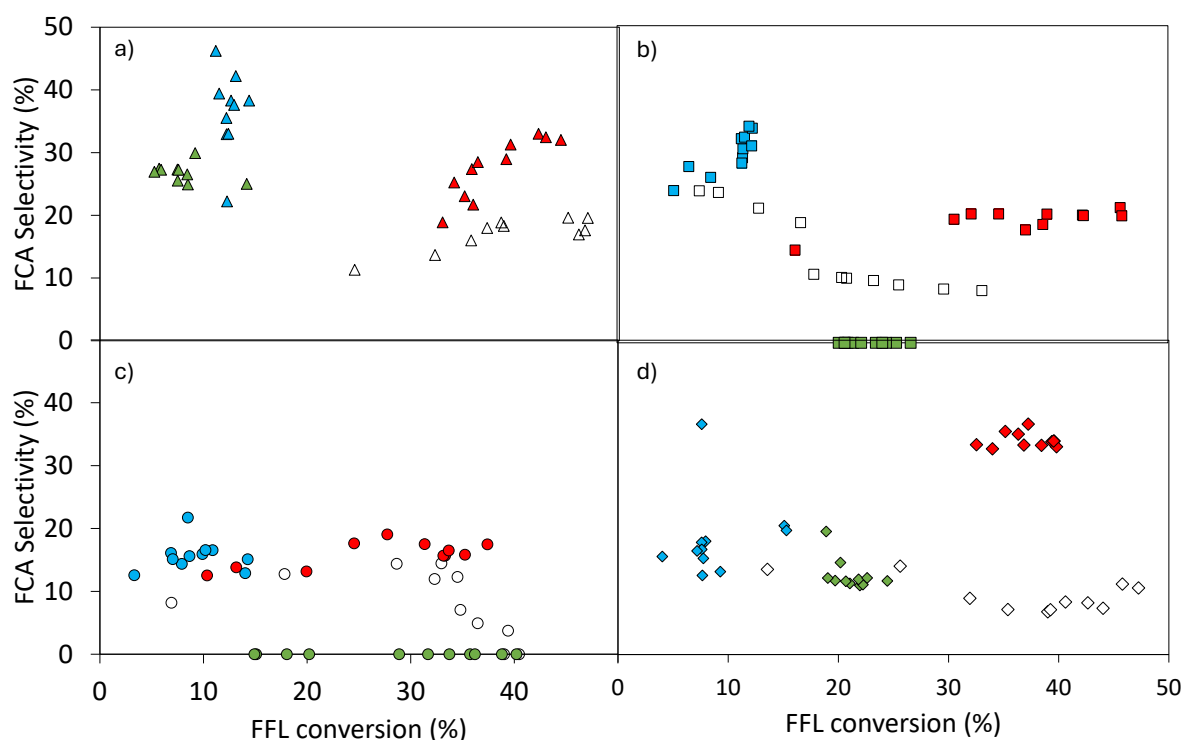


Figure 4.39 Conversion vs. FCA selectivity plots for furfural oxidation using H₂O₂ at 50 °C over (a) MgAl-supported, (b) MgZr-supported, (c) CeO₂-supported, and (d) TiO₂-supported catalysts. Red dots correspond to Au-based catalysts, green dots to Pt-based catalysts, blue dots to Pd-based catalysts, and white dots to bulk supports

Both using Pt and Pd, almost total H₂O₂ conversion is reached in less than 3h (>99%), this fact strongly affecting the distribution of the products. These results could be different modifying the reactor configuration to allow a continuous addition of H₂O₂. Despite the high interest of this configuration (previously tested in the literature [40]), the continuous change in volume limits the use of temporal data to evaluate the kinetic of the systems as well as the influence of the catalyst in the H₂O₂ decomposition rate. These points will be deeply discussed below.

Concerning the Au-modified catalysts, the maximum FCA selectivities are quite high (38.1, 24.2, 22.7, and 42%, with Au/MgAl, Au/MgZr, Au/CeO₂, and Au/TiO₂, respectively). This metal offers the maximum stability of this production, and their final FFL conversion are the highest ones (from 37 to almost 50%), resulting in the maximum FCA yields obtained with all the screening of catalysts tested in this work (8.5, 7.5 and 7.1% with Au/MgAl, Au/MgZr, and Au/TiO₂). These yields could be significantly increased by modifying the reaction configuration since FFL conversion increases by increasing the catalytic loading or recycling

the unconverted reactant. Thus, the relevance of these results is directly related to the high selectivity obtained. Concerning to H_2O_2 , although obtained conversions are very high (86.6, 97.1, 81.1, and 97.3%, with Au/MgAl, Au/MgZr, Au/CeO₂, and Au/TiO₂ after 8h), a remaining amount of oxidant is present in most of the experiments. In the same way, final carbon balances are always higher than 86% (see Table 4.9), the lack of information because of total FFL decomposition into CO₂ being not very relevant. The similar trends obtained with all the Au-modified catalysts suggests a positive role of this metal that can be discussed independently of the properties of the support (it will be analysed below). Based on these results, Au/TiO₂ is defined as the optimum catalyst to produce FCA.

Table 4.10. Furfural conversion and selectivity distribution after 8 h of reaction at 50 °C as a function of the catalyst used

	FFL Conv. (%)	Selectivity (%)			
		FCA	FN	MA	MAL
MgAl	49.2	1.8	66.6	0	0
Pd/MgAl	14.4	37.4	0	5.9	18.8
Pt/MgAl	9.2	34.8	4	3.9	10.1
Au/MgAl	49.2	37.1	2.2	17.9	0.3
MgZr	33.1	10.1	35.6	6.6	1.4
Pd/MgZr	12	37.1	0	7.7	27.5
Pt/MgZr	21.4	0	100	0	0
Au/MgZr	45.8	23.8	4	18	1.9
CeO₂	40.5	0	0	11.3	0
Pd/CeO₂	14	13.8	0	7.1	21.4
Pt/CeO₂	27.8	0	0	0	78.5
Au/CeO₂	37.4	20.9	0	5.6	0
TiO₂	45.8	13.6	6.9	66.2	2.6
Pd/TiO₂	15.3	23.0	0	76.5	0
Pt/TiO₂	22.6	14.8	6.8	9.8	7.7
Au/TiO₂	39.5	39.1	0	0	38.1

The presence of noble metals also modifies the selectivity to lineal carboxylic acids, as β -formyl-acrylic (BFA), maleic (MA) and malic (MAL) acids productions. The maximum selectivities with the corresponding FFL conversions are compared in **Figure 4.40**.

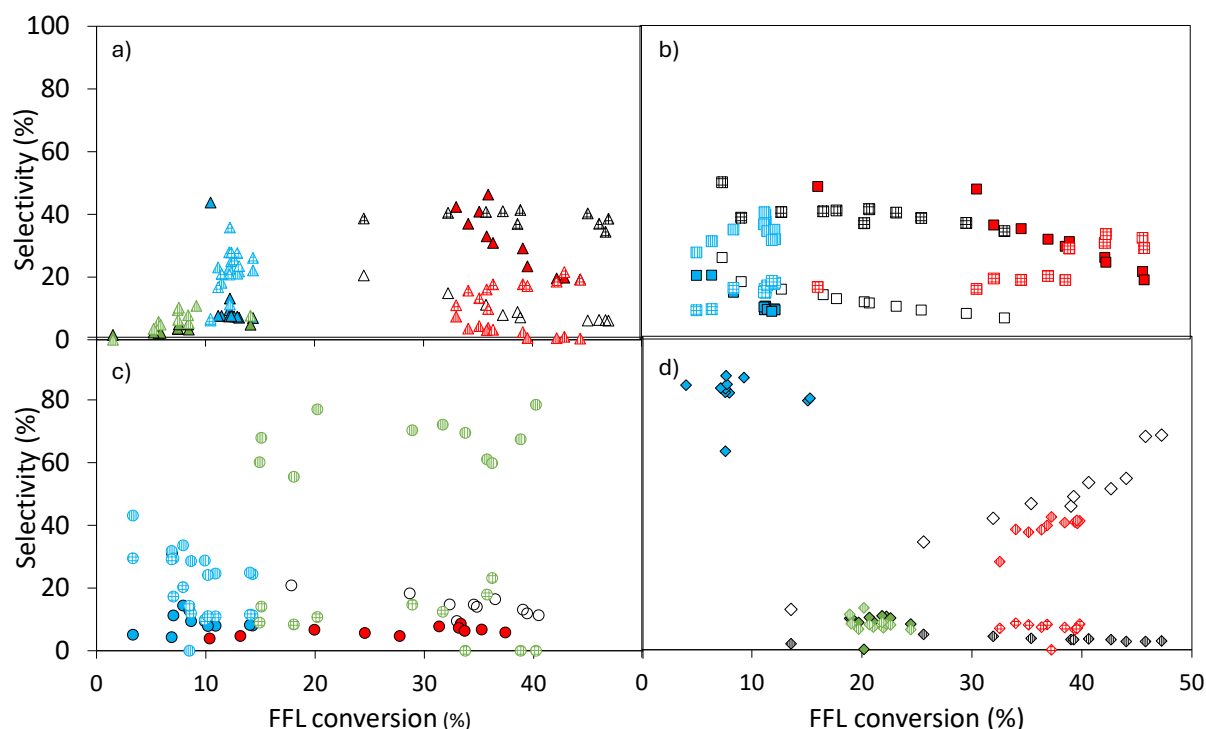


Figure 4.40. Conversion vs. selectivity plots for furfural oxidation using H_2O_2 at 50 °C over (a) MgAl-supported, (b) MgZr-supported, (c) CeO_2 -supported, and (d) TiO_2 -supported catalysts. Red dots correspond to Au-based catalysts, green dots to Pt-based catalysts, blue dots to Pd-based catalysts, and white dots to bulk supports. Solid colors correspond to MA, vertically striped symbols to MAL and squared symbols to BFA

Maleic acid (MA) is produced with almost total selectivity using Pd/ TiO_2 (84.8%), value reached after 5h that corresponds to a very low FFL conversion (7.7%). The low basicity of this material suggests a low stabilization of previous intermediates, promoting their oxidation. In this case, the chemical properties seem to be more relevant than the own activity of the metal, observing the poor results obtained when using other supports.

The maximum selectivities obtained with Au/MgAl and Au/MgZr are also quite relevant (43.9 and 46.9%), but the stability of MA with these materials is very weak, suffering a fast disappearance, discarding the gold as a good metal to obtain this compound. Pt is also discarded, observing that this metal hinders the MA route. Maleic acid (MAL) is a very unstable product that suffers fast oxidation with almost all the catalyst. Pt/ CeO_2 is the only

exception, with a constant MAL production, reaching a final selectivity of 78.5% with almost 28% of FFL conversion. This result could be a synergetic effect of its low basicity (the lowest basicity of all the catalysts tested) and a particular interaction between Pt nanoparticles and the redox surface of CeO₂. The analysis about the non-carboxylic intermediates is included in **Figure 4.41**.

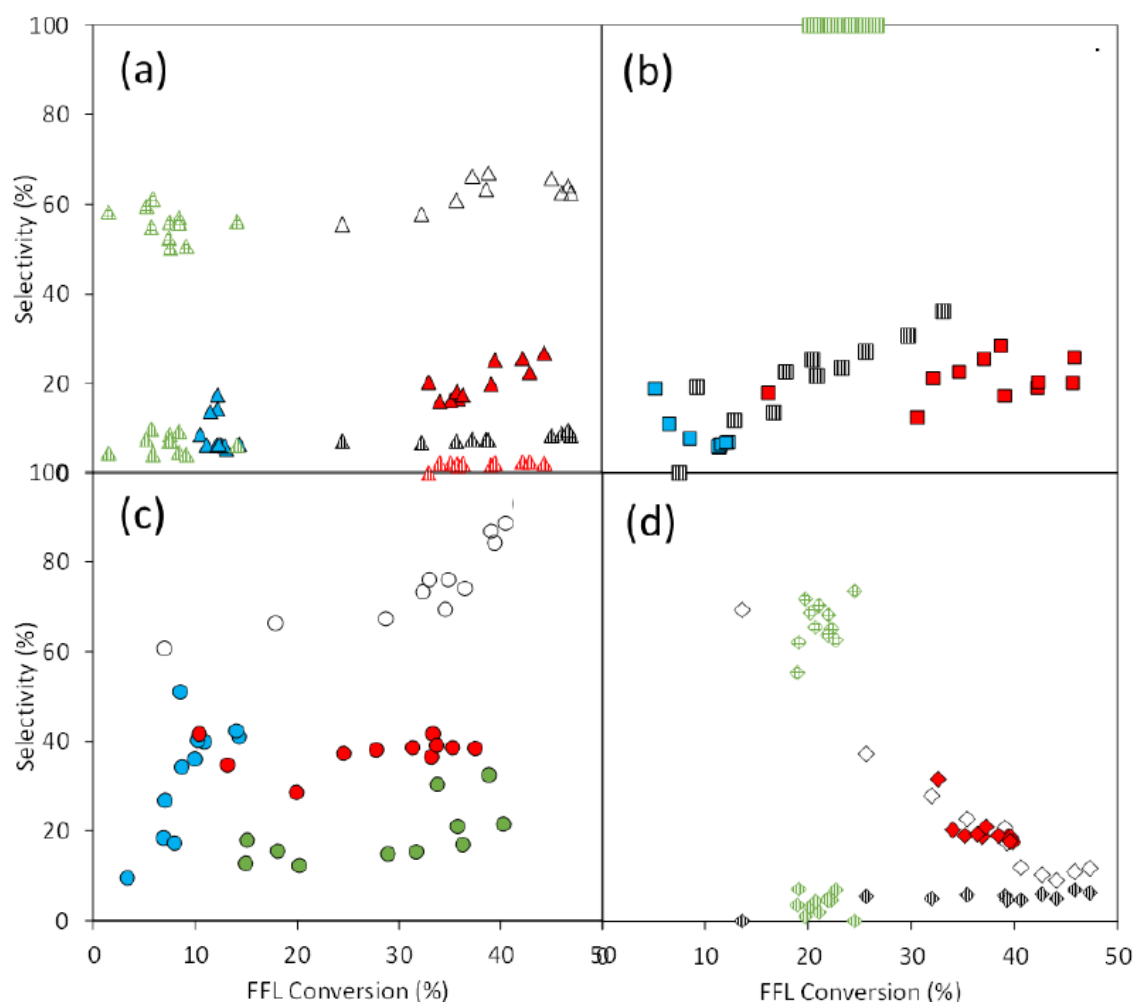


Figure 4.41. Conversion vs. selectivity plots for furfural oxidation using H₂O₂ at 50 °C over (a) MgAl-supported, (b) MgZr-supported, (c) CeO₂-supported, and (d) TiO₂-supported catalysts. Red dots correspond to Au-based catalysts, green dots to Pt-based catalysts, blue dots to Pd-based catalysts, and white dots to bulk supports. Solid colors correspond to HF, vertically striped symbols to FN and squared symbols to HFN. The formation patterns are less clear in good agreement with their more complex formation and depletion mechanism, being remarkable that TiO₂-based catalysts present a clearly decreasing trend (reactive intermediate), whereas for the other catalysts a more stable selectivity plateaus were observed, highlighting the total selectivity to FN observed for Pt/MgZr

4.3.5. Kinetic study of bifunctional catalysts

All the experimental data were fitted to the proposed kinetic model. The kinetic rates obtained for the heterogeneous contribution are summarized in **Table 4.11 and 12**. The correspondence between experimental and fitted values of the best catalysts is shown in **Figure 4.42**, whereas the other materials are included in **Figures 4.43-46**.

Table 4.11. Reaction rate constants based on the proposed reaction network (k_1 indicated in s^{-1} , the other constants in $L \cdot mol^{-1} \cdot s^{-1}$)

	Au/TiO ₂	Pd/TiO ₂	Pt/TiO ₂	Au/CeO ₂	Pd/CeO ₂	Pt/CeO ₂
k_1	$5.3 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$7.4 \cdot 10^{-5}$	-	-	$1.2 \cdot 10^{-4}$
k_2	$7.4 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$	$3.8 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$
k_3	$6.8 \cdot 10^{-4}$	$1.8 \cdot 10^{-2}$	$2 \cdot 10^{-3}$	$4.4 \cdot 10^{-4}$	$8.5 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$
k_4	-	$5.5 \cdot 10^{-5}$	-	-	$4.9 \cdot 10^{-5}$	-
k_5	-	$6.6 \cdot 10^{-4}$	-	-	-	-
k_6	$6.1 \cdot 10^{-4}$	$7.5 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$	$2.3 \cdot 10^{-4}$	$6.2 \cdot 10^{-1}$	-
k_7	$1.8 \cdot 10^{-6}$	$5.7 \cdot 10^{-1}$	$2.4 \cdot 10^{-2}$	-	$1.6 \cdot 10^{-1}$	-
$k_{7,1}$	$2.9 \cdot 10^{-4}$	$4.9 \cdot 10^{-3}$	-	-	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$
$k_{7,2}$	$3.8 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$5.8 \cdot 10^{-1}$	-	$5.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-5}$
k_8	$1.1 \cdot 10^{-3}$	$1.2 \cdot 10^0$	$6 \cdot 10^{-5}$	$9.7 \cdot 10^{-4}$	$5.8 \cdot 10^{-1}$	-
k_9	$2.5 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$	$2.3 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$2.8 \cdot 10^{-5}$	$3.7 \cdot 10^{-5}$
k_{10}	-	$1.8 \cdot 10^{-4}$	-	$4.5 \cdot 10^{-4}$	$1.7 \cdot 10^{-5}$	-
$k_{10,1}$	$9.8 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	$4.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-5}$	$1.8 \cdot 10^{-2}$	$4.7 \cdot 10^{-4}$
$k_{10,2}$	$3.1 \cdot 10^{-5}$	$2.1 \cdot 10^{-2}$	$4.2 \cdot 10^{-3}$	-	$8.1 \cdot 10^{-5}$	$5 \cdot 10^{-3}$
r^2	0.903	0.996	0.88	0.92	0.994	0.97

Table 4.12. Reaction rate constants based on the proposed reaction network (*Cont.*)

	Au/MgAl	Pd/MgAl	Pt/MgAl	Au/MgZr	Pd/MgZr	Pt/MgZr
k_1	$1.2 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$1.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
k_2	$3.6 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$
k_3	$4.5 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$5.8 \cdot 10^{-2}$
k_4	-	$6 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	-	$6.1 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$
k_5	-	$1.6 \cdot 10^{-5}$	$6 \cdot 10^{-4}$	-	-	$1.8 \cdot 10^{-3}$
k_6	-	$6.2 \cdot 10^{-2}$	$2.7 \cdot 10^{-3}$	-	$2.6 \cdot 10^{-2}$	-
k_7	-	$5.2 \cdot 10^{-2}$	$1.1 \cdot 10^{-3}$	-	$2.1 \cdot 10^{-1}$	$1.4 \cdot 10^{-3}$
$k_{7,1}$	$1.7 \cdot 10^{-4}$	$5.7 \cdot 10^{-3}$	$3.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	$1.3 \cdot 10^{-2}$	$5 \cdot 10^{-3}$
$k_{7,2}$	$4.8 \cdot 10^{-5}$	$6.2 \cdot 10^{-3}$	$1.7 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$6.8 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
k_8	-	$3.4 \cdot 10^{-1}$	-	-	$1.5 \cdot 10^{-1}$	$3.7 \cdot 10^{-2}$
k_9	$3.7 \cdot 10^{-5}$	$1.9 \cdot 10^{-3}$	$9.1 \cdot 10^{-4}$	$1.6 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$4.7 \cdot 10^{-2}$
k_{10}	-	$1.2 \cdot 10^{-2}$	$3 \cdot 10^{-3}$	-	$8.1 \cdot 10^{-3}$	$2.6 \cdot 10^{-1}$
$k_{10,1}$	$4.7 \cdot 10^{-4}$	$1.3 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$	$3 \cdot 10^{-4}$	$8.5 \cdot 10^{-3}$	$3.4 \cdot 10^{-2}$
$k_{10,2}$	$5 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-5}$	$3.8 \cdot 10^{-3}$	$2.6 \cdot 10^{-5}$	$1.1 \cdot 10^0$
r^2	0.991	0.996	0.993	0.86	0.997	0.998

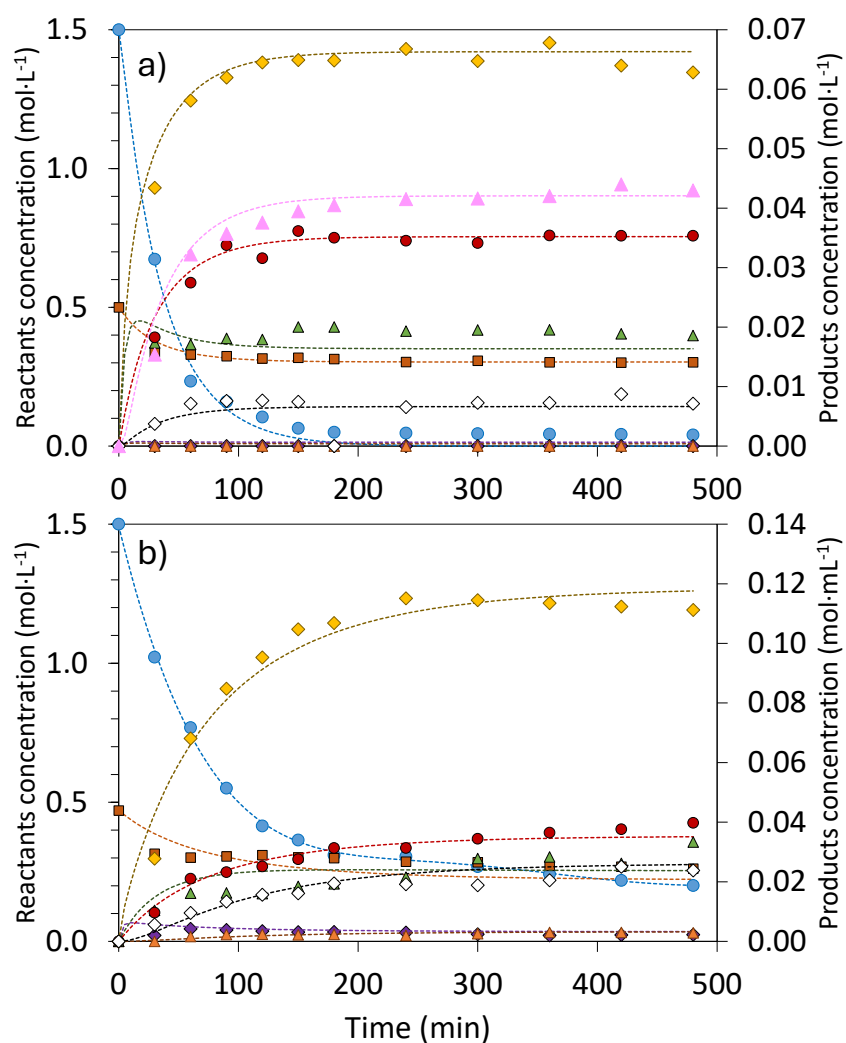


Figure 4.42. Furfural oxidation with H_2O_2 at 50 °C in presence of (a) Au/TiO_2 and (b) Au/MgAl . Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲). Broken lines correspond to the kinetic model predictions

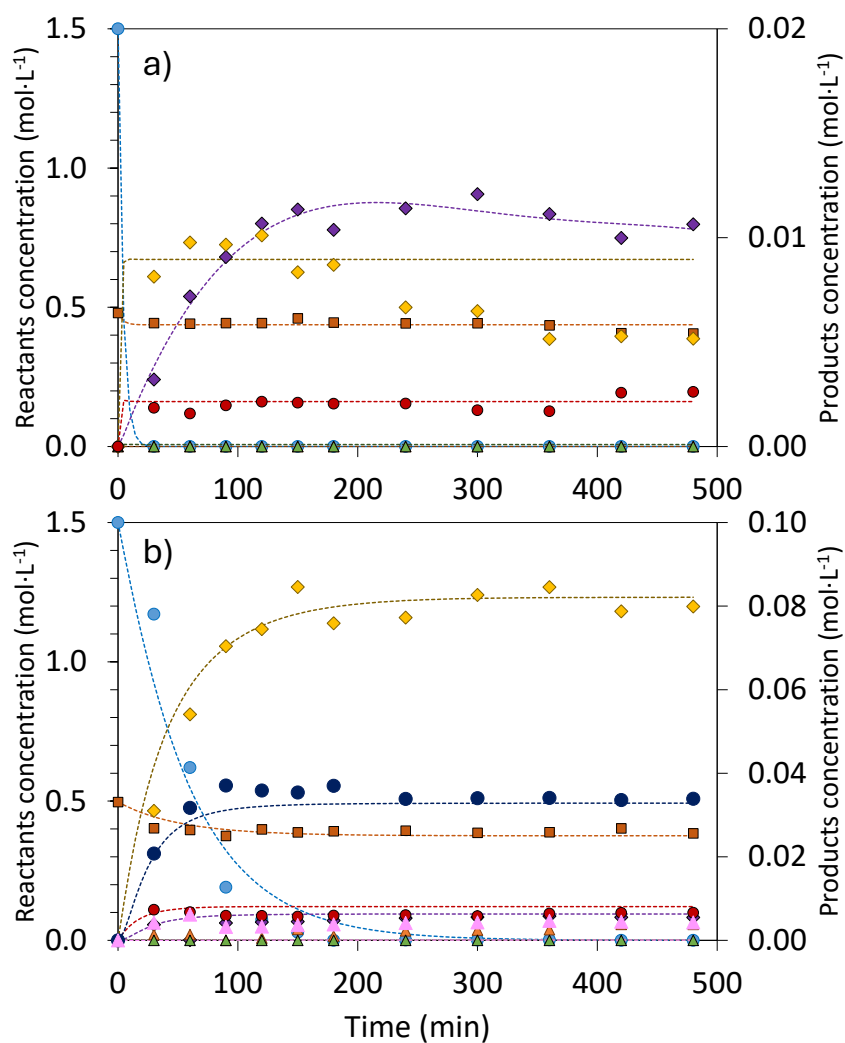


Figure 4.43. Furfural oxidation with H_2O_2 at 50 °C with a) Pd/TiO_2 , b) Pt/TiO_2 . Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲). Broken lines correspond to the kinetic model adjustment

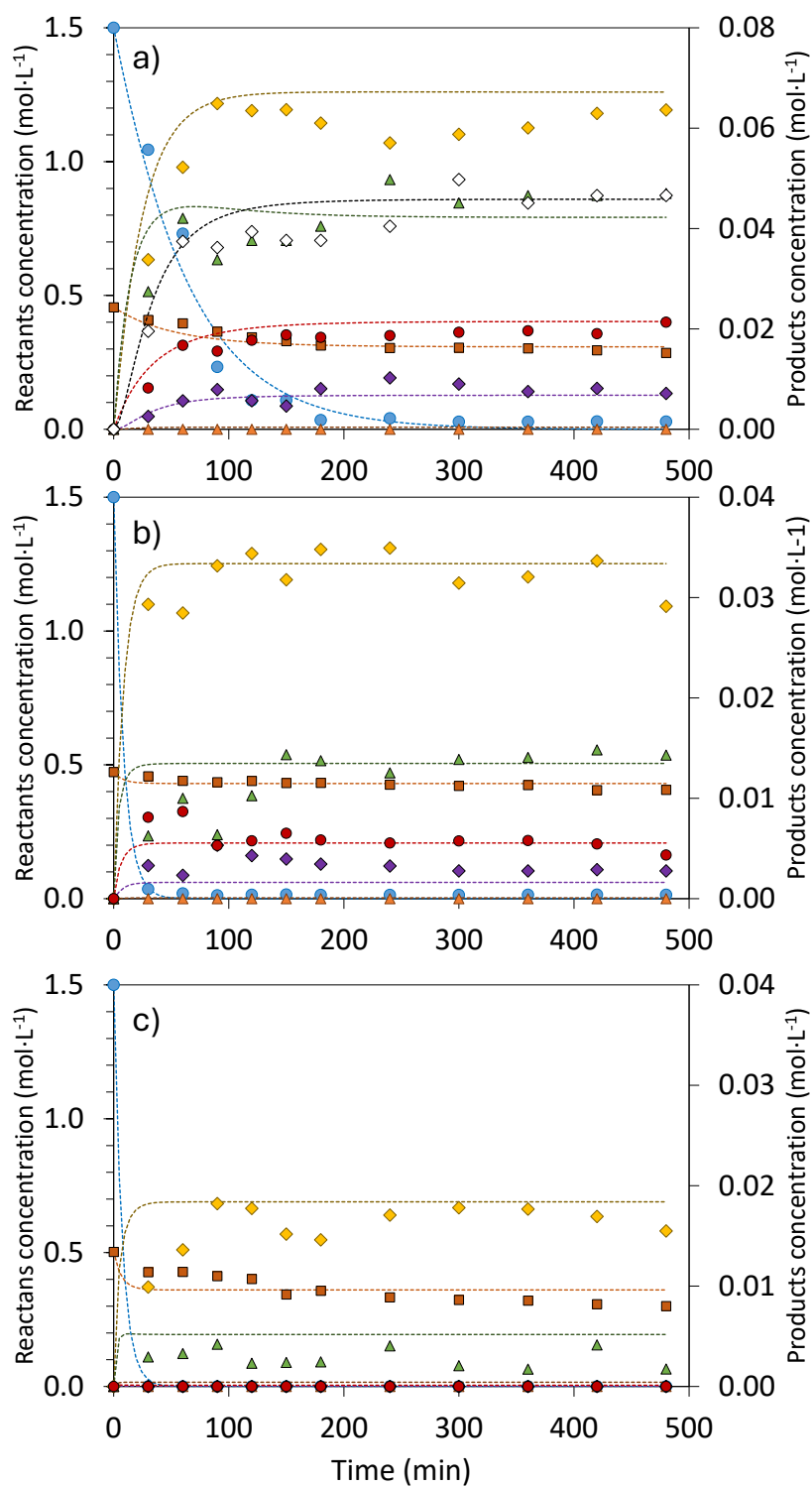


Figure 4.44. Furfural oxidation with H_2O_2 at 50°C with a) Au/CeO_2 , b) Pd/CeO_2 , c) Pt/CeO_2 . Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲). Broken lines correspond to the kinetic model adjustment

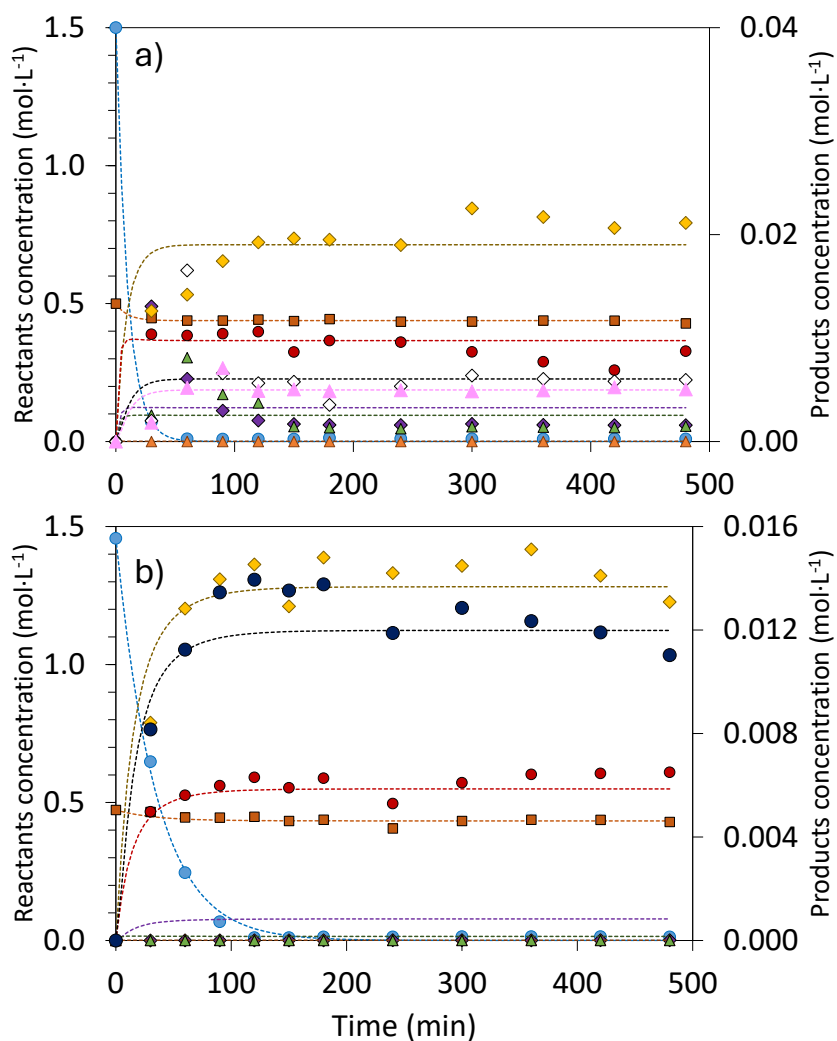


Figure 4.45. Furfural oxidation with H_2O_2 at 50 °C with a) Pd/MgAl, b) Pt/MgAl. Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲). Broken lines correspond to the kinetic model adjustment

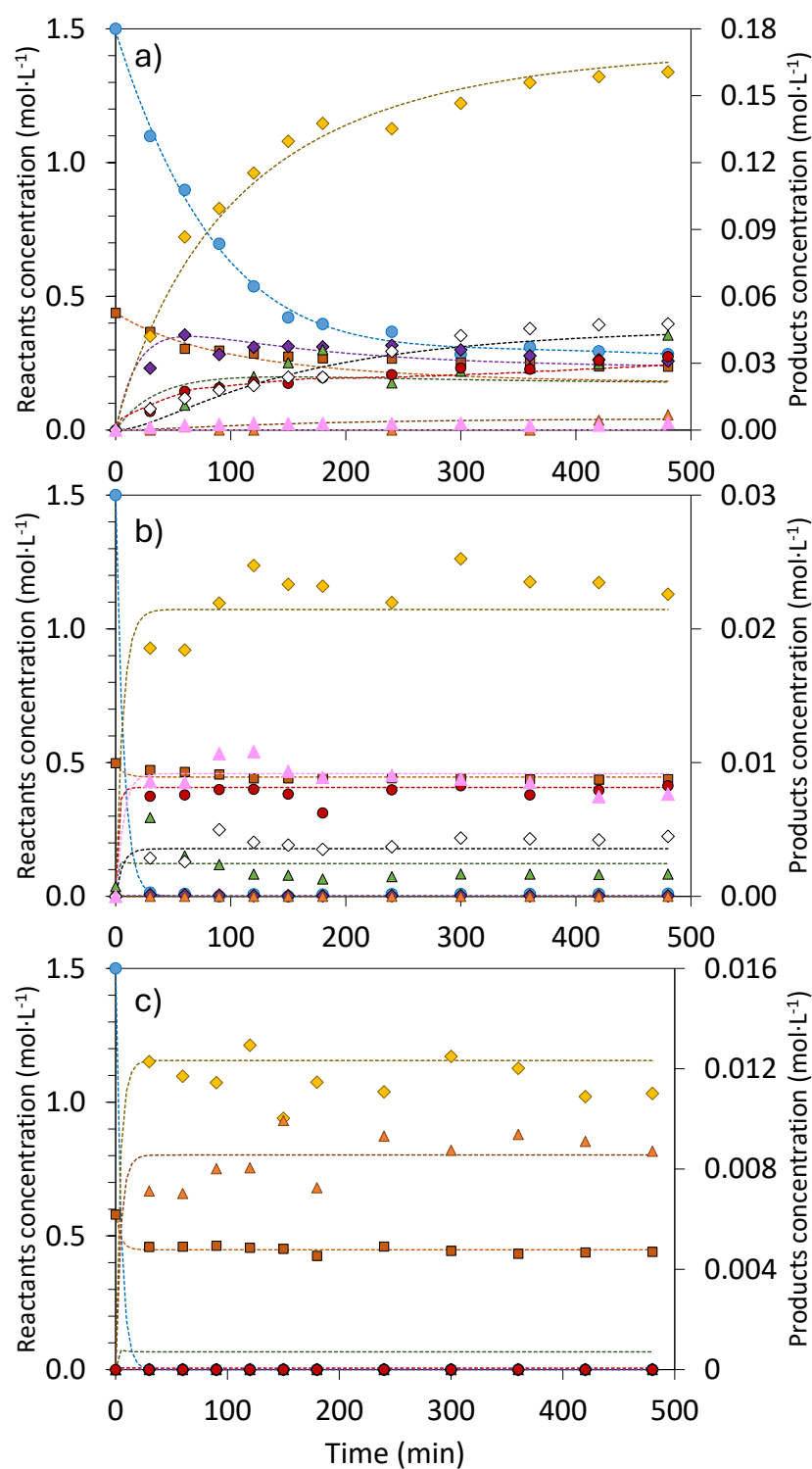


Figure 4.46. Furfural oxidation with H_2O_2 at 50°C with a) Au/MgZr, b) Pd/MgZr, c) Pt/MgZr.

Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (◇); MAL (▲).

Broken lines correspond to the kinetic model adjustment

The main conclusions derived from the kinetic study are analyzed in **Figure 4.47**. Except in the case of using CeO_2 , all the metal modified materials show higher k_1 values than the parent supports, in good agreement with the higher hydrogen peroxide conversions obtained. The lack of correspondence between the medium-strength acidity and these values suggests the prevalence of the metal activity in the H_2O_2 decomposition over the support one. The positive role of these metals in promoting hydrogen peroxide decomposition has been previously proposed in the literature [45, 58].

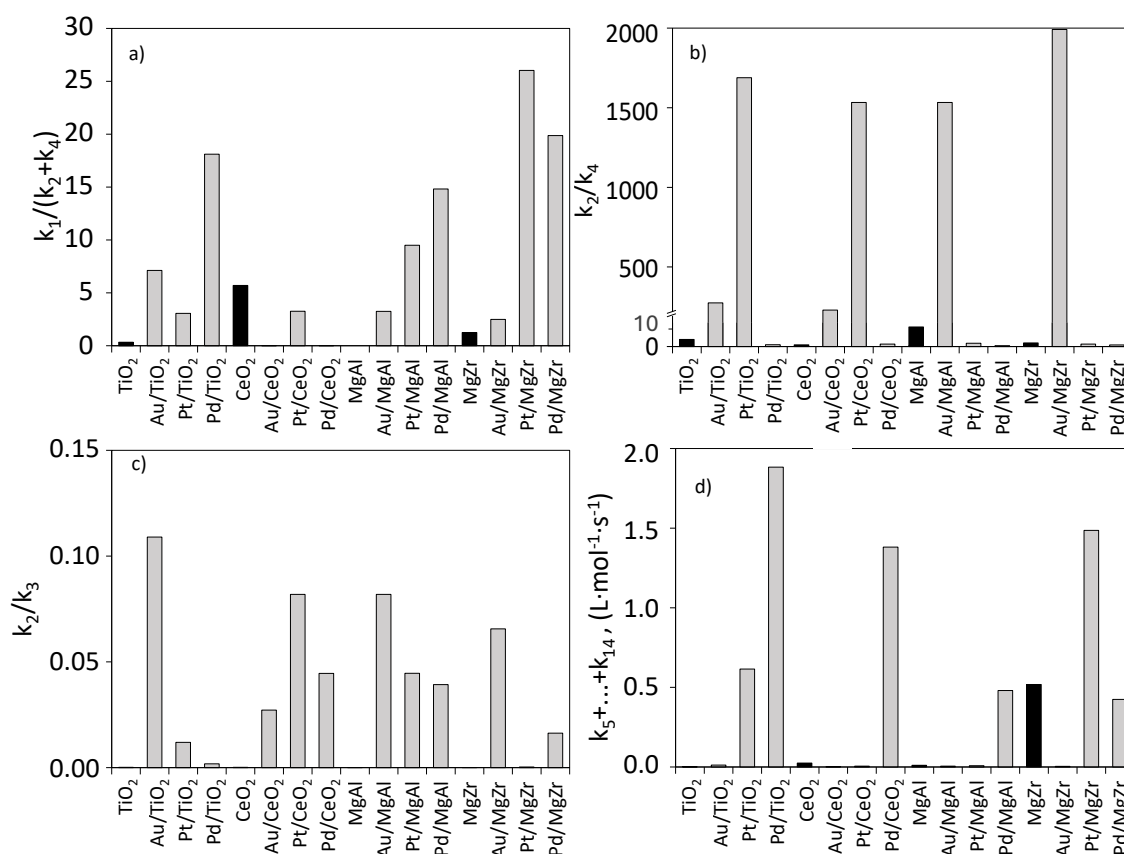


Figure 4.47. Analysis of the kinetic rates as a function of the metal-modified catalyst used

The increment in the H_2O_2 self-decomposition is more notorious than the increase in the rates of the two first steps of the main process, as illustrated in Fig. 4.47a. This effect is more relevant in those catalysts involving Pd and Pt, whereas this undesired effect is less significant when using Au-modified materials. The presence of metal nanoparticles also affects the dominant oxidizing route. A high prevalence for the furoic route is observed with Pt and Au. In the case of Pt materials, this improvement requires support with redox properties, TiO_2 or CeO_2 . On the contrary, the enhancement with Au is observed despite the

type of support used, being more significant with mixed oxides (four orders of magnitude) because, with oxides, both steps are promoted, reducing the relative differences.

The effect of using bifunctional catalysts is extended to the undesired oxidations, the different steps that decompose the two primary compounds (FCA and HF), reducing the selectivity and the carbon balance. As observed in Fig. 4.47c, the relative weight of the FCA decomposition decreases, increasing the relative k_2/k_3 value. This effect is more relevant with Au materials, mainly Au/TiO₂ and Au/MgAl. As to the secondary steps, Au is the only metal that does not produce an increment in these rates (Fig. 4.47d). The sum of all these secondary kinetic rates is significantly higher with materials containing Pd and Pt, whereas these rates globally decrease with Au-modified catalysts to obtain values lower than those reached with the bulk materials.

These results suggest the coexistence of two different oxidizing mechanisms, the effect of metal nanoparticles (mainly Au) promoting the oxidation by a redox reaction, i.e., the furoic acid production by a selective interaction between furfural and hydrogen peroxide. On the other hand, those oxidation steps that follow a decomposition mechanism, releasing a formic acid molecule are not promoted by these bifunctional catalysts. This hypothesis suggests that the metal particles (mainly Au ones) enhance the simultaneous chemisorption of both reactants required. Thus, the decomposition of H₂O₂ occurs close to the active site where the furfural is adsorbed. On the contrary, the decomposition reactions are less selective and not as sensitive to this proximity as the furoic acid (FCA).

Au is identified as the best metal to maximize FCA production, and the metal dispersion is the most relevant parameter since this determines the frequency of the correct interactions between the active site and the reactants. This hypothesis is corroborated in **Figure 4.48**, where a clear correspondence between the principal kinetic rates and the metal dispersion is observed. Not only the desired step (k_2) is promoted by a high dispersion, but also the hydrogen peroxide decomposition (k_1), the furoic acid decomposition (k_3), and the undesired 2-hydroxyfuran formation (k_4). These last two steps are less influenced than k_1 and k_2 , in agreement with the lower slope of their correlations. Thus, a medium metal dispersion must be considered, trying to reach a selective activation of the target route. Based on this premise, an intermediate dispersion (15-20%) is defined as the optimum one, a range involving Au/TiO₂ and Au/MgAl. A similar analysis with the other metals is not conclusive, no

trends for the metal dispersion being observed. This fact reinforces the hypothesis of effective chemisorption required to promote the reaction (sensitive phenomenon).

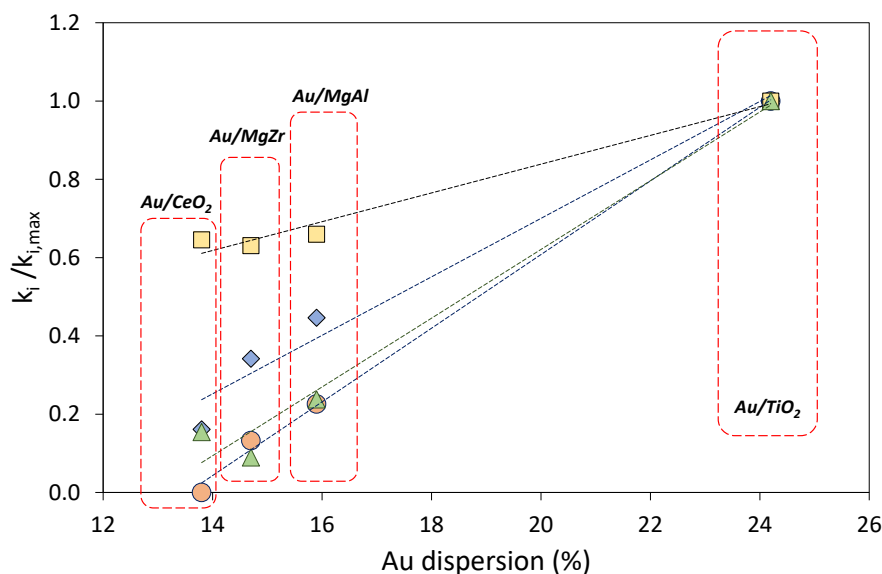


Figure 4.48: Normalized evolution of k_1 (●), k_2 (◆), k_3 (■), and k_4 (▲) kinetic rates as a function of the metal dispersion of Au-modified materials. Values obtained with Au/TiO₂ are used as reference values

4.3.6. Deactivation phenomena

Experimental results demonstrate that Au/TiO₂ is the most promising catalysts for the furfural partial oxidation to produce furoic acid, both in terms of activity and selectivity. However, the stability of this catalyst must be also evaluated since this aspect is also crucial to evaluate the technical viability of the oxidation process. This study involves not only reusability tests to evaluate the remaining activity after several cycles, but also a deep characterization of spent catalysts to identify the deactivation reasons, if applicable. By gaining insights into the factors that lead to reduced efficiency or complete catalyst failure, strategies can be developed to mitigate these effects, thereby enhancing the long-term viability and effectiveness of Au/TiO₂.

Reusability tests were performed by loading the reactor with a fresh furfural solution and the catalyst previously recovered by filtration (no regeneration process). **Figure 4.49** summarizes the main results obtained after five cycles of furfural oxidation at 50°C, using H₂O₂ as the oxidizing agent.

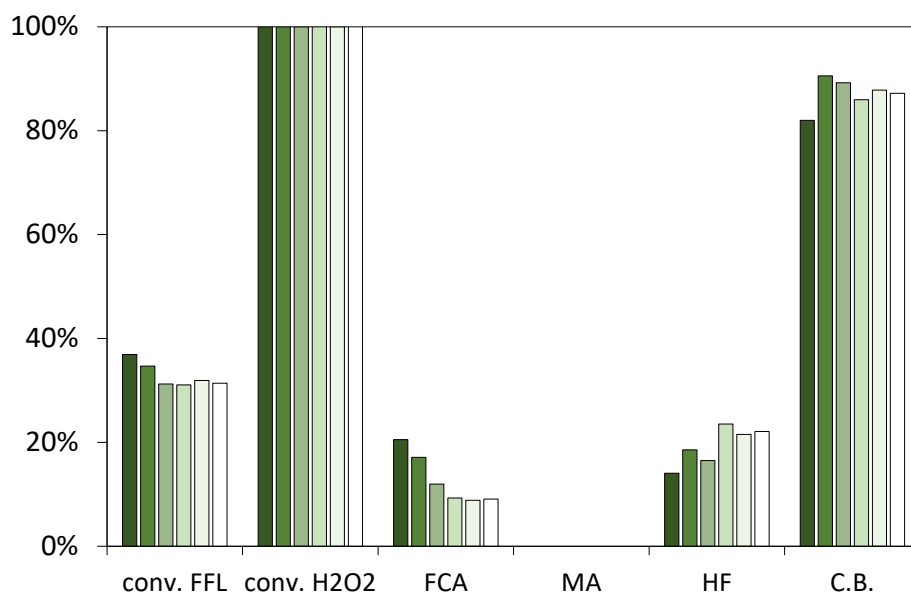


Figure 4.49. Reusability results obtained after six cycles (dark-intermediate-light colors) of 4 h of furfural oxidation at 50 °C using H₂O₂ as oxidizing agent and Au/TiO₂ as a catalyst. Legend: Product distribution in terms of selectivity

Au/TiO₂ shows a soft but clear deactivation during the first three cycles. Thus, furfural conversion after 4 h decreases from 36.9% (1st cycle) to 31.2% (3rd cycle). This deactivation also affects the products distribution, observing a significant reduction in FCA selectivity (from 20.5% to 12%), obtaining the corresponding increase in HF (from 14.1% to 18.6%). After these three cycles, experimental results suggest a stable behavior, both in conversion and FCA selectivity. The slight increase in carbon balance (from 82.25 in the first cycle to 86.3% after the sixth one) indicates that the relevance of furfural total oxidation is reduced. These results suggest that Au/TiO₂ suffers a stabilization phase with a partial loss of activity, after which the activity and selectivity remains stable.

Previous literature indicates three possible routes of catalyst deactivation when using a biomass-based molecule: structural damage by the water (used as solvent), fouling by coke, and sintering of active metal particles. A deep characterization of recovered materials was performed to identify the relevance of any of these deactivation routes. To guarantee a comprehensive analysis of these results, fresh and spent TiO₂ was also characterized. The comparison between results obtained with both materials will be helpful to identify the role of Au nanoparticles in this deactivation.

Regarding support hydrolysis or collapse, the surface area and pore volume of each material were measured by nitrogen physisorption. Results are summarized in **Table 4.13**.

Table 4.13. Results obtained by nitrogen physisorption analysis of catalysts after the first cycle

Catalyst	BET Surface Area (m ² /g)	Pore volume (cm ³ /g)
TiO ₂	49.7	0.83
Spent TiO ₂	43.0	0.49
1%wt Au-TiO ₂	51.5	0.55
Spent 1%wt Au-TiO ₂	43.0	0.45

The BET surface area of both TiO₂ and 1% wt Au-TiO₂ remains relatively stable after the reaction, showing a slight decrease from 49.7 m²/g to 43.0 m²/g for TiO₂ and from 51.5 m²/g to 43.0 m²/g for Au-loaded TiO₂. This modest reduction suggests that the structural integrity of the catalysts is largely preserved during the reaction, with minimal surface area loss. However, more significant changes are observed in the pore volume of the catalysts. The fresh TiO₂ exhibits a pore volume of 0.83 cm³/g, which decreases by approximately 50% to 0.49 cm³/g after the reaction. Similarly, the pore volume of the 1% wt Au-TiO₂ catalyst reduces from 0.55 cm³/g in the fresh catalyst to 0.45 cm³/g in the spent catalyst. This reduction in pore volume can be attributed to the exposure of TiO₂ to water during the reaction process. Fresh TiO₂, which has not previously encountered water, may form large agglomerates that are detected as pores in the physisorption analysis. Upon exposure to water, these agglomerates likely disintegrate, leading to a reduction in the measured pore volume.

To gain further insights into the morphological changes in the catalysts, X-ray diffraction (XRD) analyses were conducted on both fresh and spent materials. The results, illustrated in **Figure 4.50**, indicate that there are no significant changes in the crystalline structure of Au/TiO₂ and TiO₂ before and after the reaction. Both fresh and spent catalysts display reflections corresponding to the anatase and rutile phases of the TiO₂ support [59, 60], with no new phases or significant peak shifts observed.

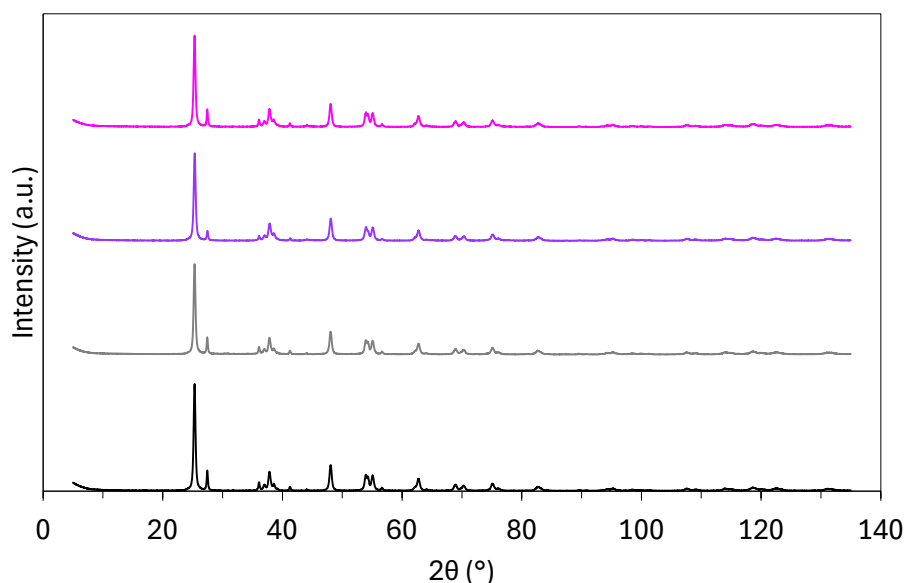


Figure 4.50. XRD diffractograms for fresh and spent TiO_2 and Au/TiO_2 . Legend: Black and grey lines represent fresh and spent TiO_2 and purple and pink lines represent fresh and spent Au/TiO_2 , respectively

Regarding carbon deposition, the Raman analysis of the TiO_2 catalyst provides insightful information about the surface composition after the reaction. The Raman spectra show no significant shifts or peaks between 1500 and 2500 cm^{-1} , which are typically associated with carbonaceous species, such as graphitic carbon or amorphous carbon deposits [59]. This absence of Raman shifts in this region strongly indicates that no significant organic molecules or carbon deposits are present on the surface of the TiO_2 after the catalytic reaction. The only observable features in the Raman spectra are the characteristic shifts related to the anatase phase of TiO_2 , confirming that the TiO_2 support remains largely unaltered in terms of its structural and chemical properties.

These Raman findings are further corroborated by the thermogravimetric analysis coupled with mass spectrometry (TG-MS), which was employed to detect any potential carbon dioxide (CO_2) release upon heating the spent catalyst. The TG-MS results showed no evidence of CO_2 evolution, further supporting the conclusion that carbon deposition did not occur during the reaction. This is a significant observation, as carbon deposition is a common cause of catalyst deactivation in many oxidation reactions, often leading to pore blockage, reduced active site availability, and overall catalyst performance degradation.

The consistency between the Raman and TG-MS analyses provides strong evidence that the TiO_2 catalyst remains free from carbon contamination after the reaction process. This absence of carbon deposition is crucial for maintaining the long-term activity and selectivity of the catalyst, as it suggests that the reaction conditions and catalyst formulation effectively minimize the risk of fouling by carbonaceous species. Consequently, the durability of the TiO_2 -supported catalyst in oxidative reactions is enhanced, potentially allowing for extended catalyst lifetimes and more efficient catalytic cycles. **Figure 4.51** visually presents the Raman analysis results, highlighting the stability of the anatase phase and the lack of carbon-related features.

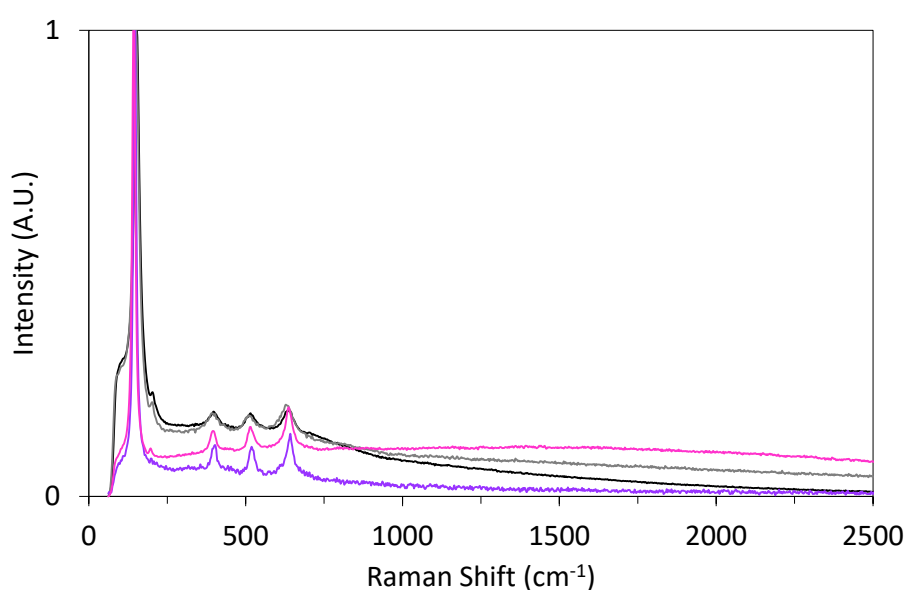


Figure 4.51. Raman spectra of (black) fresh TiO_2 , (grey) spent TiO_2 , (purple) fresh Au/TiO_2 , and (pink) spent Au/TiO_2

The vibrational bands within the 962–400 cm^{-1} range are indicative of the bending modes associated with Ti-O-Ti and Ti-O bonds, which are key to identifying the specific crystalline phases of TiO_2 . In the anatase phase, a prominent vibrational band appears at 534 cm^{-1} , serving as a distinct marker for this phase, characterized by symmetric bending of Ti-O-Ti bonds [59, 61]. This band is crucial for recognizing the anatase structure, which is noted for its high photocatalytic activity. In contrast, the rutile phase exhibits strong vibrational bands at 663 cm^{-1} , 750 cm^{-1} , and 422 cm^{-1} . These bands correspond to the unique lattice vibrations of the rutile structure, which is more compact and thermodynamically stable than anatase. The 663 cm^{-1} band is particularly associated with Ti-O bond stretching,

while the bands at 750 cm^{-1} and 422 cm^{-1} represent other characteristic modes of the rutile phase [61].

Infrared spectroscopy measurements of CO adsorption were conducted to gain deeper insights into the mechanisms of catalyst deactivation. This technique provides detailed information on the interactions between carbon monoxide and the catalytic material, enabling the identification of changes in the electronic and structural properties of the active sites. Specifically, infrared spectroscopy can reveal alterations in CO adsorption patterns that are indicative of deactivation processes, such as the formation of unwanted surface species or modifications in the geometry of active sites.

The data obtained from these measurements are summarized in **Figure 4.52**, which highlights the key differences observed between the Au-TiO₂ catalyst in its fresh state and after it has been used under reaction conditions. This figure offers a comparative view that facilitates the identification of significant changes in catalyst activity and stability, as well as the potential mechanisms responsible for its deactivation.

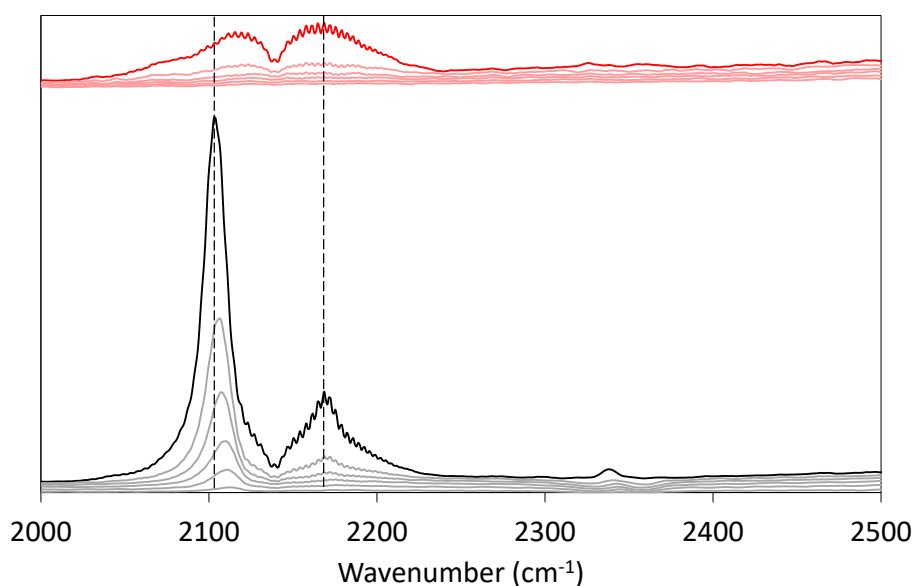


Figure 4.52. Sequence of DRIFT spectra representing the adsorbed CO species of Au/TiO₂. Legend: Spent material (red lines), fresh material (black lines)

A strong adsorption at $2103\text{--}2105\text{ cm}^{-1}$ was observed on the fresh sample, which can be attributed to CO adsorbed on metallic Au (CO–Au⁰), and the CO–Ti⁴⁺ adsorption is observed at 2170 cm^{-1} [62, 63]. Comparing analysis before and after the reaction, peaks shift

and reduce the intensity. The lower CO coverage on the spent catalyst under present adsorption conditions is attributed to a lower CO adsorption energy in the presence of TiO₂ bulk defects generated during the reaction, which is at least partly responsible also for the lower oxidation activity of these catalysts [64]. Another possible hypothesis is that Au nanoparticles change the electron structure due to interaction with radicals generated from H₂O₂ producing a “fouling” on the particles.

Regarding the phenomenon of sintering, comprehensive ex-situ TEM measurements were conducted to meticulously observe and analyze the particle shape and particle size distribution of the catalyst before and after subjecting it to the oxidation reaction. This approach provides valuable insights into how the physical characteristics of the catalyst particles evolve due to the reaction conditions. Specifically, the ex-situ TEM technique allows for high-resolution imaging, enabling the examination of particle morphology and size with precision. **Figure 4.53** presents a series of representative TEM images that capture the detailed structural changes occurring in the catalyst particles.

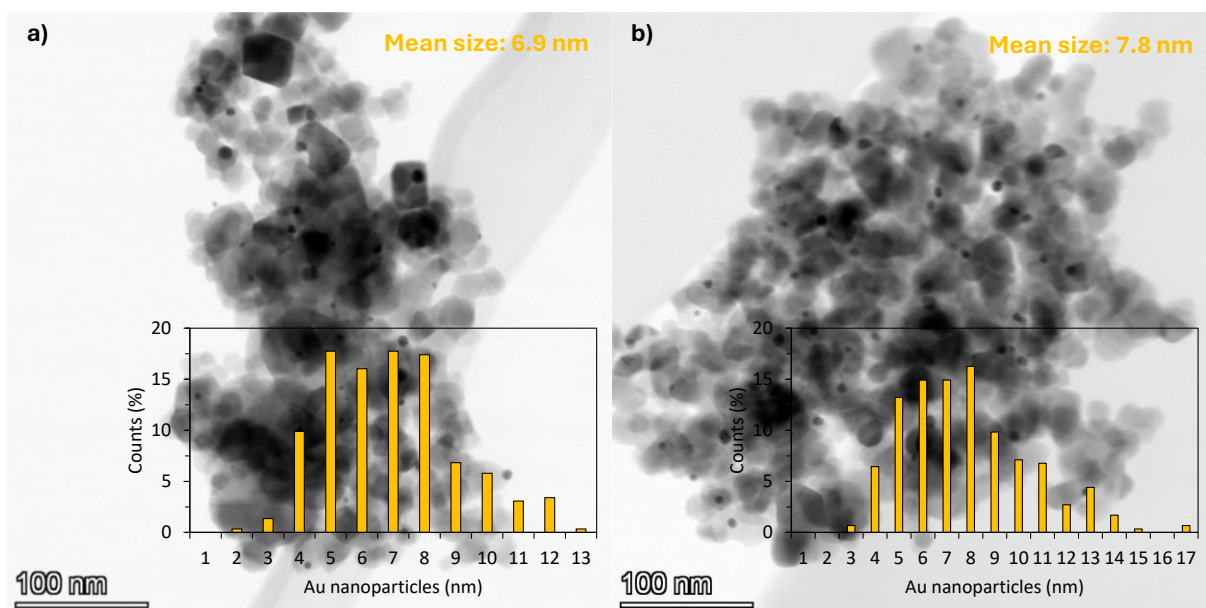


Figure 4.53. Au particle size distributions and representative high-resolution TEM images of the Au/TiO₂ catalyst. Legend: (a) Fresh catalyst, (b) spent catalyst

Alongside these images, the figure also includes the corresponding particle size distribution data, which quantitatively illustrates the shifts in particle size as a result of the oxidation process. This comprehensive analysis helps in understanding the extent of sintering and its impact on the catalytic performance, highlighting any significant changes in particle

aggregation or growth that could affect the overall efficiency and stability of the catalyst. After the oxidation reaction, there is a growth in the size of the particles, going from an average size of 6.9 nm to 7.8 nm. These results have been obtained after counting more than 300 particles in each case. Although the change in particle size is relatively small, Au is one of the noble metals most sensitive to particle size distribution and therefore this change can cause deactivation in the catalyst, resulting in a decrease in FCA selectivity. To validate and confirm the findings obtained from earlier analyses, *quasi-in-situ* reactions were conducted within a TEM reactor. This advanced experimental approach allows for real-time observation of catalyst particles under reaction conditions, providing a more accurate representation of their behavior and transformations during the reaction process. **Figure 4.54** provides a series of TEM images captured during these quasi-in-situ experiments. These images showcase the catalyst particles at various stages of the reaction, highlighting key observations such as changes in particle shape, aggregation, and other morphological transformations.

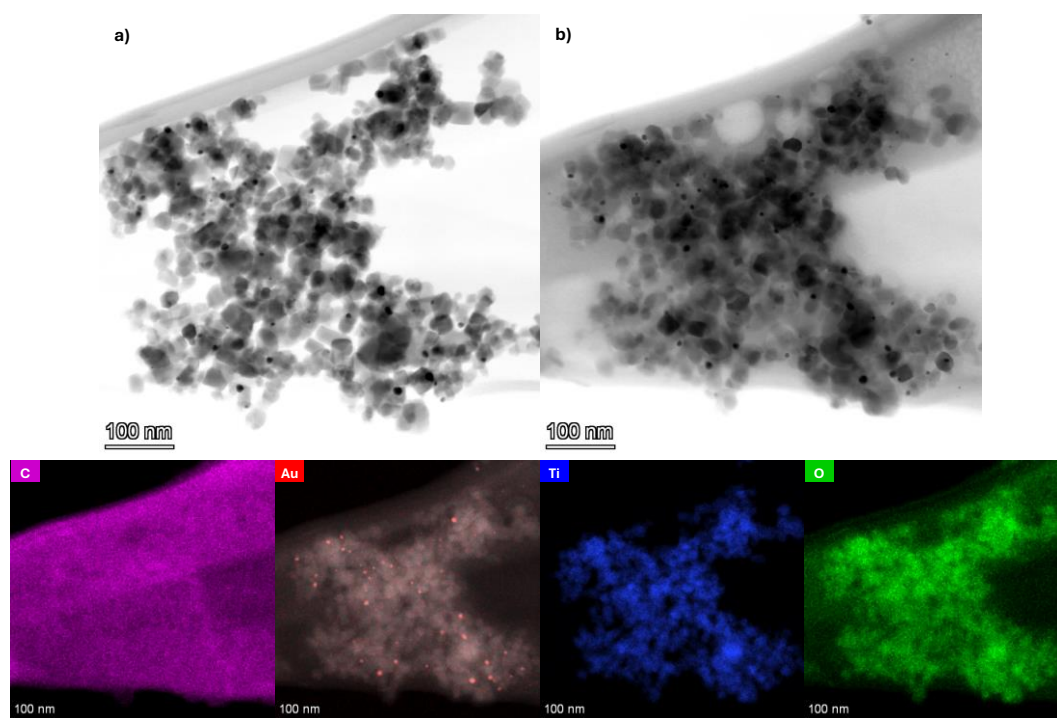
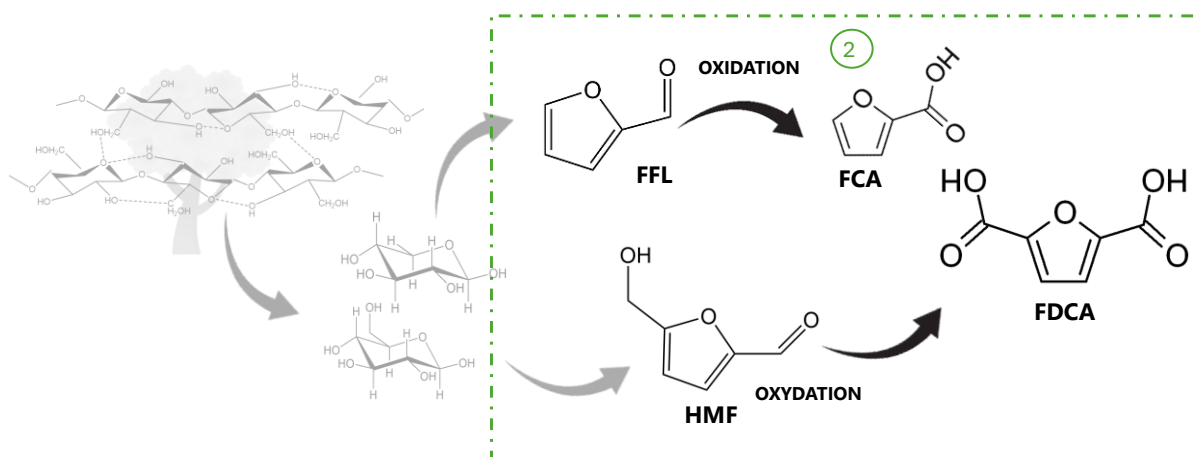


Figure 4.54. Au particle size distributions and representative high-resolution *quasi-in-situ* TEM images of the Au/TiO₂ catalyst and EDS analysis after reaction. Legend: (a) Fresh catalyst, (b) spent catalyst

Before the oxidation reaction, particle size distribution obtained is the same as in *ex-situ* analysis. After the reaction, it is not possible to wash the catalyst, and it is observed how a layer of carbonaceous deposits forms on the fibers of the grid and it is present on the

surface of the particles. This is due to the accumulation of reagent remains on the surface. In conclusion, it was observed that particle size distribution before and after the reaction is approximately the same, and deactivation cannot be attributed to this issue. However, it appears that gold nanoparticles may become saturated with radicals originating from H_2O_2 , leading to a reduction in CO adsorption experiments. This phenomenon could potentially alter the interaction of furfural, resulting in decreased selectivity towards FCA.

Since the inhibiting factors or deactivation pathways are not fully understood, further characterization through ex-situ and quasi-in-situ TEM analysis, as well as CO adsorption studies using IR spectroscopy, focusing on the interaction between gold nanoparticles and the TiO_2 support, would be interesting. According to literature findings, TiO_2 may cover the gold nanoparticles under certain redox conditions, which could contribute to catalyst deactivation.



4.4. FUROIC ACID PRODUCTION BY CATALYTIC OXIDATION OF FURFURAL WITH O₂

This research proposes the furfural partial oxidation into furoic acid using bifunctional heterogeneous catalysts and substituting the strong basic conditions by a buffer solution. Au is selected as the active metal, considering two different supports, MgAl and TiO₂. When using MgAl, a positive influence is expected due to the basic properties that stabilize the reactants and intermediates [46, 65]. In contrast, the use of TiO₂ aims to enhance oxygen activation because oxygen can be adsorbed not only on the Au nanoparticles but also on this reducible support, leading to its dissociation at the interface [66]. The analysis focuses on the main reaction parameters to optimize the selectivity and productivity of the FCA, including catalyst, reaction time, pH, O₂ pressure and temperature. The stability is also assessed through multiple consecutive tests. The main novelty of this work is considering a buffer at pH 8 to perform the reaction at softer conditions with respect to the previous literature.

The analysis of the reaction evolution is presented in terms of conversion, yield, carbon balance closure, and selectivity, according to Eq. 4.8,11,12, and 19.

$$S_i (\%) = \frac{n_i \cdot C_i}{5 \cdot (C_{FFL,0} - C_{FFL,t})} \cdot 100 \quad [4.19]$$

where "C_{FFL}" is the furfural concentration, "n_i" and "C_i" are the number of carbons and the molar concentration of each compound. All the reactions were analyzed twice and

discrepancies between analyses were lower than 5%. Due to the complexity of most figures presented, error bars are not included to facilitate the legibility of the plots.

4.4.1. Catalyst screening

A blank reaction in the absence of any catalyst was performed at 80 °C with 20 bar of O₂, using KHCO₃ to establish a constant pH (8), to evaluate the relevance of a possible autocatalytic mechanism. No products were detected after 8 h, observing a furfural conversion of 9.4 %, a value that directly corresponds to the carbon unbalance (91.5 %), suggesting a high relevance of furfural oligomerization. In good agreement with this hypothesis, the initial yellow solution is significantly darker after 8h, as well as the aspect of the solid catalyst. This undesired effect has been previously observed in the literature[67, 68].

The same results were obtained when using different supports (TiO₂, CeO₂ and MgAl), with total correspondence between conversions of 10.5, 10.2, and 9.8%, and carbon balance closure of 89.5, 89.7, and 90.1%, for TiO₂, CeO₂, and MgAl, respectively. To sum up, these catalysts are not active for the furfural oxidation at these conditions whereas they promote furfural oligomerization. These results are in good agreement with the previous literature [46, 69, 70], highlighting the high furfural oligomerization trend and the need for a noble metal catalyst to activate the oxygen dissociation required for the oxidation steps. Despite the initial assumption of TiO₂ as an active support to activate the oxygen, these results demonstrate that this activity is only relevant in the metal-TiO₂ interface [66]. Once the need for metal nanoparticles is corroborated, a set of experiments using bifunctional catalysts with different noble metals supported on TiO₂ was performed. The main results after 2 h are summarized in **Figure 4.55**.

FCA or any other products of furfural oxidation are not detected when using Ru or Rh, despite observing furfural conversion with both catalysts. Based on these results, Ru and Rh are discarded for further studies, concluding that they are not active for the target oxidation. The furfural conversions obtained with these materials are mainly caused by adsorption and decomposition into humins, in the same way as when using parent supports.

On the other hand, Pd, Pt, and Au produce furoic acid, FCA selectivity being the highest when using Au (9.6% vs. 5.8 and 4.6% of Pt and Pd after 2 h, respectively). In all the

cases, furoic acid is the only compound detected in the liquid phase. If the selectivity was expressed in terms of the relative distribution of detected products, Pd, Pt, and Au will produce 100% furoic acid. Similar selectivities are only reported when using a very complex catalyst (Au(-PVP)/Nb₂O₅-AC) and NaOH to guarantee a basic medium [56], or in a few works under free-base conditions [69, 71]. These results in free-base conditions are limited by a very relevant deactivation, a drawback prevented by this approach, as discussed below.

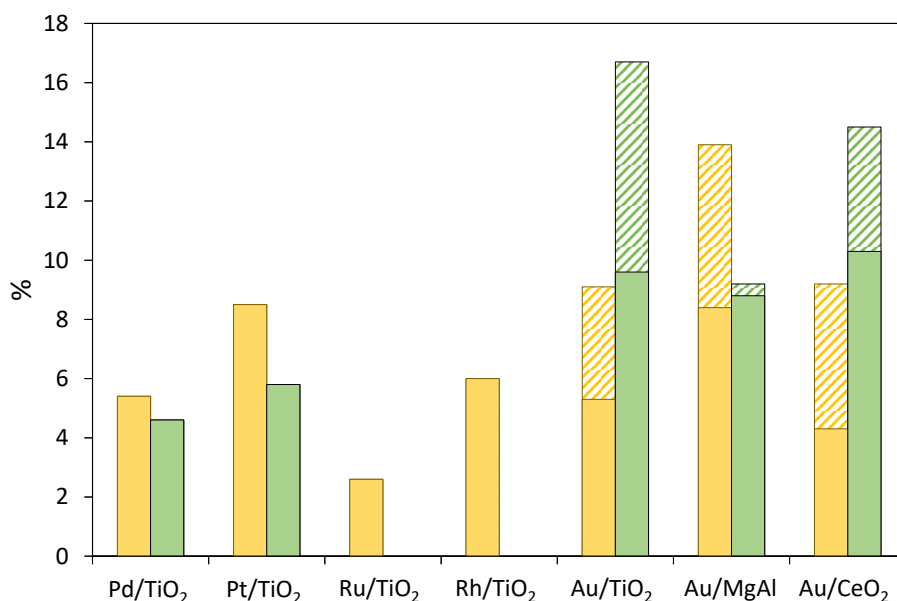


Figure 4.55. Furfural conversion (yellow) and FCA selectivity (green) obtained in the furfural oxidation at 80 °C with 20 bar of O₂ as a function of the catalyst. Results after 2 h except those shown with diagonal bars that corresponds to 8 h reaction time

Although the analysis in terms of total selectivity (based on the furfural conversion and not only on the distribution of the liquid-phase products) could mask the goodness of these results in comparison to other published studies, but this parameter also allows identifying the relative weight of humins production. To our best knowledge, the only reference with high FCA selectivity that includes the carbon balance indicates values even lower than 10% [72], suggesting a humins production higher than in this approach.

Despite the highest conversion after 2h is obtained with Pt/TiO₂ (8.5%), the FCA selectivity is almost 40% lower than the one obtained with Au/TiO₂. Thus, Au/TiO₂ shows the best compromise between activity and FCA selectivity, reaching almost double selectivity than the one obtained with Pd/TiO₂, despite the same conversion. This result suggests that this catalyst minimizes humins production.

According to this screening, Au is selected as the most promising metal. Its activity is also analyzed using other supports, such as MgAl or CeO₂. The highest conversion after 2 h reaction time is obtained for Au/MgAl (8.4%). However, this catalyst presents low FCA selectivity (8.8%), with almost 93% of the converted furfural being transformed into degradation products (humins). Similar FCA selectivities are reached with Au/TiO₂ and Au/CeO₂ (9.6 and 10.3%, respectively), observing slightly higher conversion in the case of Au/TiO₂ (5.3% vs. 4.3%). Since no conclusive results were obtained by this screening, the activity of these materials was compared at longer reaction times (8 h).

The relative increase in the furfural conversion after 8h reaction time is quite similar in all the cases, obtaining almost double values (9.1, 13.9, and 9.2 %, for Au/TiO₂, Au/MgAl, and Au/CeO₂, respectively). As to the FCA production, Au/TiO₂ is highlighted as the most selective one (16.7%), followed by Au/CeO₂ (14.5%) and, finally, Au/MgAl (9.2%). With the two first catalysts, the carbon balance closure remains over 92%, whereas a lower value (88.6%) is reached with Au/MgAl, suggesting a higher relevance of humins formation since no other product was detected in the liquid phase.

According to the literature, the metal dispersion and, subsequently, the metal nanoparticle size are the key parameters to activate the oxygen [73]. Considering the characterization results summarized in **Table 4.14**, the best Au dispersion corresponds with Au/TiO₂, a result that could justify the highest FCA selectivity reached with this material (16.7 %, 100% if considering only the products in the liquid phase). However, there is not a good correlation between these two parameters, with significant discrepancies in terms of FCA selectivity despite the similar metal dispersion of Au/MgAl and Au/CeO₂. These results suggest that the catalyst performance cannot be explained in terms of structure sensitiveness, with surface reactivity playing a key role in the selectivity evolution. Thus, the high surface acidity of MgAl is suggested as the responsible for its high humins production. The relevant role of these active sites in humins formation has been demonstrated in the literature [34, 74, 75].

To maximize the FCA production and to evaluate the relative relevance of the different active sites, the influence of reaction conditions (O₂ pressure and temperature) has been studied, considering two catalyst with opposite properties: Au/TiO₂ (the highest metal dispersion and the lowest concentration of acidic and basic sites) because of its high FCA

production, and Au/MgAl (the material with the highest concentration of acidic and basic sites) because of its high furfural conversion. If active sites related to the support are not of key relevance, working at higher pressures and temperatures could improve the results by a faster O₂ activation. On the other hand, the evaluation of these results when using Au/MgAl could be relevant to evaluate the different kinetics and mechanisms of humins formation and furfural oxidation.

Table 4.14. Summary of the main characterization properties of the different catalysts

	Surface Area (m ² ·g ⁻¹)	Pore Volume (cm ³ ·g ⁻¹)	Metal dispersion (%)	Acidity (μmolNH ₃ ·g ⁻¹)	Basicity (μmolCO ₂ ·g ⁻¹)
Pd/TiO ₂	66	0.4	13.1	104.3	68.6
Pt/TiO ₂	54	0.4	11.0	153.9	66.3
Ru/TiO ₂	48	0.4	21.0	186.2	19.3
Rh/TiO ₂	55	0.3	42.7	175.1	26.3
Au/TiO ₂	62	0.7	24.2	130.0	25.2
Au/MgAl	196	0.4	15.9	338.3	315.8
Au/CeO ₂	115	0.2	13.8	195.9	50.5

4.4.2. Influence of the oxygen partial pressure

The influence of O₂ pressure was studied from 5 to 25 bar of O₂, keeping constant the temperature at 80 °C. A different effect is observed when working with Au/TiO₂ or Au/MgAl, as shown in **Figure 4.56**.

Reaction conditions are chosen to guarantee that experimental results are not limited by oxygen availability. In reactions at 10, 15, 20, and 25 bar, the oxygen (from 0.34 to 0.85 M) is higher than the stoichiometric one (furfural requires 0.5 M of oxygen to be transformed into FCA). The fast stirring ensures a good mixture between the liquid and the gas phases, leading to the effective oxygen saturation of the liquid phase (concentrations in the liquid phase of 0.005, 0.008, 0.104, and 0.013 M, at 10, 15, 20, and 25 bar, respectively). As to the experiment at 5 bar, the O₂ concentration (0.17 M) is slightly lower than the stoichiometric one, but the conversion obtained is significantly lower than the maximum that could be obtained at these conditions. Thus, all the results can be explained based on the activity of the catalyst.

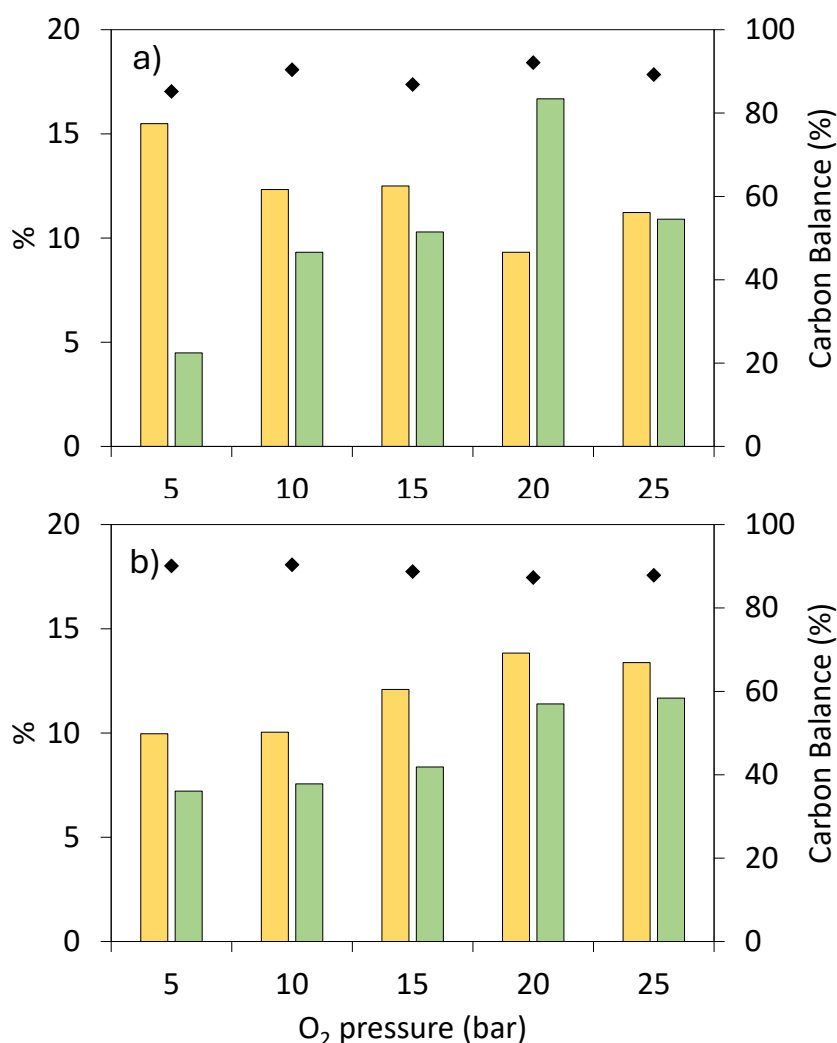


Figure 4.56. Furfural conversion (yellow), FCA selectivity (green) and carbon balance closure (◆, right axis) obtained after 8 h of furfural oxidation at 80 °C as a function of the O₂ pressures using (a) Au/TiO₂ and, (b) Au/MgAl as catalyst

In both cases, very different behaviours are observed below and above 20 bar, although with different trends depending on the catalyst. When using Au/TiO₂, the highest conversion (15.5%) is obtained at the lowest pressure (5 bar), observing a clear decreasing trend with the pressure, reaching a minimum at 20 bar (9.3%). At 25 bar, a slight increase in conversion is observed (11.3%). As to the target product, its selectivity strongly increases from 5 to 20 bar (from 4.5 to 16.7%), with a relevant decrease (10.9%) at 25 bar. These results suggest a positive effect of the O₂ pressure on the control of the main reaction explained suggesting that the surface oxygen concentration can be limiting for this step. Thus, most of the furfural converted at low pressure is transformed into humins since the low surface

oxygen concentration promotes those routes that do not require oxygen (mainly oligomerization to humins). Once the availability of the oxygen increases, humins production is hindered, increasing the selectivity for partial oxidation. The decrease in FCA selectivity observed at 25 bar is explained because the excess of O_2 and the subsequent promotion of secondary reactions degrade the FCA released in the reaction. The final product of these reactions is CO_2 (not analysed) but its intermediates in the oxidation process, maleic and formic acid, are, mainly at intermediate times (1.5% after 3.5 h). In good agreement, the maximum FCA selectivity is obtained after 3 h (11.4%), its degradation being more favourable than its production for longer times.

As for Au/MgAl, from 5 to 20 bar, there is a clear correspondence between the O_2 pressure, the furfural conversion (from 10 to 13.8%, values that correspond to activities from 12.5 to 17.3 mmol/g·h) and the FCA concentration (from 7.2 to 11.4%), suggesting that the surface concentration of oxygen is somewhat limiting the catalyst performance (opposite behavior than Au/TiO₂). At 25 bar, the FCA selectivity slightly increases (from 11.4 to 11.8%) but the furfural conversion decreases (from 13.8 to 13.4%), suggesting that the presence of oxygen is changing the properties of the metal sites or that there is a competitive adsorption between furfural and oxygen. With this catalyst, maleic and formic acid are not detected and the carbon balance obtained is only due to the presence of humins production, a process insensitive to pressure.

4.4.3. Influence of the temperature

To study the influence of temperature, furfural oxidation was studied in the range 80-150 °C keeping 20 and 25 bar of O_2 pressure and using the $KHCO_3$ buffer to guarantee a constant pH of 8. The main results obtained with both catalysts are shown in **Figure 4-57**, comparing the furfural conversion, carbon balance closure, and product distribution in selectivity terms.

Furfural conversion strongly increases when increasing the temperature, at both pressures and catalysts tested. These increments are more relevant when working at 20 bar, reaching maximum values of 85 and 69.5%, for Au/TiO₂ and Au/MgAl, respectively. The corresponding maximum values at 25 bar are 45.4 and 41%, respectively.

These rising trends match with a decrease in the carbon balance, which is in both cases more relevant when working at 25 bar. Considering the low carbon balance at 120 °C (62.6 and 41% for Au/TiO₂ and Au/MgAl, respectively), this pressure was not tested at 150 °C. At the same temperature, when working at 20 bar, the carbon balance obtained were 83 and 74%, respectively. The carbon unbalance increase suggests that, at these conditions, a relevant fraction of the furfural converted is not transformed into the target compound (FCA). On the contrary, it undergoes oligomerization, producing insoluble humins not detected in the liquid phase.

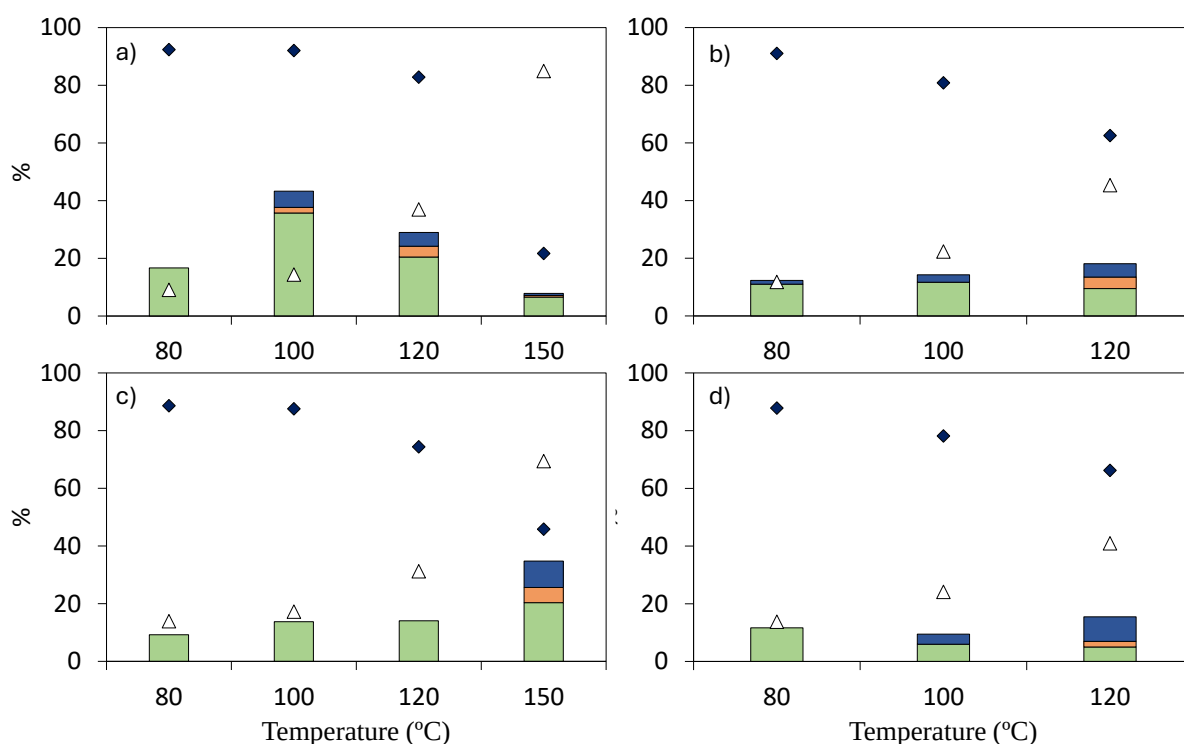


Figure 4.57. Furfural conversion (Δ), carbon balance (◆) and selectivity distribution (bars) obtained in the furfural oxidation at different temperatures (80-150 °C) for Au/TiO₂ at (a) 20 and (b) 25 bar, and Au/MgAl at (c) 20 and (d) 25 bar. Legend: FCA (green), MA (orange), FA (blue)

The presence of these humins determines the selectivity distribution since, according to the selectivity equation (Eq. (4.19)), these undesired compounds are also considered for the calculus (parameter based on the total furfural disappearance). However, this is not the only aspect to explain the carbon balance depletion. The presence of FCA oxidation compounds, such as maleic and formic acid, involves the release of CO₂, a compound involved in the carbon balance that cannot be detected with our experimental system. Moreover, the temporal profiles of these compounds (discussed in the kinetic section) suggest that the

severity of the reaction is high enough to lose control of the main reaction, producing the total oxidation of these organics into CO₂.

Looking at the effect of temperature and pressure on catalyst performance, the optimum conditions must be established by analysing the FCA selectivity and yield. In general, Au/TiO₂ presents higher oxidation activity than Au/MgAl, not only because of the higher conversion but also since maleic and formic acids are detected in relevant amounts in all the cases, except when working at 80 °C and 20 bar. Thus, mild conditions are the optimum to maximize FCA production. In good agreement, the maximum selectivity is reached at 100 °C and 20 bar (35.8%), observing a decrease in selectivity when increasing the temperature. This effect is not so well observed when working at 25 bar because the increase in conversion masks the global result. As to the production, the maximum FCA yield is obtained at 120 °C and 20 bar (7.6%). In this case, the selectivity decrease is compensated with a conversion increase. Similar selectivities are obtained at 100 °C and 150 °C, with yields of 5.3%. As to the results obtained at 25 bar, the selectivity is always significantly lower, as well as the yield, reaching the maximum value at 120 °C (4.3%).

The lower oxidation activity of Au/MgAl produces lower FCA selectivities (maximum value of 20.4 at 150 °C and 20 bar of O₂ pressure) but this compound is the only one detected in the liquid phase (i.e. the selectivity in the liquid phase is 100% for FCA) except when working at 150 °C or 25 bar. In yield terms, 120 °C and 20 bar are the optimum conditions for this catalyst, reaching 4.4% of FCA yield. However, this value is more than 40% lower than the optimum with Au/TiO₂ (same conditions).

As conclusion of this reaction conditions screening, the oxygen activation (promoted by Au/TiO₂) is identified as the key aspect to perform the furfural oxidation whereas no relevant problems related to the stability of the adsorption of reaction intermediates (aspect in which the acidic/basic properties of Au/MgAl could be crucial) is not so important.

4.4.4. Kinetics studies

To elucidate the reaction mechanism, identify all the possible routes for the furfural transformation, and discern if the same mechanism explains the results obtained by the two catalysts, **Figure 4.58** illustrates the evolution of the selectivities with conversion for the

most representative experiments (those in which a larger number of compounds are involved). At milder conditions, FCA is obtained with almost 100% selectivity in the liquid phase.

FCA, the target product, is an oxidation primary product, being the main reaction product at low conversions, and following a marked decreasing trend as the conversion increases. This conclusion is the same despite the catalyst and the reaction conditions. At low conversions, the FCA decrease coincides with the appearance of formic and maleic acid (FA and MA, respectively).

In the same way, the FCA profile reaches a flat evolution, more noticeable in the case of the reaction catalyzed with Au/TiO₂ at 120 °C and 20 bar. According to these results, the furfural oxidation into FCA and the subsequent degradation into MA and FA is identified as the main route, being common for both catalysts tested.

Results obtained with Au/TiO₂ at 25 bar and 120 °C demonstrate the presence of a parallel route, producing 2-hydroxy-2(5H)-furanone (henceforth, HFN) as a primary product. The well-marked selectivity decrease observed for HFN indicates that its degradation is a fast process. This second route is identified as relevant only for the most severe pressure and temperature conditions tested using Au/TiO₂, i.e., at 120 and 150 °C and 20 bar, and at 100 and 120 °C with 25 bar of O₂. The detailed profiles are included in **Figure 4.59-64**. On the contrary, this compound is not observed in any case when working with Au/MgAl.

It should be noted that FA selectivities are always higher than the MA ones, suggesting that FA is produced from more than one route. This fact is more evident in the case of using Au/MgAl. In this case, MA is only detected when the furfural conversion is higher than 65%, whereas FA is relevant from 20%. This observation suggests a third parallel route in which furfural is directly oxidized into formic acid, obtaining a very unstable intermediate that is only observed at trace levels at low conversions (2-hydroxyfuran, HF).

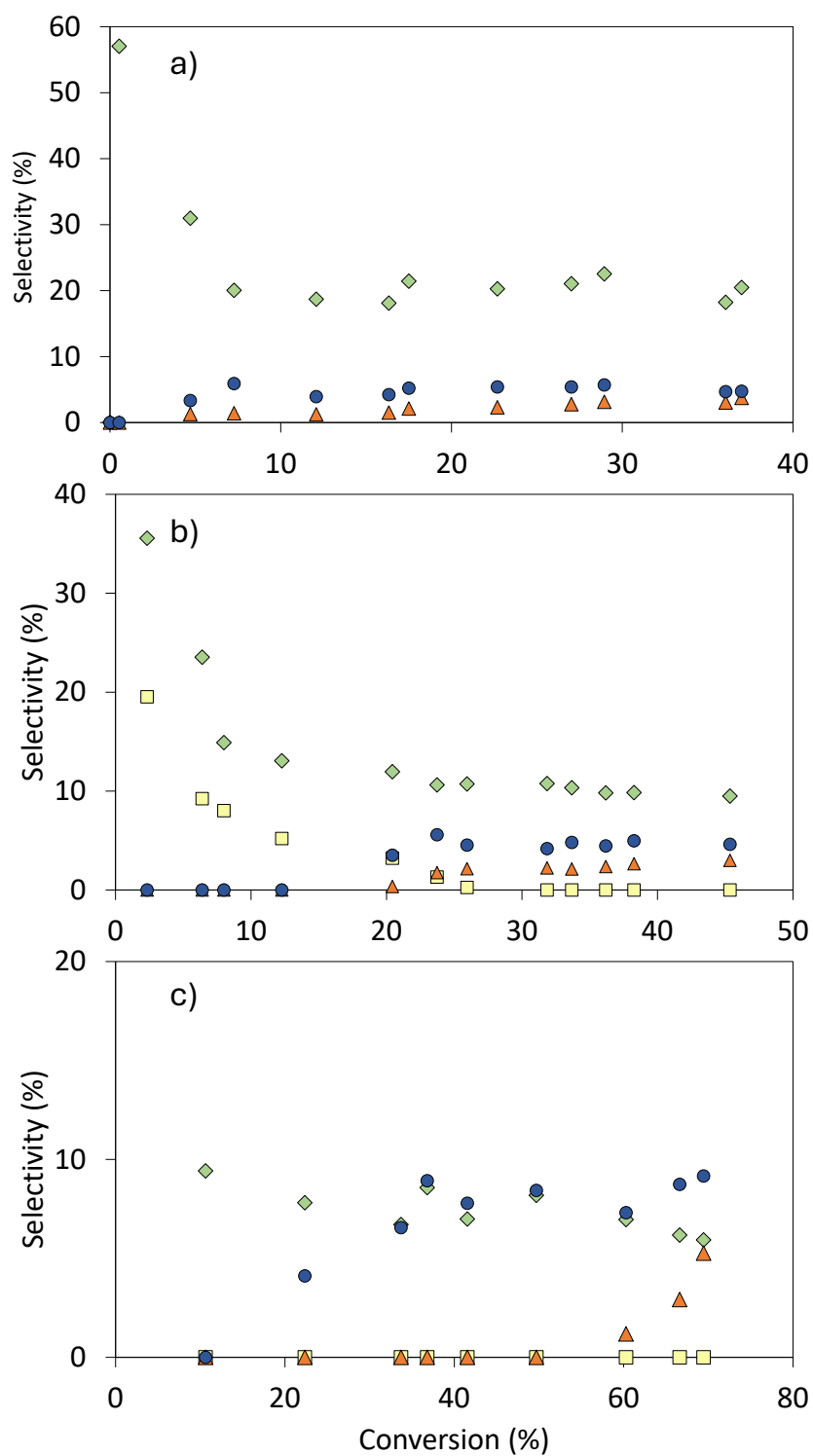


Figure 4.58. Selectivity evolution as a function of conversion. Data corresponding to: (a) Au/TiO₂ at 120 °C and 20 bar, (b) Au/TiO₂ at 120 °C and 25 bar, and (c) Au/MgAl at 150 °C and 20 bar. Symbols: FCA (◇), HFN (□), FA (●), MA (▲)

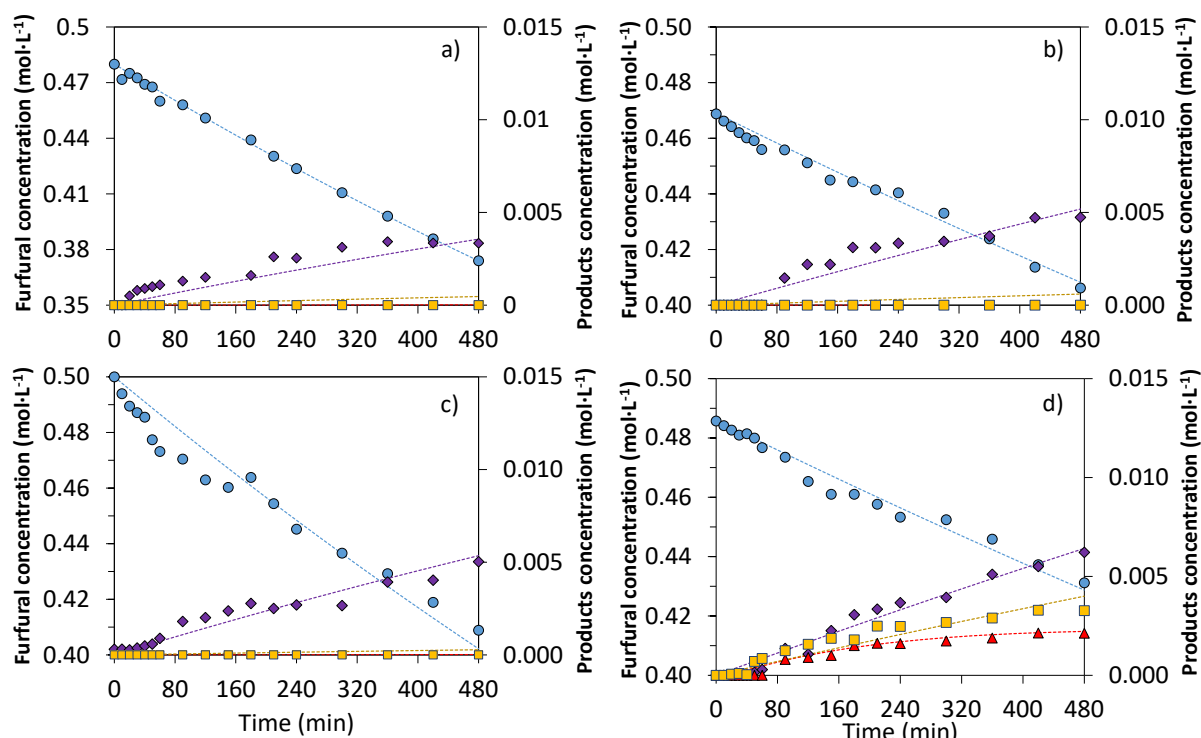


Figure 4.59. Furfural oxidation at 80 °C in presence of Au/TiO₂ modifying pressure: (a) 5 bar, (b) 10 bar, (c) 15 bar, (d) 25 bar. Symbols: FFL (●); FCA (◆); FA (■); MA (▲). Broken lines correspond to the kinetic model predictions

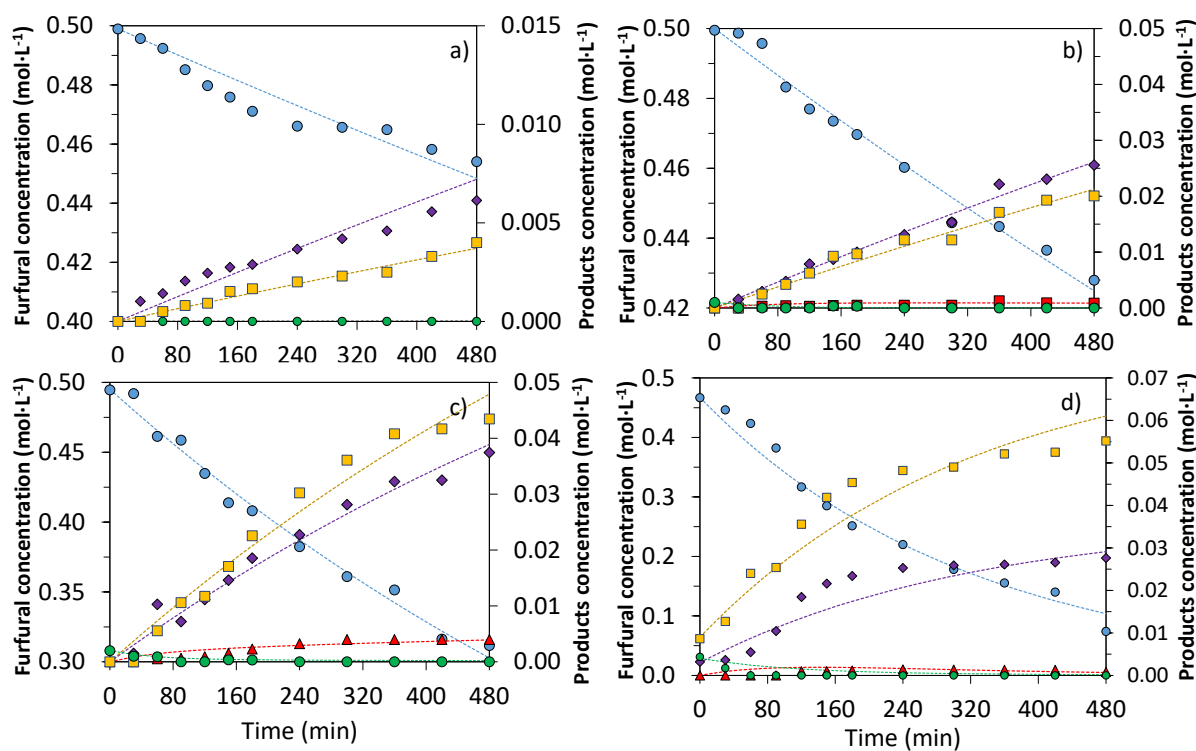


Figure 4.60. Furfural oxidation at 20 bar in presence of Au/TiO₂ modifying temperature: (a) 80 °C, (b) 100 °C, (c) 120 °C, (d) 150 °C. Symbols: FFL (●); FCA (◆); FA (■); MA (▲); HFN (●).

Broken lines correspond to the kinetic model predictions

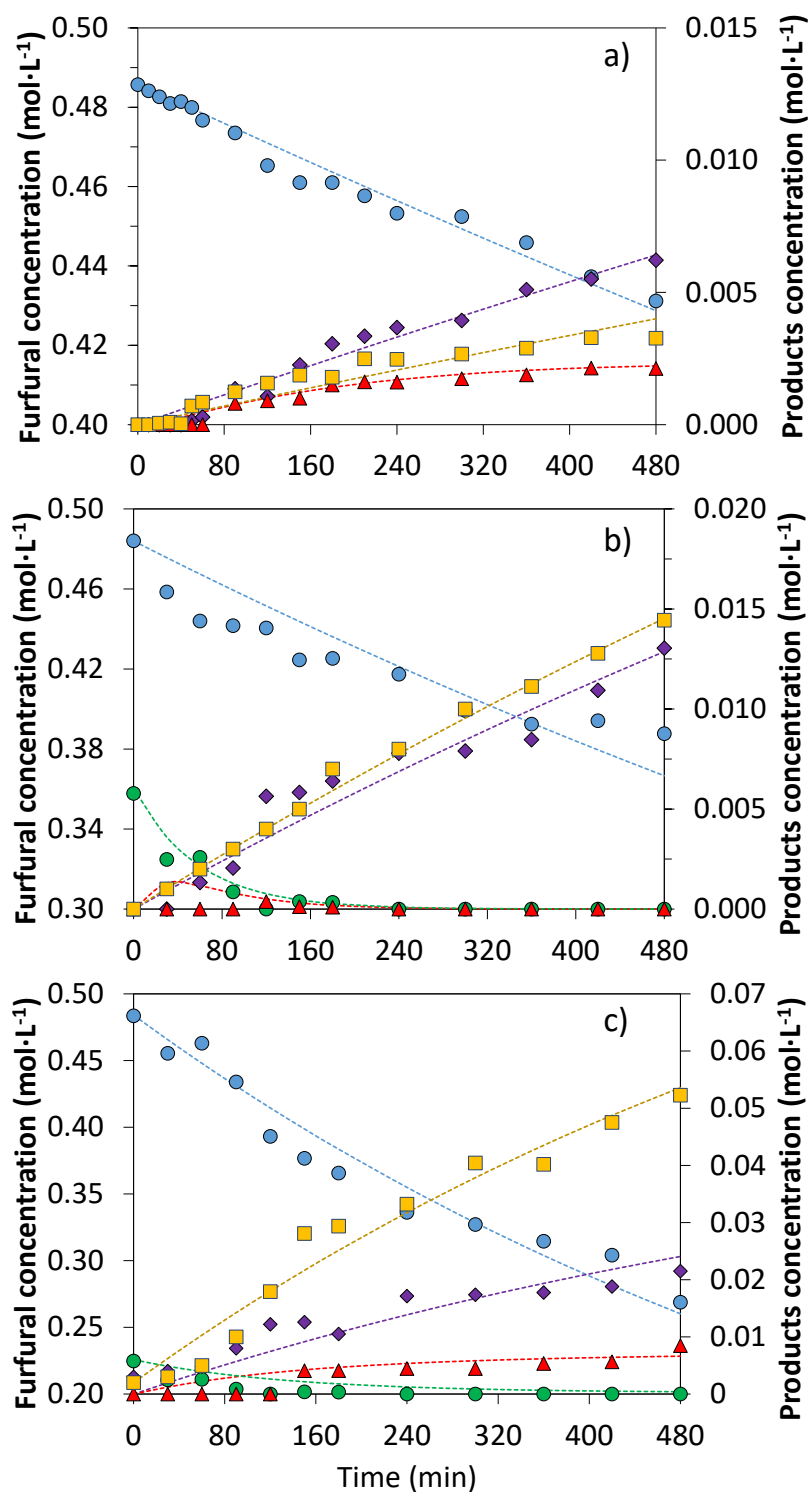


Figure 4.61. Furfural oxidation at 25 bar in presence of Au/TiO₂ modifying temperature: (a) 80 °C, (b) 100 °C, (c) 120 °C. Symbols: FFL (●); FCA (◆); FA (■); MA (▲); HFN (●). Broken lines correspond to the kinetic model predictions

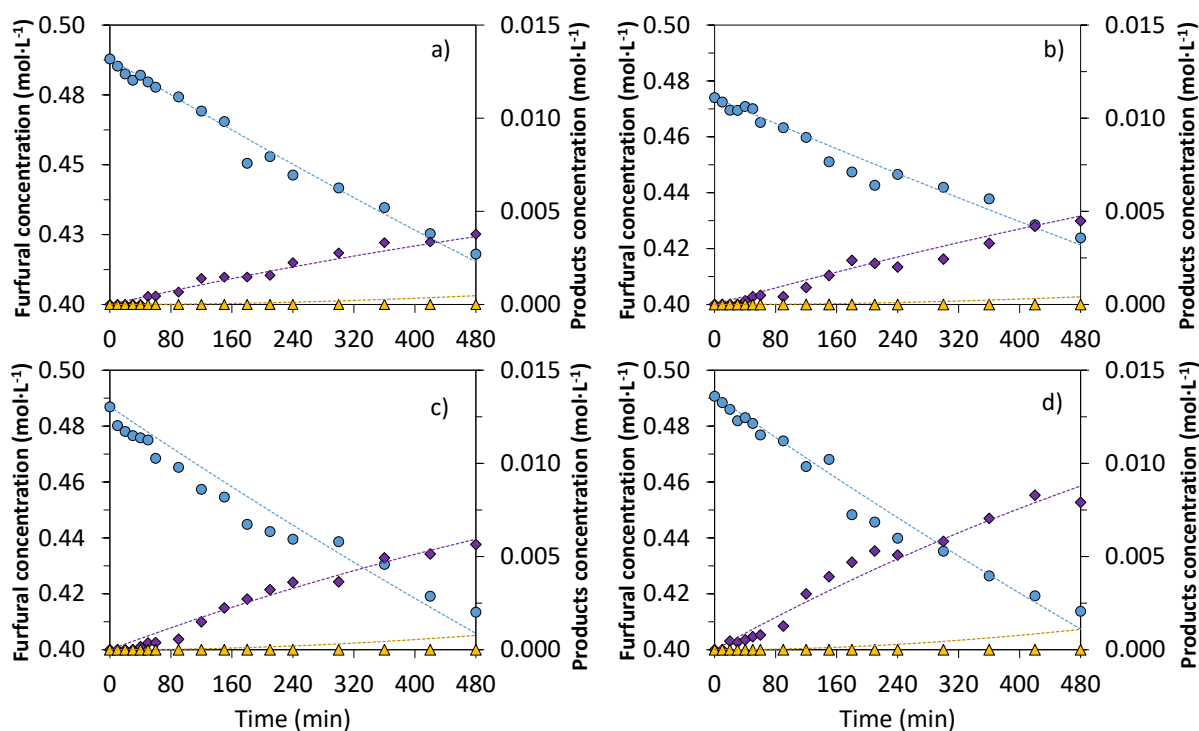


Figure 4.62. Furfural oxidation at 80 °C in presence of Au/MgAl modifying pressure: (a) 5 bar, (b) 10 bar, (c) 15 bar, (d) 25 bar. Symbols: FFL (●); FCA (◆); FA (■); MA (▲). *Broken lines correspond to the kinetic model predictions*

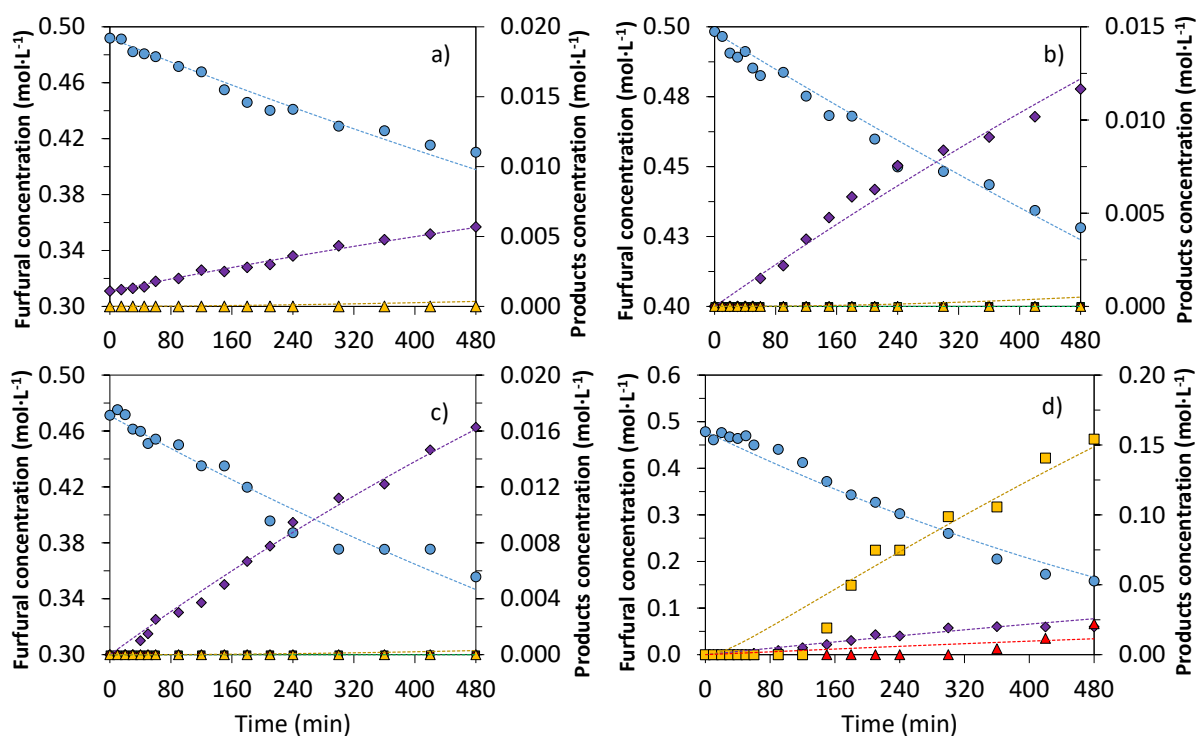


Figure 4.63. Furfural oxidation at 20 bar in presence of Au/MgAl modifying temperature: (a) 80 °C, (b) 100 °C, (c) 120 °C, (d) 150 °C. Symbols: FFL (●); FCA (◆); FA (■); MA (▲); HFN (●). *Broken lines correspond to the kinetic model predictions*

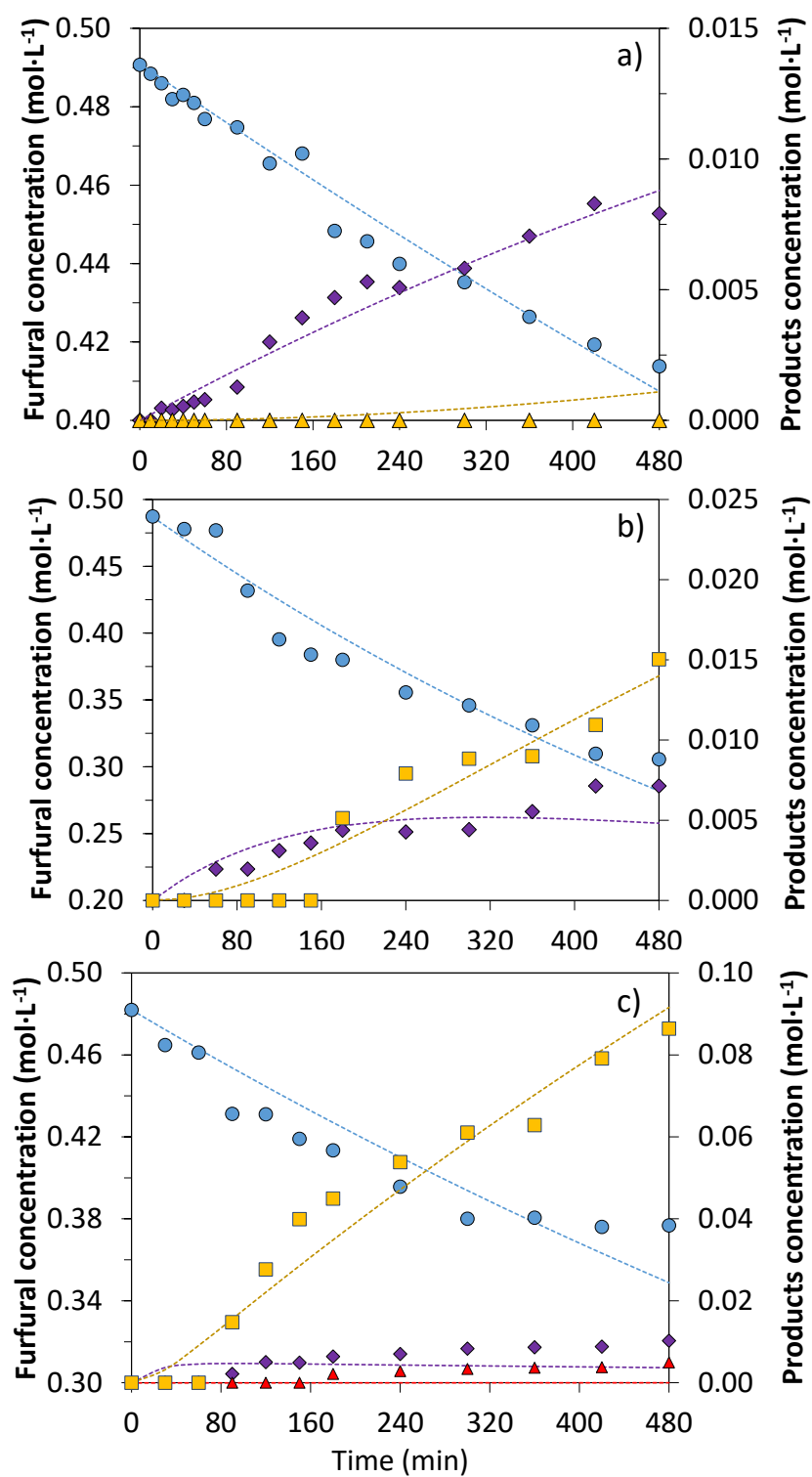


Figure 4.64. Furfural oxidation at 25 bar in presence of Au/MgAl modifying temperature: (a) 80 °C, (b) 100 °C, (c) 120 °C. Symbols: FFL (●); FCA (◆); FA (■); MA (▲); HFN (●). Broken lines correspond to the kinetic model predictions

These conclusions allow defining the reaction mechanism illustrated in **Figure 4.65**, where compounds in grey color are required to complete the carbon balance, but they are not quantitatively detected at working conditions (only in traces at the most severe ones).

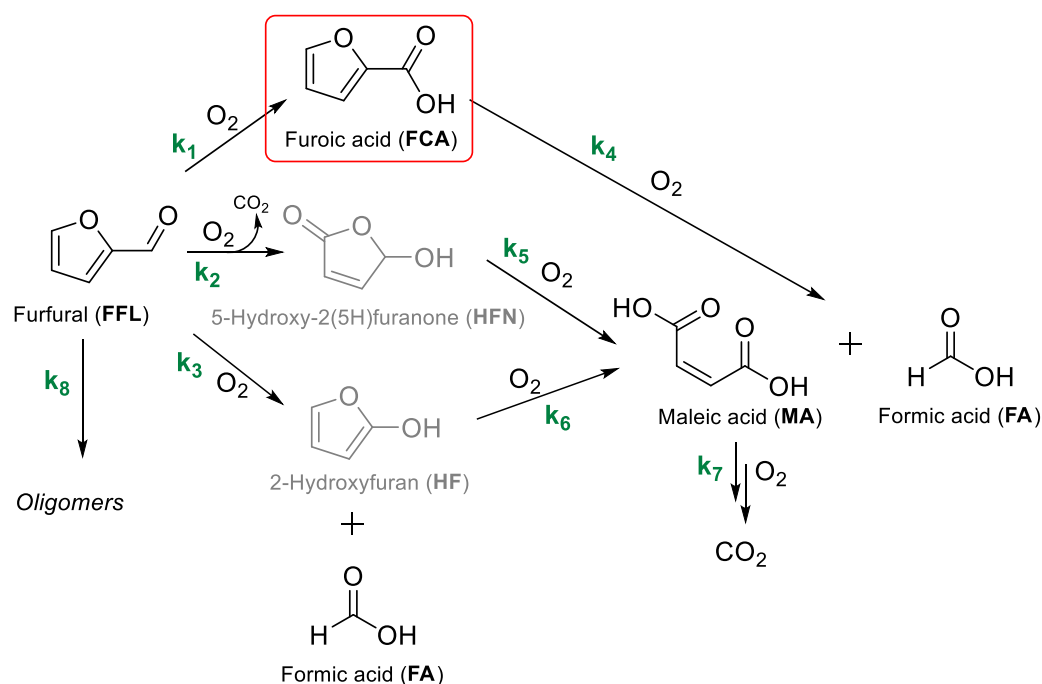


Figure 4.65. Scheme of the reaction mechanism of furfural oxidation using O_2 as oxidizing agent

Based on this mechanism, a preliminary fit of the experimental data considering all the steps were carried out for both materials and all the conditions. Experimental results were fitted to different kinetic models, the best results being obtained when considering an evolution type Langmuir-Hinshelwood for the main reactions, and a potential and independent behavior for the oligomerization and the total oxidation into CO_2 . This model is congruent with the furfural and FCA adsorptions previously discussed, a hypothesis that could be extended to all the organics involved since they have the same functional groups. Considering that O_2 is continuously provided by gas-liquid interphase transport, the concentration of this reactant can be considered constant and embedded in the apparent kinetic rate values.

The temporal evolution of all the compounds obtained with both catalysts at the different conditions tested was fit to the proposed mechanism applying the corresponding mass balances, considering the reactor as an ideal stirred batch reactor. All the equations as well as the kinetic rates and the adsorption constants are presented in Equation 4.20-25 and

Tables 4.15-20. In the same way, all the temporal profiles comparing the experimental points with the fitted data are also included in **Figure 4.59-64.**

$$\frac{dC_{FFL}}{dt} = \frac{-k_1 \cdot K_{ads, FFL} \cdot C_{FFL} - k_2 \cdot K_{ads, FFL} \cdot C_{FFL} - k_3 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - k_8 \cdot C_{FFL} \quad [4.20]$$

$$\frac{dC_{FCA}}{dt} = \frac{k_1 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - \frac{k_4 \cdot K_{ads, FCA} \cdot C_{FCA}}{1 + K_{ads, FCA} \cdot C_{FCA}} \quad [4.21]$$

$$\frac{dC_{MA}}{dt} = \frac{k_4 \cdot K_{ads, FCA} \cdot C_{FCA}}{1 + K_{ads, FCA} \cdot C_{FCA}} + \frac{k_5 \cdot K_{ads, HFN} \cdot C_{HFN}}{1 + K_{ads, HFN} \cdot C_{HFN}} + \frac{k_6 \cdot K_{ads, HF} \cdot C_{HF}}{1 + K_{ads, HF} \cdot C_{HF}} - k_7 \cdot C_{MA} \quad [4.22]$$

$$\frac{dC_{FA}}{dt} = \frac{k_3 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} + \frac{k_4 \cdot K_{ads, FCA} \cdot C_{FCA}}{1 + K_{ads, FCA} \cdot C_{FCA}} \quad [4.23]$$

$$\frac{dC_{HF}}{dt} = \frac{k_3 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - \frac{k_6 \cdot K_{ads, HF} \cdot C_{HF}}{1 + K_{ads, HF} \cdot C_{HF}} \quad [4.24]$$

$$\frac{dC_{HFN}}{dt} = \frac{k_2 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - \frac{k_5 \cdot K_{ads, HFN} \cdot C_{HFN}}{1 + K_{ads, HFN} \cdot C_{HFN}} \quad [4.25]$$

Table 4.15. Reaction rate constants based on the proposed reaction mechanism for Au/TiO₂ catalyst as function of different O₂ pressures. Units: k₁ – k₈, (h⁻¹) and K_{ads, FFL}; K_{ads, HFN}; K_{ads, HF}, and K_{ads, O₂} (L·mol⁻¹). Reaction conditions: 0.5 g Au/TiO₂, C_{0(FFL)} = 0.5 mol·L⁻¹, T = 80 °C, 700rpm, 8h reaction.

P (bar)	k ₁	k ₂	k ₃	k ₅	k ₆	k ₇	k ₈	K _{ads, FFL}	K _{ads, HFN}	K _{ads, HF}	r ²
5	0.435	0.072	0.057	0.110	0.109	0.150	0.030	0.002	0.110	0.109	0.999
10	0.458	0.068	0.053	0.111	0.110	0.150	0.015	0.003	0.111	0.110	0.988
15	0.586	0.070	0.054	0.109	0.109	0.150	0.025	0.003	0.109	0.109	0.998
20	0.556	0.001	0.286	0.225	1.180	0.149	0.010	0.003	0.225	1.180	0.999
25	0.402	0.002	0.252	0.210	2.774	0.147	0.013	0.004	0.210	2.774	0.999

Table 4.16. Reaction rate constants based on the proposed reaction mechanism for Au/TiO₂ catalyst as function of temperature. Units: $k_1 - k_8$ (h⁻¹) and $K_{ads, FFL}$; $K_{ads, HFN}$; $K_{ads, HF}$, and K_{ads, O_2} (L·mol⁻¹). Reaction conditions: 0.5 g Au/TiO₂, $C_{0(FFL)} = 0.5$ mol·L⁻¹, 20 bar O₂, 700rpm, 8h reaction.

T (°C)	k_1	k_2	k_3	k_5	k_6	k_7	k_8	$K_{ads, FFL}$	$K_{ads, HFN}$	$K_{ads, HF}$	r^2
80	0.556	0.001	0.286	0.225	1.180	0.149	0.010	0.003	0.225	1.180	0.999
100	0.449	0.001	0.365	0.915	3.210	0.021	0.007	0.016	0.915	3.208	0.999
120	0.407	0.032	0.501	1.049	3.226	0.045	0.033	0.031	1.049	3.221	0.999
150	0.446	0.026	0.888	1.033	3.609	1.033	0.147	0.031	1.032	3.602	0.995

Table 4.17. Reaction rate constants based on the proposed reaction mechanism for Au/TiO₂ catalyst as function of temperature. Units: $k_1 - k_8$ (h⁻¹) and $K_{ads, FFL}$; $K_{ads, HFN}$; $K_{ads, HF}$, and K_{ads, O_2} (L·mol⁻¹). Reaction conditions: 0.5 g Au/TiO₂, $C_{0(FFL)} = 0.5$ mol·L⁻¹, 25 bar O₂, 700rpm, 8h reaction.

T (°C)	k_1	k_2	k_3	k_5	k_6	k_7	k_8	$K_{ads, FFL}$	$K_{ads, HFN}$	$K_{ads, HF}$	r^2
80	0.402	0.002	0.252	0.210	2.774	0.147	0.013	0.004	0.210	2.774	0.999
100	0.512	0.012	0.578	1.016	2.222	2.505	0.027	0.007	1.014	2.221	0.998
120	0.324	0.014	0.694	0.688	2.259	0.000	0.051	0.026	0.663	2.254	0.997

Table 4.18. Reaction rate constants based on the proposed reaction mechanism for Au/MgAl catalyst as function of different O₂ pressures. Units: $k_1 - k_8$, (h⁻¹) and $K_{ads, FFL}$; $K_{ads, HFN}$; $K_{ads, HF}$; $K_{ads, FCA}$; and K_{ads, O_2} (L·mol⁻¹). Reaction conditions: 0.5 g Au/MgAl, $C_{0(FFL)} = 0.5 \text{ mol} \cdot \text{L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, 700rpm, 8h reaction.

P (bar)	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	$K_{ads, FFL}$	$K_{ads, HFN}$	$K_{ads, HF}$	$K_{ads, FCA}$	r^2
5	0.061	0.000	0.000	0.139	0.000	0.000	0.300	0.019	0.019	0.000	0.000	0.219	0.997
10	0.065	0.000	0.000	0.131	0.000	0.000	0.100	0.016	0.022	0.000	0.000	0.130	0.999
15	0.071	0.000	0.000	0.134	0.000	0.000	0.100	0.021	0.040	0.000	0.000	0.216	0.998
20	0.069	0.000	0.000	0.113	0.000	0.000	0.100	0.025	0.020	0.000	0.000	0.113	0.999
25	0.075	0.000	0.000	0.117	0.000	0.000	0.100	0.017	0.047	0.000	0.000	0.084	0.998

Relevant conclusions can be drawn from this comprehensive study, allowing a significant simplification of this complex model. The values obtained for " k_2 " (HFN formation step) are systematically lower than those values obtained for " k_1 " (FCA formation step), being zero in most of the cases and more than two orders of magnitude lower than " k_1 " in the other cases. Moreover, the " k_5 " (HFN decomposition) values are significantly higher than the " k_2 " ones. In the same way, " k_6 " (HF decomposition) values are one or two orders of magnitude higher than " k_3 " (HF formation). In fact, this last constant has null values for all the reactions carried out with Au/MgAl. With this context and considering the negligible concentration of HF and HFN intermediates, the production of maleic and formic acid can be assimilated to a primary step, being directly obtained from furfural, without distinguishing if the formation route is from HF or HFM. With this simplification, " $K_{ads, HFN}$ " and " $K_{ads, HF}$ " are also neglected in the simplified model.

The profiles of the FCA discard a relevant decomposition of this compound when using Au/TiO₂. In good agreement, negligible values for " k_4 " and " $K_{ads, FCA}$ " were obtained. However, to define a common mechanism for both catalysts, the FCA decomposition into MA and FA is considered. Based on the conclusions of this detailed study, the reaction mechanism can be simplified to the one shown in **Figure 4.66**, and the kinetic model can be

expressed according to the following equations (Eq. 4.25-28), in which only the relevant kinetic steps and adsorption processes are considered.

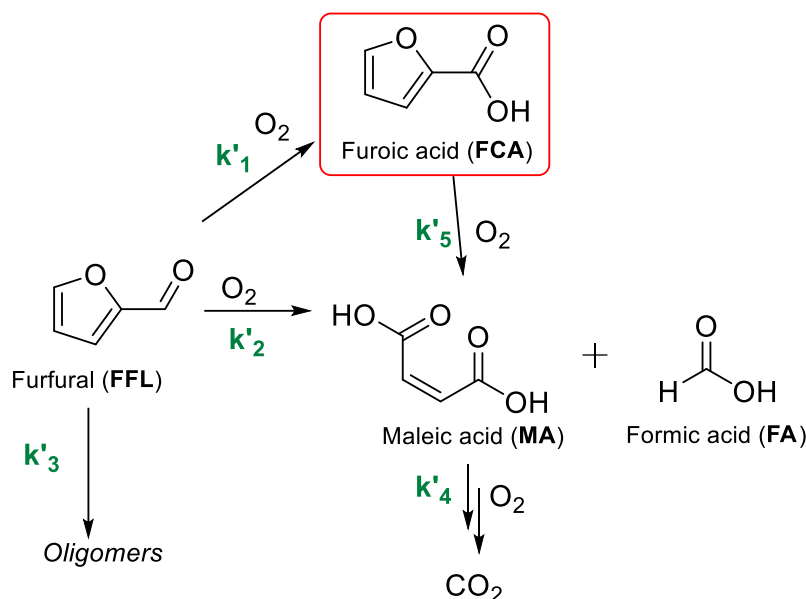


Figure 4.66. Scheme of the simplified reaction mechanism of furfural oxidation using O_2 as oxidizing agent according to the preliminary analysis of the complex mechanism

$$\frac{dC_{FFL}}{dt} = \frac{-k'_1 \cdot K_{ads, FFL} \cdot C_{FFL} - k'_2 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - k'_3 \cdot C_{FFL} \quad [4.25]$$

$$\frac{dC_{FCA}}{dt} = \frac{k'_1 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - k'_5 \cdot C_{FCA} \quad [4.26]$$

$$\frac{dC_{MA}}{dt} = \frac{k'_2 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} - k'_4 \cdot C_{MA} + k'_5 \cdot C_{FCA} \quad [4.27]$$

$$\frac{dC_{FA}}{dt} = \frac{k'_2 \cdot K_{ads, FFL} \cdot C_{FFL}}{1 + K_{ads, FFL} \cdot C_{FFL}} \quad [4.28]$$

After comparing different types of kinetics and analyzing the fit of all the reactions tested, some steps are considered with a Langmuir-Hinshelwood model, whereas other steps follow first-order behavior. For the adsorption processes, the best fit was obtained considering that both oxidation routes involving furfural require the adsorption of this reactant on the same type of active sites. In all the cases, apparent rates are considered, involving in these constants the oxygen concentration, since, as commented before, oxygen concentration will be constant throughout each entire experiment.

The kinetic constants obtained for Au/TiO₂ are summarized in **Table 4.19**. This model represents the temporal evolution of all the compounds obtained in reactions at the most severe conditions whereas, for all the reactions at 80 °C (and most of those at 100 °C), the presence of only one product (FCA) reduces the number of steps involved, with null values for k'_2 , k'_4 y k'_5 . The corresponding values for Au/MgAl are shown in **Table 4.20**, observing slightly higher values for almost all the kinetic rate constants.

Figures 4.67 and **68** show the good fit of experimental values to those predicted by the model for the most representative experiments, with Au/TiO₂ and Au/MgAl, respectively. The adjustment of each reaction is shown in **Figures 4.69-72**.

Table 4.19. Reaction rate constants based on the simplified reaction mechanism for Au/TiO₂ catalyst as function of different O₂ pressures and reaction temperatures.

P (bar)	T (°C)	k'_1 (mol·L ⁻¹ ·s ⁻¹)	k'_2 (mol·L ⁻¹ ·s ⁻¹)	k'_3 (s ⁻¹)	k'_4 (s ⁻¹)	k'_5 (s ⁻¹)	$K_{ads, FFL}$ (L·mol ⁻¹)	r ²
5	80	0.0017	-	8.3·10 ⁻⁶	-	-	0.00036	0.9999
10	80	0.0015	-	5.5·10 ⁻⁶	-	-	0.00034	0.9999
15	80	0.0017	-	5.2·10 ⁻⁶	-	-	0.00030	0.9995
20	80	0.0017	-	4.3·10 ⁻⁶	-	-	0.00029	0.9998
25	80	0.0017	-	3.9·10 ⁻⁶	-	-	0.00028	0.9999
20	100	0.0142	0.012	7.4·10 ⁻⁶	0.105	8·10 ⁻⁸	0.00015	0.9999
25	100	0.0110	0.010	5.1·10 ⁻⁶	0.141	1.7·10 ⁻⁶	0.00012	0.9984
20	120	0.0944	0.140	1.4·10 ⁻⁵	0.111	1.2·10 ⁻⁶	4·10 ⁻⁵	0.9996
25	120	0.0750	0.101	8.9·10 ⁻⁶	0.250	2.2·10 ⁻⁵	4·10 ⁻⁵	0.9977
20	150	0.2148	0.414	3.8·10 ⁻⁵	0.240	5·10 ⁻⁶	2·10 ⁻⁵	0.9942

Table 4.20. Reaction rate constants based on the simplified reaction mechanism for Au/MgAl catalyst as function of different O₂ pressures and reaction temperatures.

P (bar)	T (°C)	k'_1 (mol·L ⁻¹ ·s ⁻¹)	k'_2 (mol·L ⁻¹ ·s ⁻¹)	k'_3 (s ⁻¹)	k'_4 (s ⁻¹)	k'_5 (s ⁻¹)	$K_{ads, FFL}$ (L·mol ⁻¹)	r ²
5	80	0.0051	-	7.6·10 ⁻⁶	-	-	1.0·10 ⁻⁵	0.9999
10	80	0.0073	-	7.3·10 ⁻⁶	-	-	1.4·10 ⁻⁵	0.9996
15	80	0.0082	-	6.0·10 ⁻⁶	-	-	1.4·10 ⁻⁵	0.9997
20	80	0.0090	-	6.6·10 ⁻⁶	-	-	9.2·10 ⁻⁶	0.9997
25	80	0.0011	-	5.9·10 ⁻⁶	-	-	1.1·10 ⁻⁵	0.9998
20	100	0.0012	-	8.1·10 ⁻⁶	-	-	1.3·10 ⁻⁵	0.9992
25	100	0.0039	0.0046	1.7·10 ⁻⁵	0.030	3.4·10 ⁻⁵	1.5·10 ⁻⁶	0.9979
20	120	0.0035	-	9.3·10 ⁻⁶	-	-	1.5·10 ⁻⁶	0.9953
25	120	0.0099	0.0764	2.8·10 ⁻⁵	0.076	8.0·10 ⁻⁵	1.6·10 ⁻⁶	0.9986
20	150	0.0156	0.0886	1.6·10 ⁻⁵	0.018	5.3·10 ⁻⁶	0.8·10 ⁻⁶	0.9998

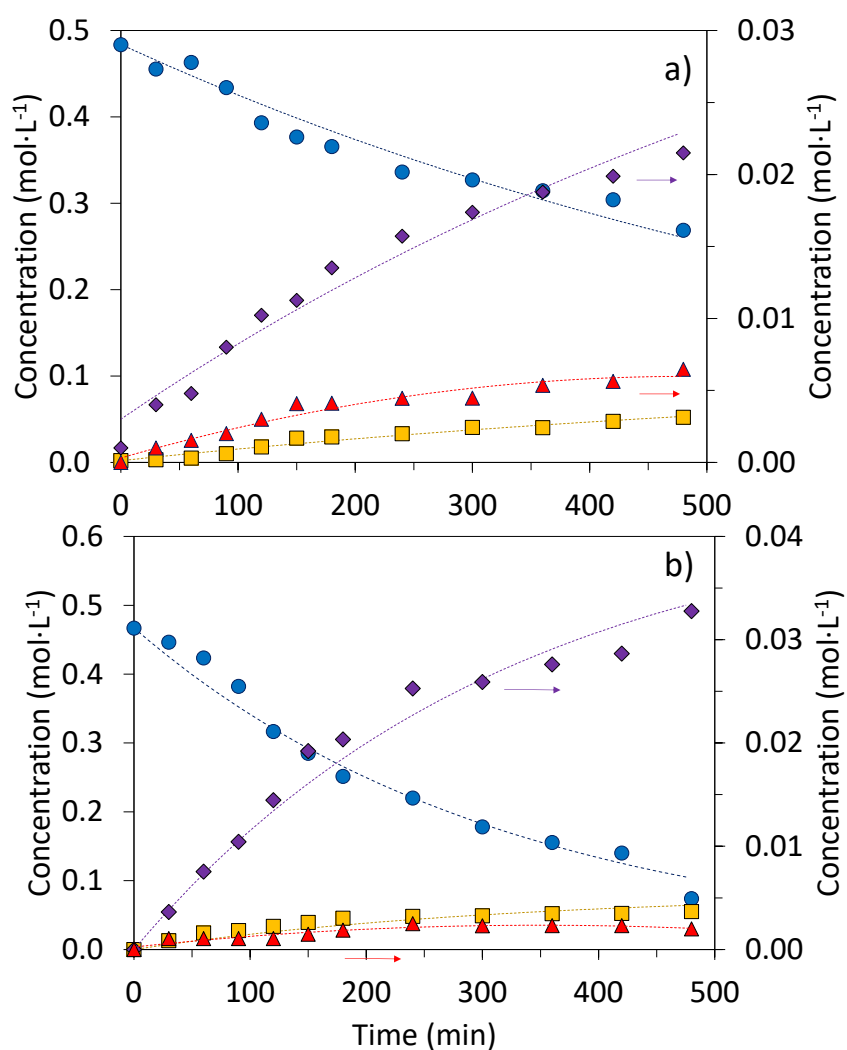


Figure 4.67. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of all the compounds involved in the furfural oxidation catalyzed by Au/TiO₂ at (a) 120 °C and 25 bar, and (b) 150 °C and 20 bar. Symbols: FFL (●), FCA (◆), MA (▲), and FA (■)

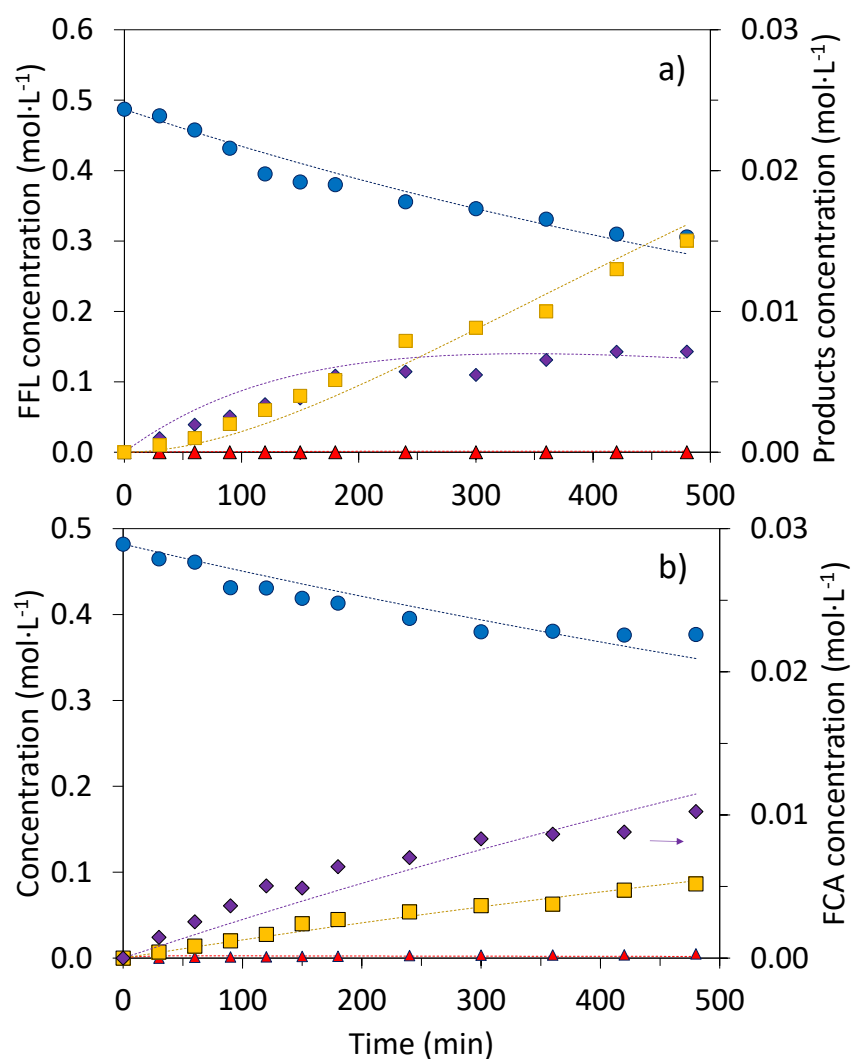


Figure 4.68. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of all the compounds involved in the furfural oxidation catalyzed by Au/MgAl at (a) 100 °C and 25 bar, and (b) 120 °C and 25 bar. Symbols: FFL (●), FCA (◆), MA (▲), and FA (■)

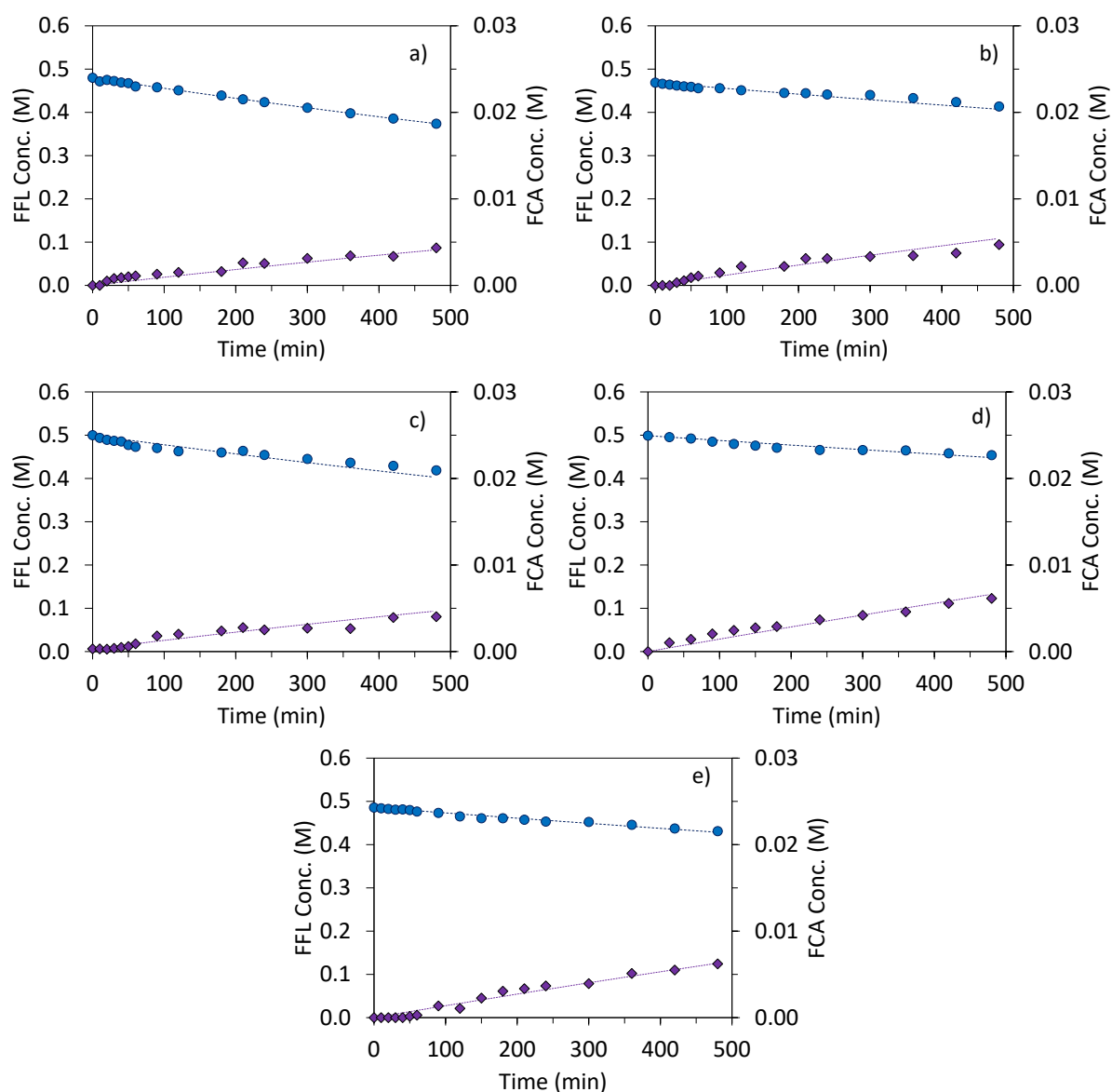


Figure 4.69. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of the furfural oxidation catalyzed by Au/TiO₂ at 80 °C as a function of the O_2 pressure: (a) 5 bar, (b) 10 bar, (c) 15 bar, (d) 20 bar, and (e) 25 bar. Symbols: FFL (●), FCA (◆)

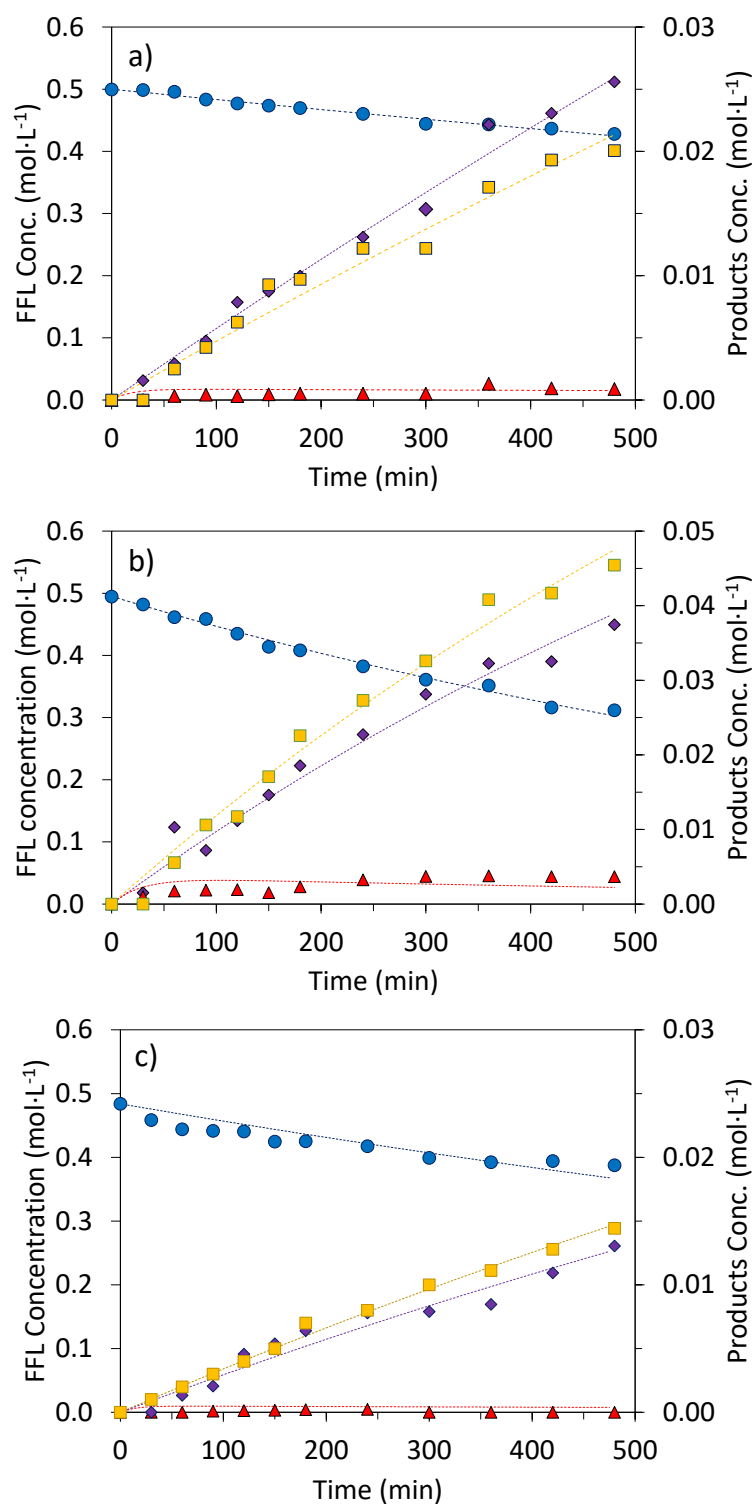


Figure 4.70. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of the furfural oxidation catalyzed by Au/TiO₂ at: (a) 100 °C, 20 bar; (b) 120 °C, 20 bar; and (c) 100 °C, 25 bar. Symbols: FFL (●), FCA (◆), MA (▲), and FA (■)

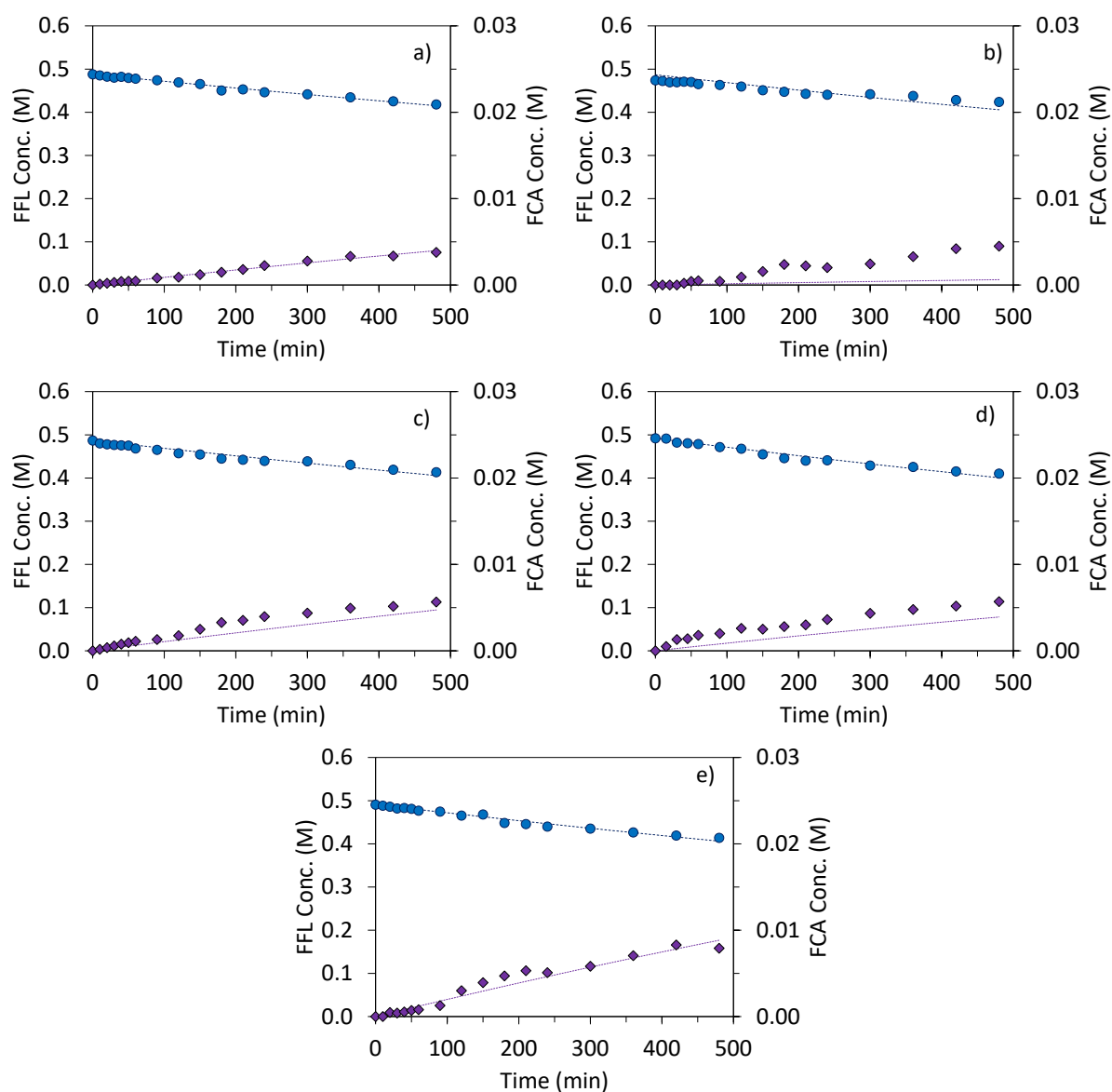


Figure 4.71. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of the furfural oxidation catalyzed by Au/MgAl at 80 °C as a function of the O_2 pressure: (a) 5 bar, (b) 10 bar, (c) 15 bar, (d) 20 bar, and (e) 25 bar. Symbols: FFL (●), FCA (◆)

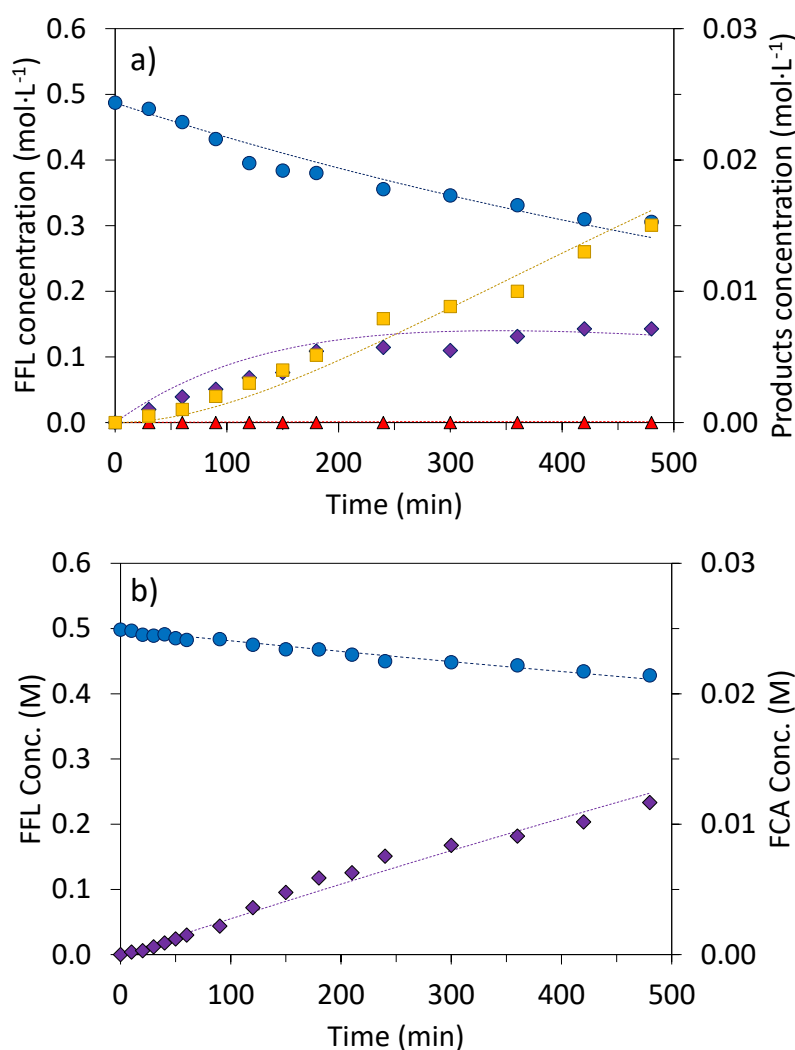


Figure 4.72. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of the furfural oxidation catalyzed by Au/MgAl at: (a) 100 °C, 20 bar and (b) 100 °C, 25 bar. Symbols: FFL (●), FCA (◆), MA (▲), and FA (■)

As analyzed in **Figure 4.73**, using Au/TiO₂ at the lowest temperature (80°C), the direct production of FCA from furfural (k'_1) does not depend on the oxygen pressure, obtaining very similar rate constant values at all the studied pressures. This fact suggests that oxygen surface concentration is large enough for not being a limiting reactant and does not lead to any kind of inhibition or modification of furfural adsorption sites. However, a different trend was observed at higher temperatures (100-120 °C), observing that total pressure negatively affects this step (Table 19). This result suggests that oxygen hinders the oxidation reaction at these conditions, that could be at first insight, unexpected for an oxidation reaction. This

apparent contradiction can be explained by two different causes: a competitive adsorption of oxygen and furfural at higher temperatures (plausible if temperature has a more marked negative effect on furfural adsorption than for oxygen adsorption) or that higher oxygen concentrations at the highest studied temperatures can lead to an overoxidation of the Au atoms, decreasing its intrinsic activity for this reaction.

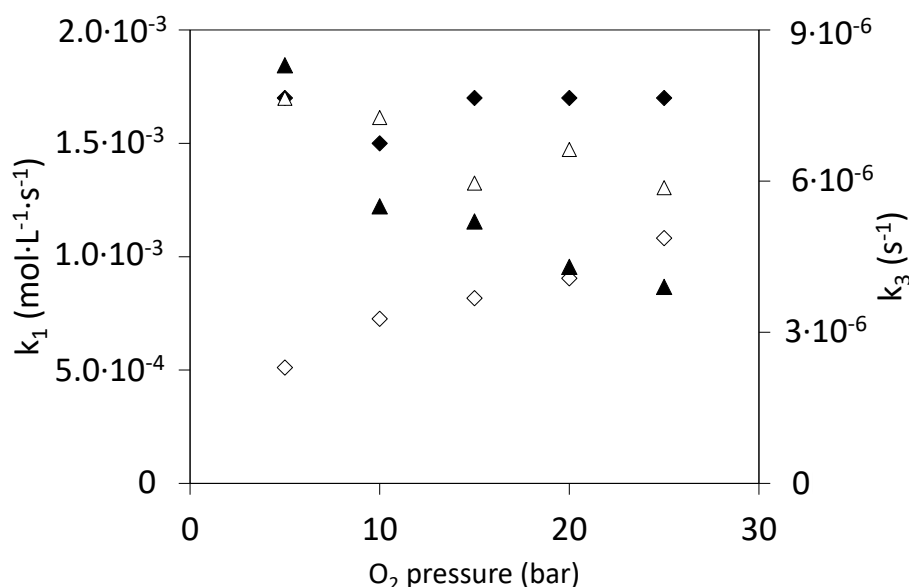


Figure 4.73. Evolution of k_1 (diamonds) and k_3 (triangles) with the O_2 pressure. Data corresponding to Au/TiO₂ (black) and Au/MgAl (white)

A decreasing trend with total oxygen pressure is observed for the furfural oligomerization (k'_3). According to the initial comparison of results in the absence of a catalyst and using the different supports, the furfural oligomerization has a relevant homogeneous component, but the solid catalysts also contribute to this reaction (mainly catalysts with acid properties). Both mechanisms have been previously identified in the literature [67, 73, 76]. The evolution of k'_3 (constant that involves both mechanisms) with the pressure indicates that the furfural oligomerization is inhibited by the presence of oxygen. If this analysis is extended to higher temperatures, the comparison between kinetic rates obtained at 20 and 25 bar demonstrates that the role of oxygen concentration cannot be discarded. Thus, minor discrepancies are obtained, with slightly higher values at 20 bar in comparison to the same step at 25 bar and the same temperature. In global terms, working with high pressure enhances the selective FCA production with k_1/k_3 ratios from 206 to 430, at 5 and 25 bar, respectively.

In the case of the reactions catalyzed with Au/MgAl, the kinetic study demonstrates a positive effect of the oxygen pressure enhancing the target reaction, with increasing k'_1 values with increasing O_2 pressures at all the studied temperatures. This trend is the opposite of that observed for Au/TiO₂ catalysts and suggests that oxygen surface concentration can be limiting for this step when working with Mg-Al supported catalysts. It should be noted that the absence of redox properties of the MgAl support hinders oxygen mobility from metal sites where O_2 is activated to the support (several authors suggest that furfural can be adsorbed in basic sites of the support in this kind of materials [77]). This fact makes surface oxygen concentration more limiting and justifies that increasing pressures lead to higher reaction rates. The chemical differences between Mg-Al oxide (with a higher concentration of basic sites that can promote furfural adsorption but inactive for activating oxygen) and TiO₂ (which has a lower affinity for furfural adsorption but higher electron mobility that can promote overoxidation of the metal sites at the highest temperatures) appear to be responsible for the differential effect of oxygen pressure.

Regarding the furfural oligomerization, the second relevant reaction with this material, the decreasing trend defined for Au/TiO₂ is also observed, with slightly higher values. This result is in good agreement with the role of acid sites promoting oligomerization [76]. With this catalyst, the other steps are only significant when working in the most severe conditions, not obtaining data enough to complete a deep analysis.

As to the influence of the temperature, both at 20 and 25 bar, kinetic rates demonstrate a clear increasing trend, coherently with an Arrhenius dependence. This correspondence verifies the initial assumptions considered when deciding which steps follow an exponential model and which adsorption constants are relevant (opposite behavior of kinetic rates and adsorption constants with the temperature). Although not all the steps are relevant at mild conditions, all the rates obtained were adjusted to the Arrhenius model, obtaining the activation energies summarized in **Figure 4.74**. Although the activation energy should be independent of the pressure, it must be noted that the analysis is done considering the apparent kinetic constants, which involve the oxygen pressure.

The highest activation energy is obtained for the FCA decomposition (k'_5), in good agreement with the fact that this step is only relevant at the most severe conditions. No relevant differences were obtained with the two parallel steps involving the furfural to

produce FCA and MA (k'_1 and k'_2 , respectively), with typical values of catalytic reactions. Similar activation energies are also obtained for the FFL oligomerization (k'_3) and MA total oxidation (k'_4), but in this case with values congruent with a non-catalytic character of these steps.

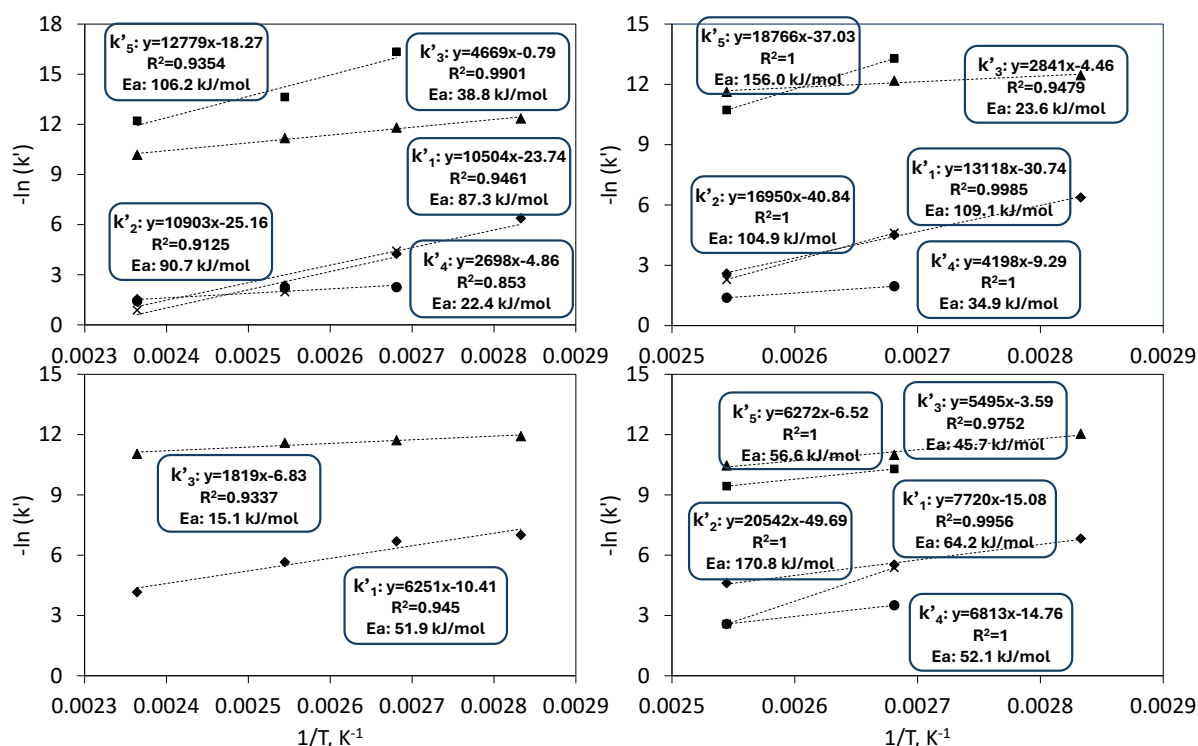


Figure 4.74. Activation energy (Ea) values according to the Arrhenius model (N/A = non available). Data corresponding to (a) Au/TiO₂ 20 bar; (b) Au/TiO₂ 25 bar; (c) Au/MgAl 20 bar; (d) Au/MgAl 25 bar. Symbols: k'_1 (◆); k'_2 (×); k'_3 (▲); k'_4 (●); k'_5 (■)

The activation energies obtained with this material are lower than those obtained with Au/TiO₂. These results suggest that the slower kinetics obtained are due to significantly lower values of the pre-exponential constants, values related to the probability of constructive interactions between both reactants.

To sum up, the oxygen availability in the vicinity of adsorbed furfural is suggested as the main factor controlling the kinetics of the furfural oxidation to produce furoic acid when using Au/MgAl, obtaining significantly better results when working with Au/TiO₂ because of the higher oxygen mobility in the support. Thus, at the same conditions, FCA productions 160 % higher than those obtained with Au/MgAl are reached when using TiO₂ as support.

4.4.5. Catalyst reusability

Activity studies performed with Au/TiO₂ working under controlled pH conditions (buffered solution) demonstrate that this new approach allows obtaining a relevant increase in terms of furoic acid selectivity (100% in the liquid phase except when working at too high temperatures) concerning previous literature at pH 14 [56, 78]. Moreover, the relevance of humins production is reduced. However, to compare this configuration with the base-free one, stability is a key factor to consider. Literature under uncontrolled pH demonstrates a high FCA selectivity but a strong deactivation due to the permanent adsorption of this acid and the catalytic leaching due to the low pH [46, 65, 70, 71].

To study the catalytic stability, the catalyst after the reaction with Au/TiO₂ at 100 °C and 20 bar was recovered by filtration, washed with water, and introduced in subsequent cycles with fresh solutions of furfural without any previous reactivation. Results obtained after 8h of reaction are summarized in **Figure 4.75**, in terms of furfural conversion, furoic acid selectivity, and carbon balance closure. Strong stability is observed, with negligible decreases in the furfural conversion (14.6% after the fourth cycle) and constant furoic acid selectivities of 35%. The slight increase in the carbon balance closure suggests that the humins formation is slightly hindered, maybe because of the permanent adsorption of these solids on the active catalytic sites.

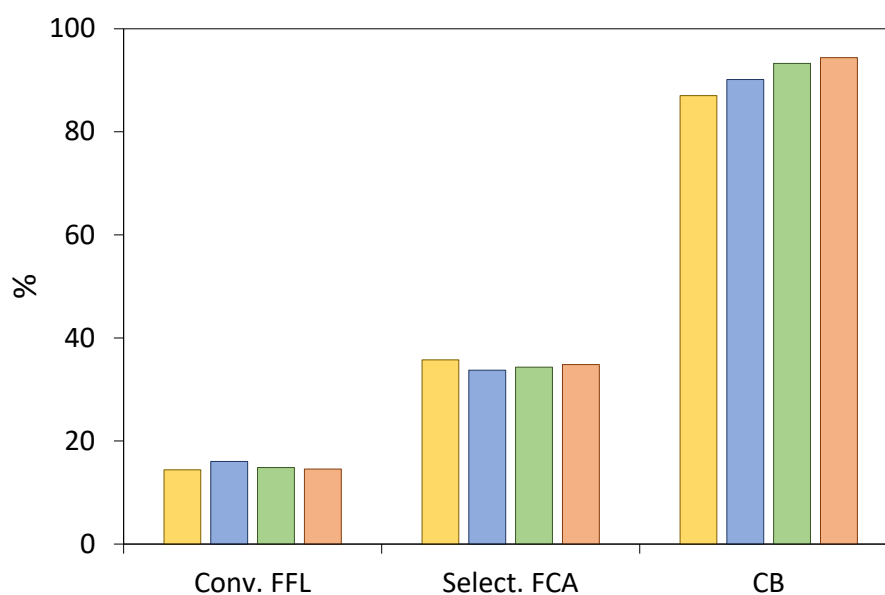
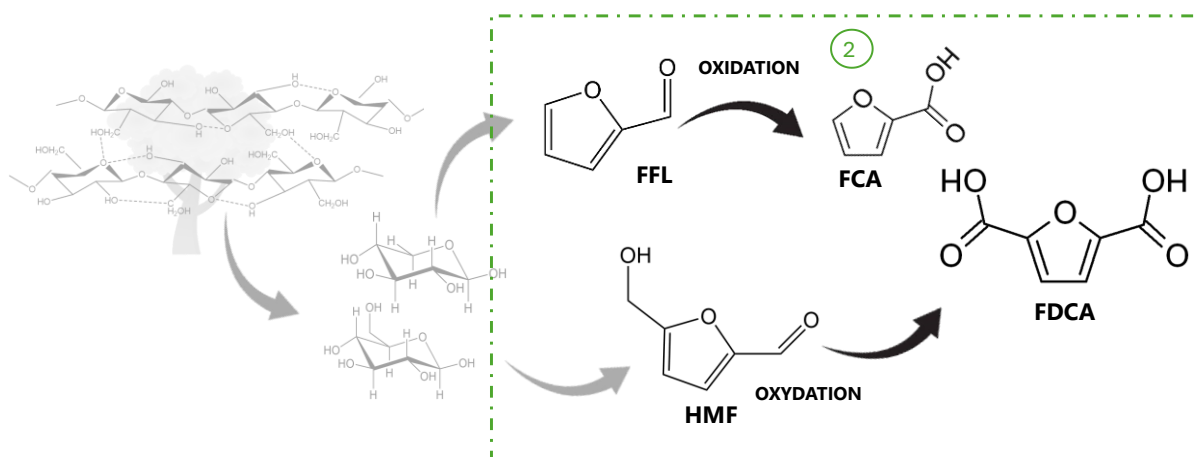


Figure 4.75. Stability results obtained with Au/TiO₂ at 100 °C and 20 bar. Results corresponding to data after 8h with the first (yellow), second (blue), third (green), and fourth (orange) cycle

These results demonstrate that the catalytic leaching and the deactivation by permanent adsorption of FCA are prevented by working with a buffer solution at pH 8. This strong stability contrasts with the results published when working under uncontrolled pH, which is a clear advantage of this configuration.



4.5. PRODUCTION OF 2,5-FURANDICARBOXYLIC ACID BY OXIDATION OF 5-HYDROXYMETHYLFURFURAL AND FRUCTOSE

This study aims to conduct a comprehensive analysis of the impact of various reaction conditions (including temperature, oxygen pressure, NaOH:HMF ratio, and HMF initial concentration) on the oxidation of HMF to FDCA over Au/TiO₂ catalysts. The objective is to identify the optimal conditions that achieve a balance between activity, selectivity, and sustainability. Subsequently, we evaluate the feasibility of directly producing FDCA from fructose in a one-pot configuration. This evaluation involves assessing whether the conclusions drawn from the study using commercial HMF remain applicable when using biomass-related feedstocks.

The analyses of the reactions are present in terms of conversion, selectivity, and carbon balance closure, according to the following expressions:

$$x (\%) = \frac{C_{i,0} - C_{i,t}}{C_{i,0}} \cdot 100 \quad [4.29]$$

$$S_i (\%) = \frac{n_j \cdot C_j}{(C_{i,0} - C_{i,t})} \cdot 100 \quad [4.30]$$

$$Yield (\%) = \frac{n_j \cdot C_j}{n_i \cdot C_{i,0}} \cdot 100 \quad [4.31]$$

$$C.B. (\%) = \frac{\sum(n_j \cdot C_j)}{\sum(n_i \cdot C_i)} \cdot 100 \quad [4.32]$$

where " n_i " and " C_i " are the number of carbons and the molar concentration of each reactant and " n_j " and " C_j " are the number of carbons and the molar concentration of each compound.

As preliminary studies, the possible HMF oxidation and/or degradation promoted by basic conditions has been tested considering two different configurations, both in the absence of any solid catalyst. On the one hand, the HMF self-degradation was evaluated at room temperature and atmospheric pressure using the most basic conditions considered in this work (0.04 M NaOH, 4:1 NaOH/HMF). After 24 h, more 50% of the initial HMF disappears but no products are detected, with the subsequent decrease in the carbon balance (47.5%). The dark color of the solution is congruent with these results, suggesting a high HMF polymerization trend (humins formation), even in the absence of oxidizing conditions. Humins remain soluble at high pH levels due to their coiled conformations, which are cross-linked by weak forces such as Van der Waals bonds [79, 80].

The same experiment was also performed under oxidizing condition (20 bar of O_2). After 1h, 98.4% of HMF conversion is reached, but the carbon balance decreases to 6.8%, suggesting that the HMF oligomerization, the only reaction taking place at these conditions, is significantly promoted by oxidizing conditions. No products were detected by increasing the temperature to 80 °C.

Both experiments indicate the need for a metal catalyst to steer the reaction toward the production of FDCA by activating the oxygen dissociation required for oxidation steps [79, 81-83]. The systematic study about the reaction conditions that allow reaching the maximum FDCA yield with the minimum severity is then studied using in all the cases Au/TiO₂ (2 g·L⁻¹).

4.5.1. Influence of the reaction temperature on the 5-hydroxymethylfurfural oxidation

Figure 4.76 shows the temporal profiles obtained in the aerobic oxidation of a 0.1M HMF solution as a function of the temperature (range studied 60-100 °C). The high O_2 pressure chosen (20 bar) ensures the theoretical excess of this reactant, whereas the fast stirring (700 rpm) promotes the oxygen transfer from the gas to the liquid phase, discarding mass transfer limitations as relevant in the discussion of the results. The NaOH:HMF ratio (4:1) has been chosen considering the literature [81] to promote the reaction and to keep the

humins soluble, preventing their precipitation on the catalyst surface, with the subsequent catalytic deactivation by pore blockage.

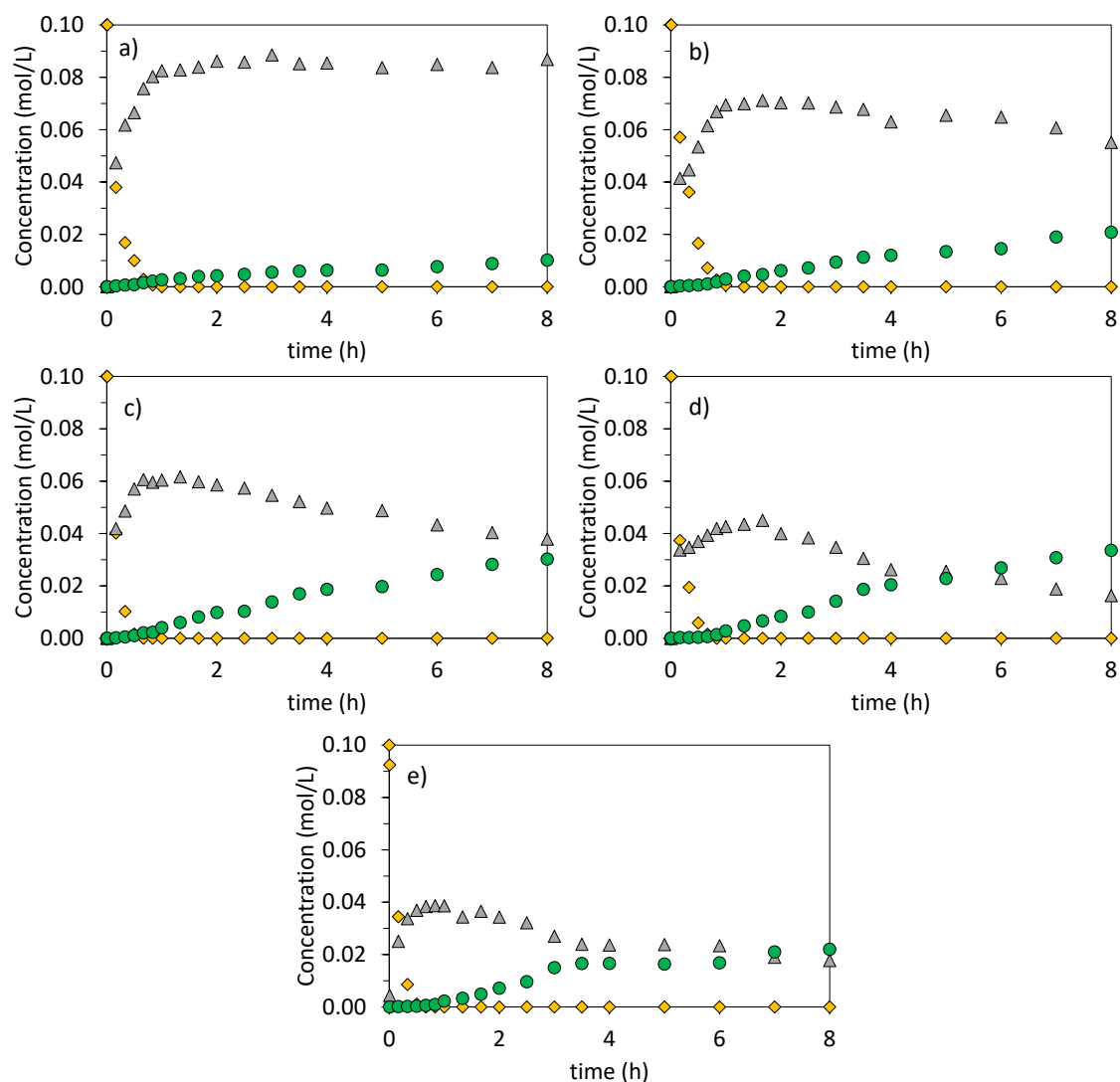


Figure 4.76. Temporal evolution of all the compounds involved in the 0.1 M HMF oxidation as a function of temperature at 20 bar and NaOH:HMF 4:1 ratio over Au/TiO₂ (2 g·L⁻¹). Legend: (a) 60 °C, (b) 70 °C, (c) 80 °C, (d) 90 °C, and (e) 100 °C. Symbols: HMF (◆), HMFCa (▲), and FDCA (●)

Total HMF conversion is reached in less than 1 h, regardless of the temperature. HMFCa is the first component detected, discarding the parallel route of DFF. This intermediate has the typical profile of a primary reaction product, reaching its maximum in less than one hour, with concentrations that correspond to more than 80% of the HMF converted at 60 °C. As the temperature increases, the maximum decreases (70% at 70 °C, 67% at 80 °C, 44% at 90 °C, 38% at 100 °C), suggesting a higher relevance of humins formation. Reaction at 60 °C has not severity enough to promote the second oxidation step,

FDCA being obtained in traces (<10% after 8 h). Increasing the temperature, HMFCFA decreases because of the formation of FDCA. There is total correspondence between the HMFCFA disappeared and the FDCA formation, which suggests that HMF is the only humins precursor. Consequently, the carbon balance has been constant since the first hour, obtaining a well-marked decreasing trend with the temperature, from 97% at 60 °C to 40% at 100 °C. This parameter, as well as the selectivity distribution obtained after 8h are compared in **Figure 4.77**.

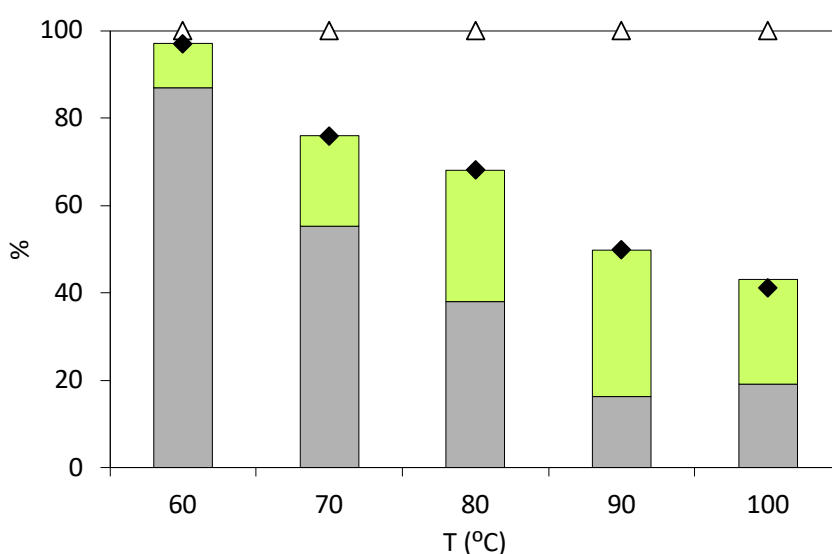


Figure 4.77. HMF conversion (Δ), carbon balance (◆), and selectivity distribution (bars) obtained after 8 h of 0.1 M HMF oxidation at different temperatures (60-100 °C) over Au/TiO₂ (2 g·L⁻¹) at 20 bar and 4:1 molar ratio NaOH:HMF. Legend: HMFCFA (grey) FDCA (green)

The comparison after 8 h reaction time reflects that the second oxidation is not enough promoted at temperatures below 80 °C, being the solution enriched in HMFCFA. The maximum FDCA selectivity is observed at 90 °C (33.5% of the total HMF converted, a value that represents 67.3% of the products detected in the liquid phase). However, the carbon balance (49.8%) obtained at this temperature indicates that these conditions are also favourable for the humins formation. This effect is even more relevant at 100 °C. The balance between maximizing the activity and minimizing the humins formation seems to be obtained at 80 °C. Although after 8h the relative selectivity of FDCA is only 44%, the higher carbon balance closure (67%) and the temporal profiles suggest that longer times could significantly improve this value with a limited humins formation. These conditions are considered as the base case for further studies. This study allows concluding some relevant aspects that

condition the following studies: (1) humins are generated by the polymerization of HMF but other oxidized compounds are not involved; (2) although temperature promotes both reactions, humins formation is more sensitive to this factor than the oxidation steps, being required to modify other parameters to maximize the FDCA yield, and (3) Minimizing humins formation should be prioritized over maximizing FDCA yield as the primary criterion when selecting optimum conditions to prevent catalytic deactivation (decreasing as much as possible the NaOH usage for avoiding humins precipitation).

4.5.2. Influence of O₂ pressure on the 5-hydroxymethylfurfural oxidation

The optimization of O₂ pressure is interesting because of two opposite aspects. On the one hand, since 20 bar of O₂ represents a high excess concerning the theoretical consumption required to promote the complete oxidation of HMF, trying to minimize the pressure would represent an effort to improve the economy of the process. On the contrary, higher O₂ pressure could enhance the interaction of this molecule with the metal sites, promoting oxygen dissociation and, subsequently, the oxidation pathway over the humins formation. The influence of O₂ pressure was studied from 15 to 30 bar of O₂, keeping constant the optimum temperature at 80 °C. Temporal profiles, shown in **Figure 4.78**, demonstrate that the reaction mechanism remains unaltered. Thus, total HMF conversion is reached after 1 h and HMFCFA is the only intermediate detected. However, the product distribution changes significantly, also affecting the carbon balance, which indicates that the pressure of oxygen plays a key role in the process, despite the large excess theoretically used in all the cases. To facilitate the discussion of this effect results after 0.5 h (before reaching total HMF conversion) and 8 h are compared in **Figure 4.79**.

As anticipated, the decrease in the carbon balance occurs during the first 0.5 h of the reaction, no observing more evolution once the HMF conversion is complete. This fact indicates that HMF plays a crucial role in humins formation. From 15 to 25 bar, results after 0.5 h indicate a positive effect of O₂ pressure tuning the reaction to the desired oxidation, reducing the humins formation, and observing an increase in the carbon balance from 50% to 63%. Considering the short reaction time evaluated, the almost total selectivity of the HMFCFA is explained by its character as a primary compound (not enough time to promote the second step). Results obtained at 30 bar suggest a possible inhibition effect that could

indicate that all the Au sites are covered by O_2 molecules, disturbing the HMF adsorption. Thus, there is less HMF adsorbed, reducing the frequency of interaction between the two reactants (lowest HMF conversion). This effect would be more relevant at increasing pressures, discarding this approach.

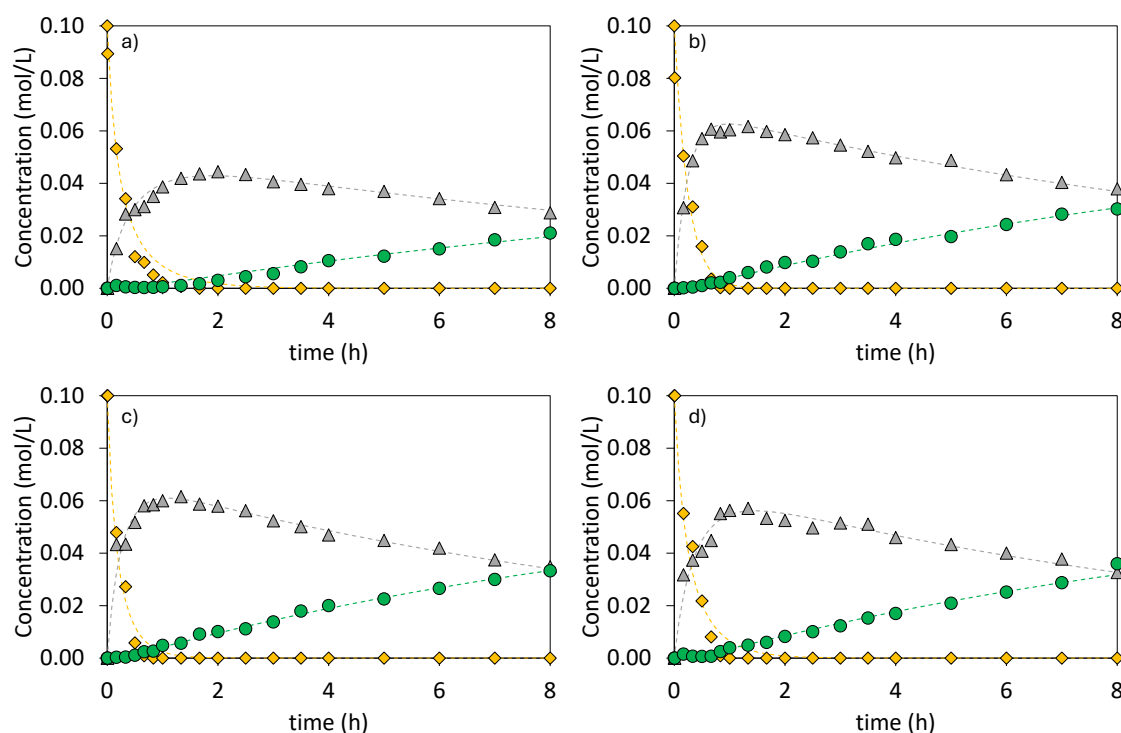


Figure 4.78. Temporal evolution of all the compounds involved in the HMF oxidation as a function of pressure at 80 °C and 4:1 ratio NaOH:HMF. Legend: (a) 15 bar, (b) 20 bar, (c) 25 bar, and (d) 30 bar.

Symbols: HMF (◆), HMFCFA (▲), and FDCA (●). Broken lines represent the kinetic model

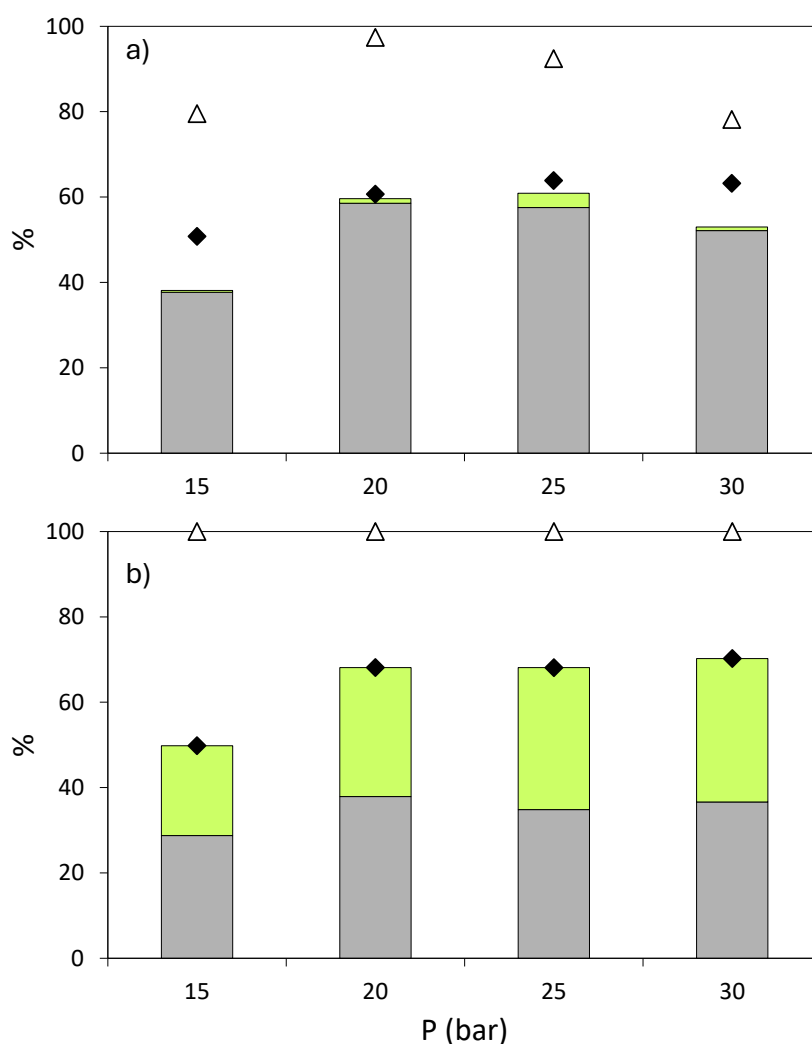


Figure 4.79. HMF conversion (Δ), carbon balance ($\blacklozenge$), and selectivity distribution (bars) obtained after (a) 0.5 h and (b) 8 h of 0.1 M HMF oxidation at 80 °C as a function of the O₂ pressures using Au/TiO₂ and a NaOH:HMF molar ratio of 4:1. Legend: HMFCa (grey) FDCA (green)

The expected evolution to the second step is observed after 8 h. The analysis of these results suggests a lower effect of O₂ pressure on the second step, and the ratio FDCA/HMFCa increases from 0.4 at 15 bar to 0.5 at 25 bar. As in the previous analysis, this trend is not observed at 30 bar, reinforcing the inhibition.

Comparing the results at 0.5 and 8 h, a slight increase in the carbon balance is observed, except when working at 15 bar: from 60.7 to 68.1%, from 63.9 to 68.4%, and from 63.2 to 70.2%, respectively. Reversible HMF adsorption is discarded as the main reason for this effect since the increase is more relevant at 30 bar, conditions at which the O₂ adsorption competes with the HMF one. Then, this fact suggests certain reversibility of the oligomers formation. The decomposition of soft humins under an oxidizing atmosphere at mild

conditions has been previously considered in the literature [84]. Thus, once there is no more HMF in the reaction medium (1 h), the HMFCa is still produced by the decomposition of these “weak” oligomers. This hypothesis is supported by several pieces of evidence, mainly at 30 bar: (1) there is no correspondence between the HMF disappearance and the HMFCa maximum, this point being displaced to 80 minutes, and (2) the total yield of HMFCa and FDCA increases with the time, suggesting a continuous incorporation of more HMFCa, and not only the transformation observed in the other cases.

To reinforce this discussion, a simplified kinetic analysis of results obtained at different pressures has been performed. The experimental results are consistent with a reaction mechanism composed of two consecutive oxidation steps, with HMFCa being the unique intermediate detected in the FDCA formation. Irreversible first-order kinetics has been observed for both successive steps. The high excess of oxygen in all the experiments (the fast stirring and the pressure excess guarantees the saturation) allows considering constant oxygen concentration in each experiment, the effect of oxygen on reaction kinetic being embedded in the apparent kinetic rate constant. With these established premises, the kinetic modelling was performed using the following mass balance equations:

$$\frac{d[HMF]}{dt} = -k_1 \cdot [HMF] - k_3 \cdot [HMF]^2 \quad [4.33]$$

$$\frac{d[HMFCa]}{dt} = k_1 \cdot [HMF] - k_2 \cdot [HMFCa] \quad [4.34]$$

$$\frac{d[FDCA]}{dt} = k_2 \cdot [HMFCa] \quad [4.35]$$

In these equations, the effect of undesired consumptions because of the HMF transformation into insoluble compounds (humins) is considered in the “ k_3 ” term, proposing a second-order reaction, which corresponds to a bimolecular process. First-order oligomerization kinetics was also evaluated, obtaining a poorer model prediction. **Table 4.21** summarizes the apparent kinetic rate constants obtained for experiments at different pressures, as well as the corresponding regression coefficients. The high values obtained (>0.98 in all the cases) indicate good correspondence between the theoretical model proposed and the experimental data. This fact is also corroborated by the good fit observed

in all the graphs including temporal profiles (Fig 4.78), the theoretical values being plotted with broken lines.

Table 4.21. Apparent reaction rate constants based on reaction mechanism for Au/TiO₂ catalyst (2 g·L⁻¹) as a function of different O₂ pressures when using 0.1 M of initial HMF concentration and a 4:1 NaOH:HMF ratio

P (bar)	k' ₁ (h ⁻¹)	k' ₂ (h ⁻¹)	k' ₃ (L·mol ⁻¹ ·h ⁻¹)	r ²
15	1.52	0.065	25.9	0.9892
20	2.76	0.080	28.3	0.9893
25	2.96	0.088	32.5	0.9913
30	1.98	0.090	25.2	0.9871

Since all the experiments were performed at the same temperature and oxygen is at large excess (close to saturation concentration), oxygen concentration can be considered as a constant at a given pressure. However, this concentration increases as operation pressure increases, allowing to correlate reactivity trends with oxygen concentration. The significant differences observed corroborate the role of this reactant, with different impacts in three evaluated reactions. Thus, each apparent kinetic constant can be expressed as a function of the oxygen concentration according to this expression, estimating oxygen concentration with the Henry law for the oxygen-water system:

$$k_i = k'_i \cdot [O_2]^n \quad [4.36]$$

The linearization of this expression is shown in **Figure 4.80**. The value of k₁ obtained at 30 bar was excluded from this analysis since experimental results demonstrate an inhibition effect of the oxygen adsorbed when working at so high pressure, shielding the effect on the reaction rate.

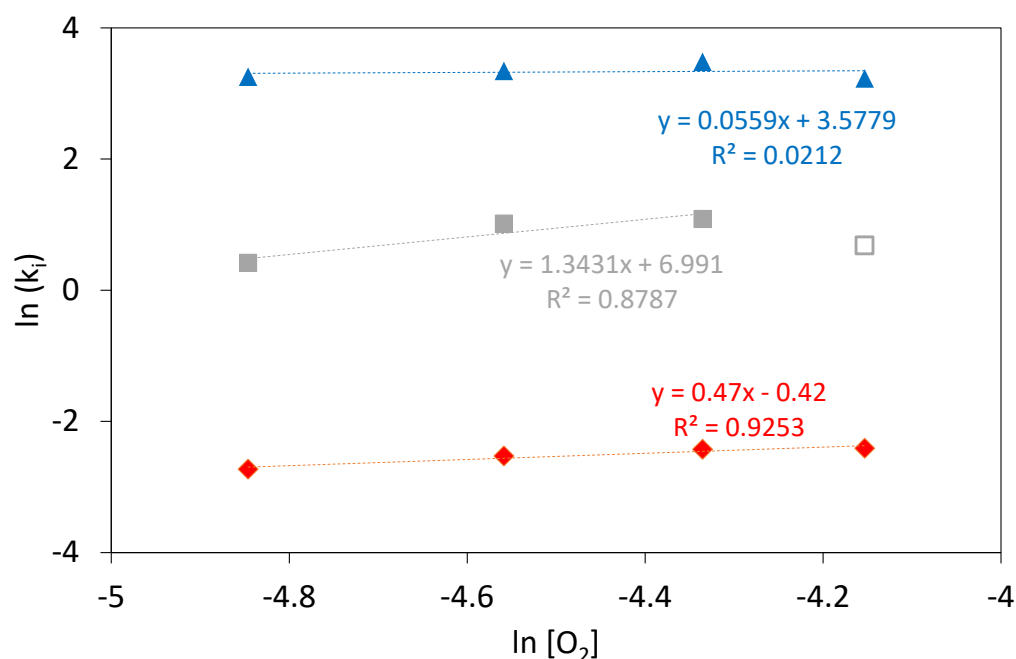


Figure 4.80. Evolution of kinetic constants with the O_2 when performing the HMF oxidation with $2 \text{ g} \cdot \text{L}^{-1}$ of Au/TiO_2 at 80°C with a NaOH:HMF ratio of 4:1. Legend: (■) k_1 ; (♦) k_2 ; (▲) k_3

Results indicate a more relevant effect of the oxygen in the first step of the reaction (HMFCFA formation), whereas the HMFCFA oxidation is less sensitive to oxygen concentration. Considering the few points available for fitting the first step (complete conversion in 1 h), the kinetic order of the second step (0.5) is considered more robust than the corresponding one for the first step (1.3 which could correspond to a real 1.5). In both cases, the oxygen adsorption and subsequent dissociation seem to be relevant, explaining these reaction orders. As suggested in the discussion of experimental results, a negligible role of oxygen in the humins formation is demonstrated. The intrinsic kinetic rate values obtained ($k_1 = 1090 \text{ L}^{1.5} \cdot \text{mol}^{-1.5} \cdot \text{h}^{-1}$; $k_2 = 0.66 \text{ L}^{0.5} \cdot \text{mol}^{-0.5} \cdot \text{h}^{-1}$; and $k_3 = 36 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$) are in good agreement with the literature [85, 86]. Thus, the first step is significantly faster than the second one, being promoted by NaOH (the direct comparison is not possible because of the different kinetic orders).

4.5.3. Influence of NaOH and 5-hydroxymethylfurfural concentration

Results at different pressures and temperatures suggest that longer times could improve the FDCA yield. However, longer times could increase the complexity of humins, resulting in heavy compounds insoluble even at high pH values. This fact is a potential

inconvenience that discourages this option, highlighting the importance of optimizing other operating conditions that may prevent the original formation of these humins.

Strategies to reduce their formation require analyzing the effect of working at different initial HMF concentrations (in good agreement with the second reaction order of the humins formation step, reducing the HMF concentration could decrease the relative weight of their formation) or NaOH:HMF ratios (a relevant effect would suggest that humins formation is homogeneously catalyzed). The effect of the HMF concentration has been studied considering two reactions with lower initial HMF concentration (0.05 and 0.01 M) but keeping constant the NaOH:HMF ratio (4:1). This study was performed at 80 °C and under 25 bar of O₂. Temporal profiles are detailed in **Figure 4.81**.

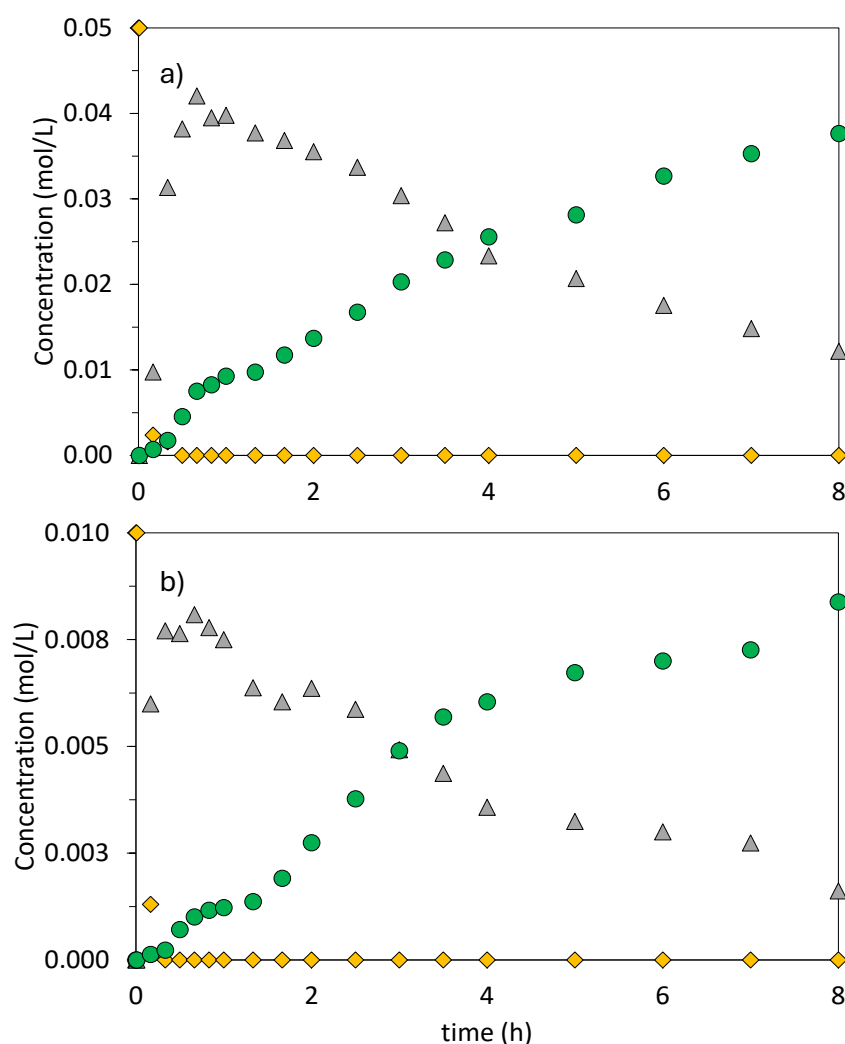


Figure 4.81. Temporal evolution of all the compounds involved in the HMF oxidation at 25 bar, 80 °C, and 4:1 ratio NaOH:HMF as a function of HMF concentration. Legend: (a) 0.05M HMF, and (b) 0.01M HMF. Symbols: HMF (◆), HMFCa (▲), and FDCA (●)

As anticipated, total HMF conversion was reached at shorter times, after 30 and 20 minutes, respectively, times that correspond to the maximum HMFCFA. Longer times are required to transform this intermediate into the FDCA, obtaining a continuous increase and final yields after 8 h of 75.3% and 83.8%, respectively, see **Figure 4.82**.

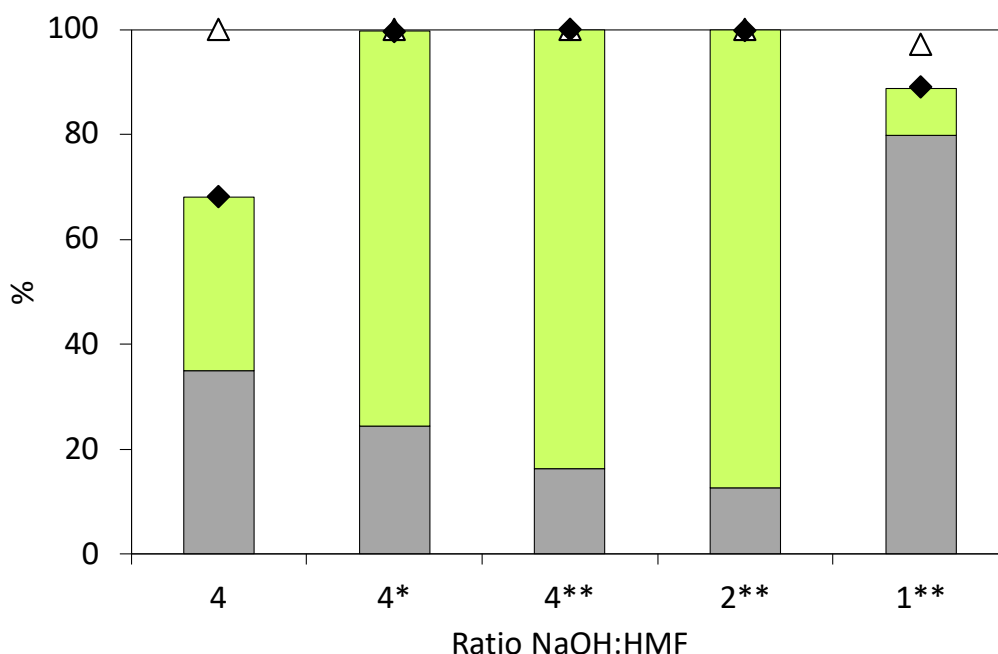


Figure 4.82. HMF conversion (Δ), carbon balance ($\blacklozenge$), HMFCFA selectivity (grey bars), and FDCA selectivity (green bars) obtained after 8h of HMF oxidation at 80 °C over Au/TiO₂ (2 g·L⁻¹) with 25 bar of O₂ as a function of the NaOH:HMF ratio. (*) initial HMF concentration 0.05 M; (**) initial HMF concentration 0.01M. Base case (4): 80 °C, 25 bar, 0.1 M of HMF and NaOH:HMF 4:1

The most relevant result of this study is the total disappearance of humins, with carbon balances higher than 99.7% during all the experiments. This fact is congruent with a predominance of oxidation over oligomerization at diluted conditions (higher oxygen/HMF ratios), promoting oxidative pathways. In the same way, lower HMF concentrations also lead to lower humins formation (second-order dependence).

Based on these results, the role of NaOH in promoting the humins is clear. However, the literature indicates that an alkaline pH is required to promote oxidation stabilizing the intermediates. Considering that the use of alkaline solutions is against the Principles of Green Chemistry because of the wastewater generated, the possibility of reducing the excess of NaOH is considered a good practice. For this study, an initial concentration of HMF of 0.01M was used, due to the maximum FDCA yield obtained with these diluted conditions. Temporal

profiles working with 4:1, 2:1, and 1:1 ratios (values that correspond to initial pH of 14, 14, and 10, respectively) are plotted in **Figure 4.83**, whereas results after 8 h are summarized in Fig. 4.82 for a better comparison.

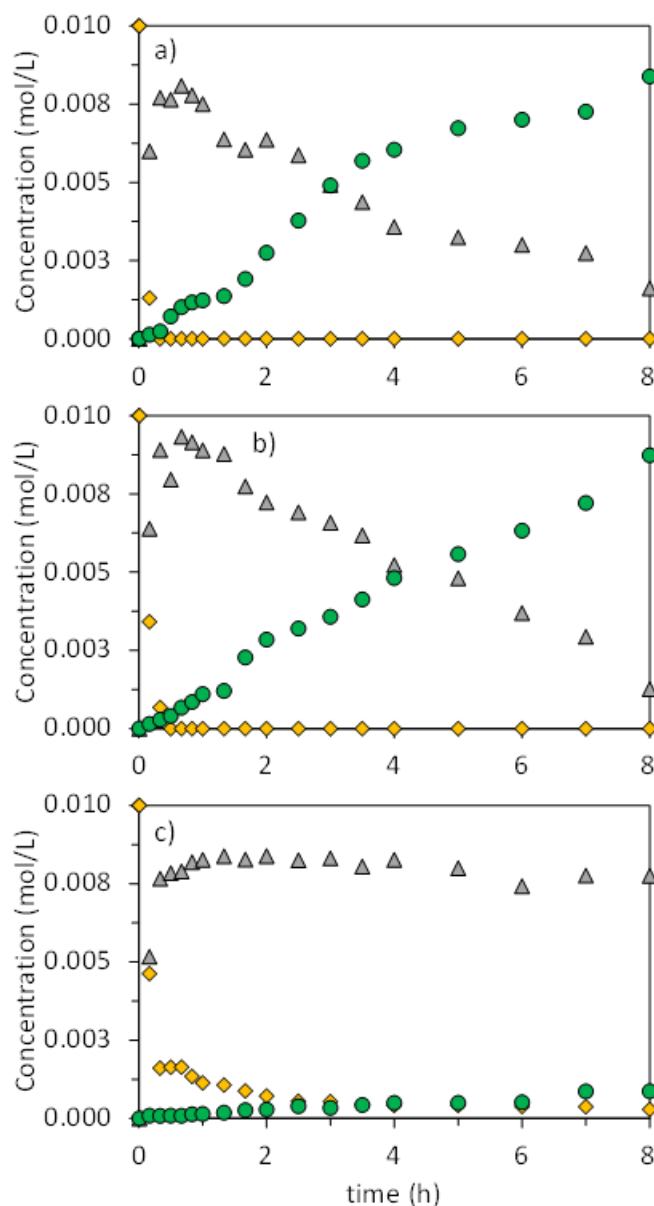


Figure 4.83. Temporal evolution of the compounds involved in the HMF oxidation as a function of NaOH concentration over Au/TiO_2 ($2 \text{ g} \cdot \text{L}^{-1}$) at 25 bar O_2 , 80 °C, and 0.01M HMF. Legend: (a) 0.04M, (b) 0.02M, and (c) 0.01M. Symbols: HMF (◆), HMFCa (▲), and FDCA (●)

In terms of the HMF evolution, a negligible effect of reducing the NaOH excess from 4:1 to 2:1 is observed, with total conversion in 20 minutes. However, working with equimolar amounts of both compounds significantly reduces the HMF oxidation rate, requiring more than 3h to obtain more than 90% of conversion. Even after 8h, traces of HMF are detected

(97% of conversion). HMFCa and FDCA are the only compounds detected, discarding a different mechanism because of the different pH. At 2:1 condition, the carbon balance remains close to 100% during all the reactions, and more than 87% of FDCA is reached after 8h. On the contrary, at 1:1, the low basicity prevails in the second oxidation step, HMFCa being the main product detected (80% after 8h). At these conditions, there is a soft but continuous decrease in the carbon balance, with final values of 89%. This result could be explained by the permanent adsorption of HMFCa or FDCA on the catalytic surface because the pH is not alkaline enough to promote their desorption.

Based on these results, 80 °C and 25 bar of O₂, working with an initial HMF concentration of 0.01M and a NaOH:HMF ratio of 2:1 are defined as the optimal conditions when using pure HMF as a reactant. However, isolating HMF from sugar hydrolysis is quite complex because of the high HMF reactivity that promotes its rehydration into levulinic and formic acid. Considering this bottleneck, the possibility of integrating as a one-pot reaction the hydrolysis and oxidation was evaluated. It is expected that promoting the HMF oxidation limits its degradation. Obtaining good results in this approach could imply a relevant improvement in the economic feasibility of the process, considering the cost savings derived from the one-pot configuration.

4.5.4. One-pot synthesis of 2,5-furandicarboxylic from fructose

Fructose is used as the model sugar to evaluate the one-pot configuration. This sugar is present in biomass, can be obtained from cellulose through hydrolysis and inversion reactions, and is the direct precursor of HMF. There are many references analyzing the dehydration of fructose to obtain HMF, mainly using HCl as a catalyst [1, 4, 87]. Based on our previous studies, a one-pot approach is proposed considering a first step under dehydration conditions of 3 h (time at which the maximum HMF was reached) [4]. After 3h at 120 °C under an inert atmosphere (20 bar of N₂), a solution of NaOH was added to the reaction medium to neutralize the previous acidic conditions and to reach a 2:1 theoretical ratio (based on the expected HMF concentration). In this solution, the required amount of Au/TiO₂ was suspended to guarantee the presence of Au nanoparticles required to promote the oxidation. The temperature is then decreased to 80 °C, introducing an oxidizing atmosphere of 25 bar of O₂. The main results are summarized in **Figure 4.84**.

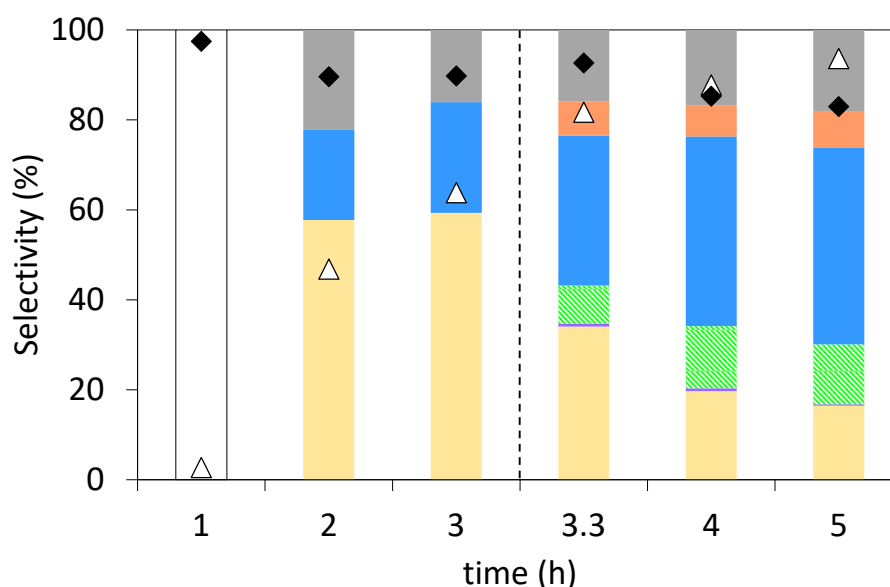


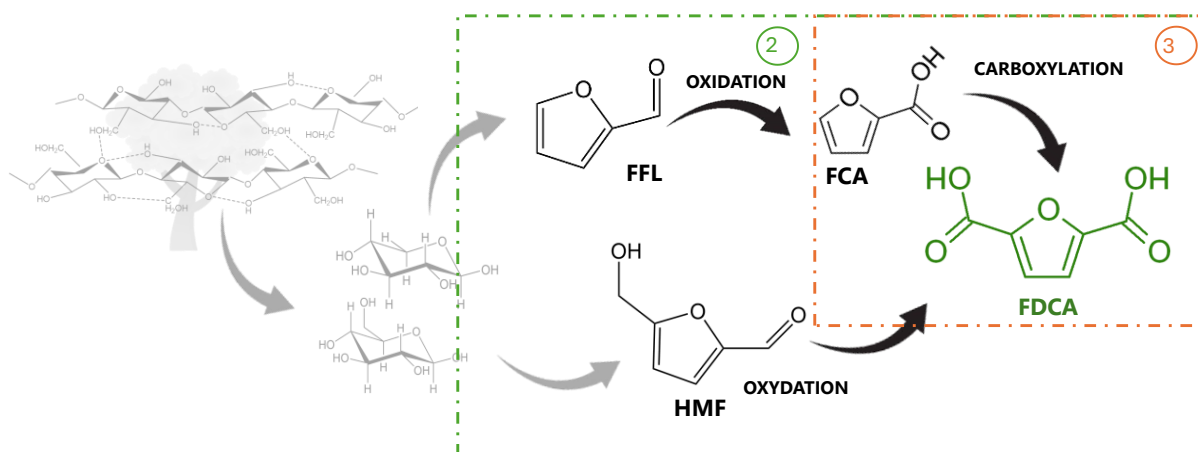
Figure 4.84. Fructose conversion (Δ), carbon balance ($\blacklozenge$), and selectivity distribution of products obtained in dehydration of fructose combined with oxidation of HMF. Legend: HMF (yellow), HMFA (purple), FDCA (dashed green), LA (blue), FA (orange), and others (grey). The broken line indicates the change from dehydration to oxidation conditions

After 1h, there is a total correspondence between fructose conversion and carbon balance closure (2.7% and 97.5%). However, no products in the liquid phase were detected, suggesting a partial fructose oligomerization. After 3 h (still under hydrolytic conditions), fructose conversion reaches 64% and HMF is obtained with more than 59% selectivity. This time was chosen to switch to oxidizing conditions since levulinic acid is already obtained with 25% of selectivity and longer times are expected to increase this value. The carbon balance at this point is 90%, which is congruent with the lack of signal of formic acid (the acid that is simultaneously produced with levulinic acid). It is suggested that this acid could be decomposed or incorporated into the sugar oligomer's structure as a part of the humins precursor.

Once under oxidizing conditions, only traces of HMFA are observed (selectivity lower than 1% during all the reaction), but the total oxidation is observed, yielding 14% of FDCA after 4 h. Longer times do not improve this selectivity because of the formation of levulinic and formic acids, reaching up to 44% and 9%, respectively. The effect of high pH promoting levulinic acid formation has been previously reported in the literature [1].

The kinetic model proposed for HMF oxidation does predict FDCA concentration obtained in the one-pot experiment (0.014 mol/L vs. 0.012 mol/L, theoretical vs. experimental value), with quite good correspondence during all the reactions. However, relevant differences are observed when comparing expected and experimental values for HMF and HMFCa. On the one hand, the kinetic model predicts total HMF conversion, whereas experimental data demonstrate a significant HMF concentration due to the continuous incorporation of more HMF by fructose dehydration. In addition, the kinetic model predicts a stream enriched in the HMFCa intermediate, whereas this compound is negligible in the real sample. This result indicates a different interaction between the reactants (HMF and oxygen) and the catalyst, promoting the step less sensitive to the oxygen adsorbed (HMFCa oxidation to FDCA). This fact could be explained by the high salinity obtained when neutralizing the initial HCl and possible interaction with the oxidizing catalyst, by the interaction of fructose and primary derivatives with the active phase, or by a different nature of the fructose-derived humins leading to a more severe deactivation.

According to these results, the one-pot fructose hydrolysis and HMF oxidation process is feasible, but the optimum conditions proposed for HMF oxidation are not applicable in this system, requiring a particular study to maximize the FDCA yield, promoting the first oxidation step and reducing the relevance of levulinic acid production.



4.6. OXIDATION OF HMF/FURFURAL MIXTURES TO FURANIC ACIDS OVER Au/TiO₂ AND FUROIC ACID CARBOXYLATION

From the perspective of industrial implementation of lignocellulosic biomass waste utilization, the study of simultaneous HMF and FFL oxidation has a key role since both compounds are simultaneously produced by acid hydrolysis. Thus, developing an oxidation process involving both platform molecules would have a positive impact on the total system reducing the purification requirements. Results discussed in previous sections suggest the use of oxygen as a reductant (higher control on the reaction), at 80°C and 1 wt% Au/TiO₂ as the catalyst, but also indicate that optimum conditions to obtain furoic acid are different from those required to produce FDCA. Thus, a system considering the simultaneous valorization of both aldehydes needs a specific optimization, considering the high polymerization and decomposition trend of HMF (NaOH is required to minimize both aspects) as well as the intermediate reactive character of furoic acid and the subsequently expected negative effect of too severe conditions.

Based on these premises, the simultaneous oxidation of both aldehydes in the presence of NaOH is studied at 30 bar of O₂, using Au/TiO₂ as the catalyst. For the quantitative analyses of these results, carbon balance, conversions, and selectivities are calculated in two ways: (1) independently since there are not common compounds that can be obtained from both routes according to equations 4.29-32 and (2) carbon balances and selectivities are also

calculated considering the total moles converted from both reactants according to equations 4.37-38.

$$S_i (\%) = \frac{n_j \cdot C_j}{6 \cdot (C_{HMF,0} - C_{HMF,t}) + 5 \cdot (C_{FFL,0} - C_{FFL,t})} \cdot 100 \quad [4.37]$$

$$C.B. (\%) = \frac{\sum(n_j \cdot C_j)}{6 \cdot (C_{HMF,0} - C_{HMF,t}) + 5 \cdot (C_{FFL,0} - C_{FFL,t})} \cdot 100 \quad [4.38]$$

where " n_j " and " C_j " are the number of carbons and the molar concentration of each compound involved in mixtures oxidation; $C_{HMF,0}$ and $C_{FFL,0}$ are the initial concentrations on each reactant, and $C_{HMF,t}$ and $C_{FFL,t}$ are the concentration at each time point considered.

For individual oxidation, two different configurations were considered: buffer solutions for furfural, and high basicity for HMF. This second route is proposed for mixtures since FDCA (final compound of HMF oxidation) has a very low solubility in neutral pH. Moreover, the presence of furfural in the solution would decrease the pH, with a significant reduction in the FDCA solubility. Optimum results with HMF suggest using a NaOH concentration of 0.02M. In this case, a higher excess is proposed (0.03M) considering the possible partial neutralization due to the furfural and acids obtained, as well as to ensure that furfural oxidation is performed through a Cannizzaro mechanism, avoiding the complex mixture of intermediates that would be obtained if both mechanisms take place simultaneously.

Before considering the catalytic system, a blank test was carried out at 80°C and 30 bar of O₂ in an aqueous solution using initial concentrations of FFL and HMF of 0.01 M, and 0.03 M NaOH. No products were detected. However, the carbon balance closure decreased to 81% after 8 hours of reaction obtaining a conversion of HMF and FFL of 23 and 12 %, respectively. These results are congruent with an uncontrolled degradation of both compounds into humins, in good agreement with results indicated by previous literature [81, 88]. Comparing these results with the previous blank experiment performed with HMF (see page 224), a significant decrease in HMF oligomerization was observed. This fact can be due to the lower basicity of this test (0.03M NaOH for mixtures, 0.4M NaOH for HMF) or by a positive effect of furfural reducing the oligomerization trend. In any case, a promoted

polymerization by the copresence of both aldehydes is discarded, and humins seem to be produced by the individual polymerization of any reactant.

4.6.1. Influence of furfural and HMF concentration in oxidation of mixtures

Real mixtures obtained from biomass hydrolysis can yield different HMF:FFL ratio as a function of different parameters, including the initial cellulose/hemicellulose ratio in the biomass, as well as the hydrolysis conditions (furfural is a stable compound whereas HMF could be degraded into levulinic and formic acid if time, temperature and acidity is not perfectly controlled). Trying to evaluate possible real situations in which different HMF:FFL ratios could be obtained; first analyses were conducted at different aldehyde ratios. This study is also useful to identify possible inhibition effects, determining the optimum ratio to carry out simultaneous partial oxidation. Experiments were performed with a constant NaOH concentration of 0.03 M with HMF:FFL ratios from 1:1 to 2:1. The different ratios also affect the total organic concentration, from 0.02 M in 1:1 reaction to 0.03 M in 2:1 and 1:2 experiments. As a typical example of the results obtained, the temporal profile of the reaction at ratio 1:2 HMF:FFL is illustrated in **Figure 4.85**. This ratio corresponds to the most common ratio obtained in hydrolysis [89 -91].

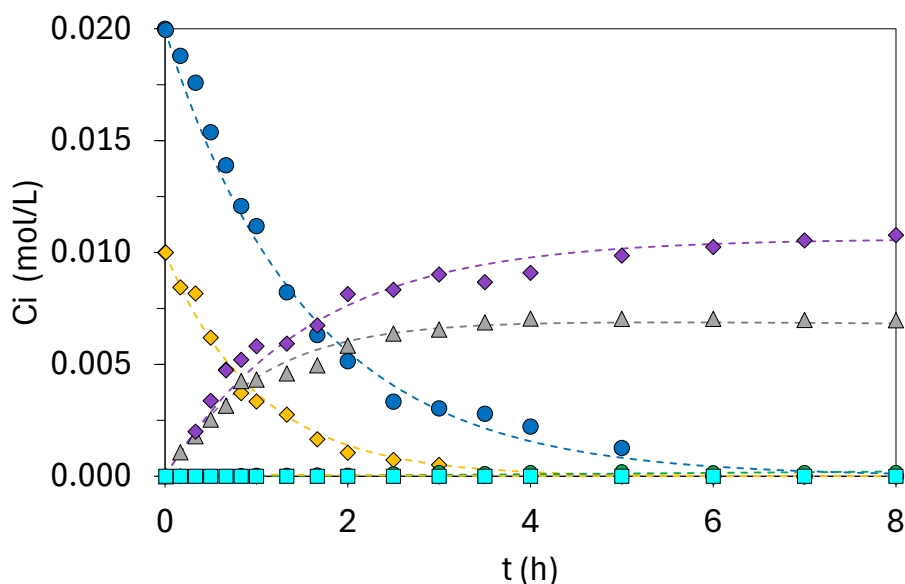


Figure 4.85. Temporal evolution of the compounds involved in the HMF:FFL mixture oxidation at ratio HMF:FFL 1:2, 0.03M NaOH, 30 bar of O₂ and over Au/TiO₂ (2 g·L⁻¹). Symbols: HMF (◆), HMFA (▲), FDCA (●), FFL (●), FCA (◆), and FOH (■)

Regarding HMF, total conversion is observed after less than 4 h, obtaining a continuous and soft increasing trend of the reaction intermediate HMFCa. This compound represents 23% of global selectivity in the final mixture after 8 h (humins are also considered in this result since the selectivity is calculated as the concentration of the target compound divided by the total moles of reactants converted, see Eq.37). This value corresponds to 69.7% of the HMF converted. Based on these results, it could be concluded that HMF oxidations compete with its oligomerization, i.e., humins formation (final partial carbon balance of 71.8%). FDCA is only observed in traces (0.7% of global selectivity, 2% of partial one). An individual experiment with only HMF and NaOH was performed to identify if reaction conditions do not allow the FDCA oxidation or if the FDCA production is inhibited by the presence of furfural or any of its acid derivatives. The temporal profile of this reaction is included in **Figure 4.86**.

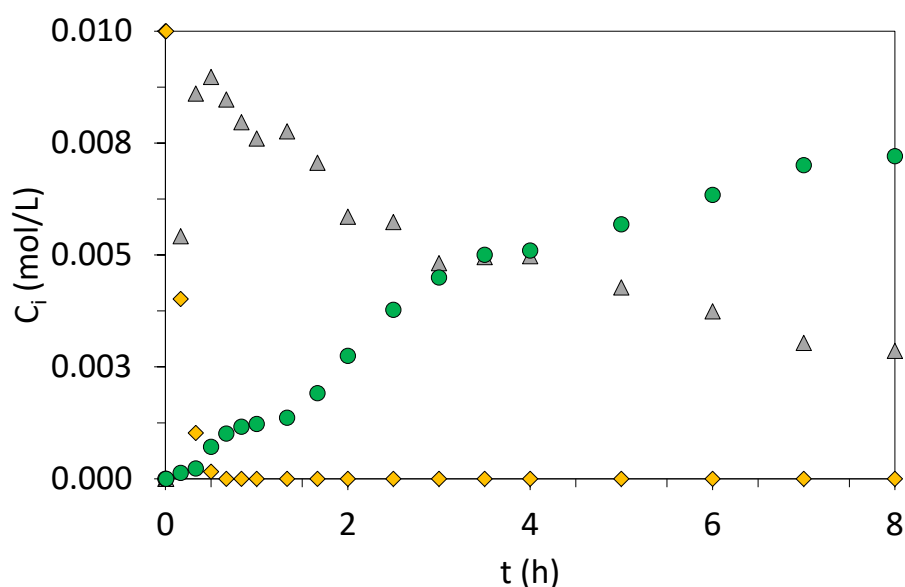


Figure 4.86. Temporal evolution of the compounds involved in the individual HMF oxidation 80°C and 30 bar of O₂ over Au/TiO₂ (2 g·L⁻¹). Symbols: HMF (◆), HMFCa (▲), FDCA (●)

In this reaction, HMFCa follows the typical behavior of a reaction intermediate, reaching its maximum in selectivity at short times (0.5 h), observing a marked decreasing trend because of its oxidation into FDCA. The comparison between both profiles (HMF and HMF:FFL mixture) allows concluding that (1) furfural and HMF oxidations are competitive reactions because the HMF conversion is significantly slower in presence of furfural, and (2)

this inhibition is more marked in the second step of the HMF oxidation, affecting the production of the target FDCA.

As to furfural, complete conversion is reached after 7 h, only observing the FCA as the direct product. This compound has a continuous increasing trend to reach 36% of global selectivity (61% of the organics in the liquid phase). The partial analysis of the furfural route indicates that this concentration corresponds to 53.9% of the furfural converted. According to the Cannizzaro mechanism, furfuryl alcohol is expected to be formed in equimolar quantities than furoic acid. The negligible concentration of this compound during all the experiment could be justified by its reoxidation into furfural and the high polymerization trend of this alcohol. Both reactions are favored by basic conditions and the availability of O₂, as indicated in the literature [92]. The reoxidation of furfuryl alcohol into furfural would result in an enrichment in furoic acid in the final mixture. Thus, the low increase over equimolar production (from 50 to 54%) experimentally detected suggests a high relevance of oligomerization (humins formation) and an almost negligible role of the reoxidation, at least in these conditions. The high polymerization trend of furfuryl alcohol has been previously reported in the literature [93,94].

However, reoxidation cannot be discarded since, as shown in **Table 4.22**, the partial FCA selectivity (only considering the mass balance to C₅ adducts) increases to almost 100% when reducing the furfural excess from 1:2 to 2:1 (HMF excess). This high selectivity can only be obtained if reoxidation prevails over oligomerization. Thus, both decomposition steps coexist in these reactions, with a different relative weight as a function of the aldehydes ratio.

Table 4.22. Carbon balance of C₅ and C₆ oxidation routes and partial selectivities obtained at different HMF:FFL ratios for FCA, HMFCa, and FDCA after 8h reaction at 0.03M of NaOH

HMF:FFL	X _{FFL} (%)	X _{HMF} (%)	S _{FCA} (%)	S _{FOH} (%)	S _{HMFCa} (%)	S _{FDCA} (%)	C.B. C ₅ (%)	C.B. C ₆ (%)	C.B. (%)
2:1	100	81.3	99.8	0	55.5	18.4	99.8	63.8	84.1
1:1	66.9	100	97.5	47.2	29.7	3.1	130	32.9	79.3
1:1.5	100	100	71.9	0	58.9	1.8	71.9	65.3	65.6
1:2	100	100	53.9	0	69.7	2.0	53.9	71.8	60.7

Concerning the HMF oxidation, complete conversion is obtained in all cases with the only exception of 2:1, in which HMF is in clear excess. Working with a ratio HMF:FFL 1:1, HMF reaches complete conversion after 5h, while in the ratio 1:1.5 and 1:2, full conversion is achieved after 3 h. These evolutions are congruent with the lower concentration of HMF in these configurations. FDCA selectivity increases with the increase in HMF, reaching its maximum at 2:1 ratio, with a partial selectivity close to 20%. This fact suggests that higher FFL concentration limits the oxidation of HMFCa possibly due to a competitive adsorption of both aldehydes on the same type of active sites, prevailing the furfural one.

The low C6 carbon balances (<72%), linked to HMF oxidation, indicate a high relevance of polymerization in this route. The temporal profile of C6 carbon balance indicated a continuous decrease with time, reaching constant values once achieving complete HMF conversion. This fact suggests that HMF is the main humins precursor in this route. Levulinic acid or formic acid are not detected, discarding the decomposition of this compound into these acids. C5 polymerizations cannot be discarded but, in this case, they are less relevant than the HMF ones and mainly promoted by furfuryl alcohol. Furfural oligomerization is almost negligible, as indicated by quantitative formation of furoic acid in 2:1 reaction. As the relative weight of furfural in the initial mixture increases, the carbon balance decreases, but the correspondence between furfural conversion and furoic acid production remains constant, and the carbon balance shows a soft but continuous decrease even after reaching total furfural conversion. This effect indicates that products are the main humins precursors and not the furfural.

Equimolar conditions (1:1) represent a particular case in this discussion. The C5 partial carbon balance reaches an unexpected value of 130% after 8 h (values over 100% after 30 min, reaching a maximum of 140% after 4h, with a soft decrease at longer times). The inconsistent partial C5 carbon balance and the low C6 one suggests that part of the C6 compounds decompose into C5 ones (global carbon balance 79.3%). On the other hand, and only in these conditions (1:1), furfuryl alcohol is detected in relevant amount during all the reaction, suggesting a particular synergetic effect of this ratio of aldehydes that stabilizes this side compound (negligible concentration of this compound at other HMF:FFL ratios). Moreover, the partial selectivity of furfuryl alcohol evolves from almost 100% (i.e., the concentration of this compound corresponds to the total amount of furfural converted) to 47% (close to the

theoretical amount predicted by the Cannizzaro mechanism). This profile suggests that Cannizzaro route competes with another mechanism in which furfuryl alcohol is independently produced. This mechanism is expected to require the copresence of both reactants since the preferential adsorption of any of them (rest of aldehydes ratio studied) shields it. A possible option is a Meerweing-Ponndorf-Verley & Oppenover (MPV-O) mechanism for which the alcohol group of HMF reacts with the carbonyl group of furfural, producing a rearrangement that yields furfuryl alcohol and 2,5-diformylfuran (DFF). This reaction has been proposed in the literature, highlighting the high selectivity obtained at soft conditions (this reaction is performed at 80°C) in presence of acid catalysts [95]. In the presence of metal and basic catalysts, the reaction is possible but significantly slower, which justifies that it is relevant only when both aldehydes are simultaneously adsorbed on the catalytic surface [96, 97]. This double aldehyde suffers an oxidative decarbonylation, yielding FCA and releasing CO₂. The reaction mechanism is plotted in **Figure 4.87**. The final effect of these two steps is the accumulation of C₅ compound, as well as an increase in the FCA and furfuryl alcohol production. Although furfuryl alcohol reoxidation and oligomerization are still relevant, the high amount of this alcohol produced at these conditions justifies that this compound is detected in the liquid phase.

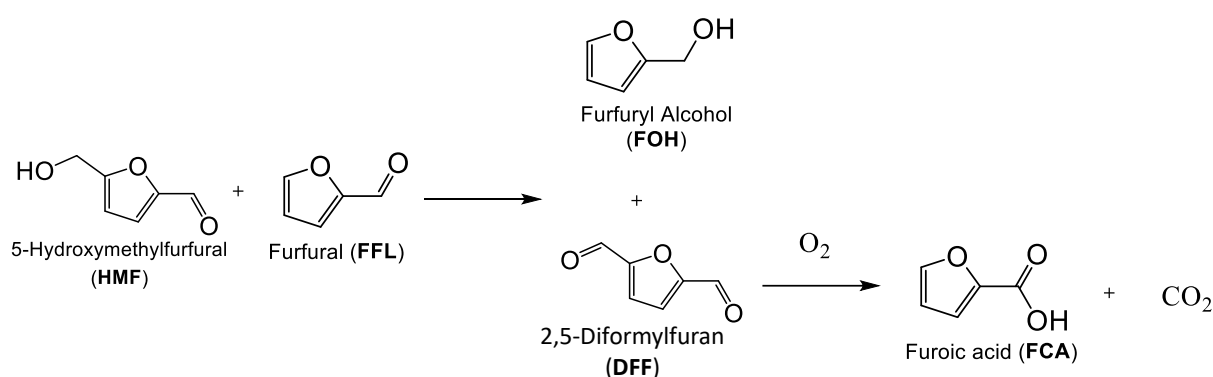


Figure 4.87. Scheme of MPV-O and oxidative decarbonylation mechanism proposed for the simultaneous conversion of HMF and FFL

Based on these conclusions, the 1:1 HMF:FFL ratio is identified as a particular case in which the interaction between both aldehydes is the maximum one, affecting the reaction mechanism and producing an enrichment in the C₅ oxidation compounds. Globally, these results demonstrate that the HMF:FFL ratio significantly influences the reaction mechanism, and conclusions obtained in individual studies cannot be directly extrapolated to mixtures.

The oxidation of these aldehydes into acids with the subsequent production of protons is expected to affect possible adsorptions and oligomerizations, with a clear impact in the reaction mechanism. Based on this hypothesis, the influence of the amount of NaOH was analyzed.

4.6.2. Influence of NaOH concentration in mixtures oxidation

With the aim to identify if the basicity of the reaction medium influences the reaction results, experiments with 0.02 and 0.04 M of this compound were performed, using 1:1 and 1:2 as HMF:FFL ratios. These conditions were chosen, not because of being identified as the best ones in the previous experiments (mixtures enriched in HMF produce more FCA and FDCA) but because they better represent the expected concentration obtained in a real hydrolysis of soft biomass. Remarkable results for different basicity tests are summarized in **Table 4.23**.

Table 4.23. Carbon balance of C₅ and C₆ oxidation routes and partial selectivities obtained at different NaOH concentrations tested for FCA, HMFCA, and FDCA after 8h reaction

C _{NaOH} (M)	HMF:FFL	X _{FFL} (%)	X _{HMF} (%)	S _{FCA} (%)	S _{FOH} (%)	S _{HMFCA} (%)	S _{FDCA} (%)	C.B.C ₅ (%)	C.B.C ₆ (%)	C.B. (%)
0.02	1:1	63.6	100	70.8	91.9	29.7	0.7	139.9	30.4	80.2
	1:2	89.0	100	63.9	0	42.5	0.7	67.9	43.3	58.1
0.03	1:1	66.9	100	97.5	47.2	29.7	3.1	130	32.9	79.3
	1:2	100	100	53.9	0	69.7	2.0	53.9	71.8	60.7
0.04	1:1	100	100	93.3	24.1	63.6	5.6	109.2	69.2	99.1
	1:2	100	100	99.6	0	61.2	31.1	99.6	88.7	95.5

Complete HMF conversion was obtained in all cases, requiring shorter times to reach it as the basicity increases (from 8 h working with 0.02 M of NaOH to 2 h when doubling the NaOH concentration). On the other hand, furfural requires a minimum of basicity to disappear completely, with conversions lower than 70% when working with less than 0.04 M. Considering the excess of furfural in 1:2 reaction, higher conversion of this aldehyde would be expected when working at 1:1. However, experimental results contrast to this theoretical

analysis, and conversion at 1:2 ratios are higher than when working in equimolar conditions, nevertheless the basicity. These results support the profiles discussed in the previous subsection, discarding experimental errors. The coexistence of Cannizzaro and MPV-O mechanisms justifies this unexpected effect. Working at equimolar conditions, both aldehydes interact by a slower route, with the subsequent reduction in the net furfural consumption rate. In good agreement with this hypothesis, 1:1 corresponds to the only experiments in which furfuryl alcohol is observed in relevant amounts, reaching partial selectivities after 8 h of 92%, 55% and 24% with 0.02, 0.03 and 0.04 M of NaOH, respectively. These results support the previous hypothesis about a strong interaction between both aldehydes when working in equimolar concentration, this interaction being less relevant as the basicity increases.

As anticipated, NaOH strongly influences this reaction, not only in terms of conversion but also in the products distribution. FCA selectivity increases at increasing basicity, from 66.1 % to 93.3% when working at 1:1, and from 63.9% to 99.6% with 1:2 ratios. The same trend is observed with the FDCA, in this case with an influence significantly more marked, especially when working in 1:2 aldehyde ratio (from 0.7% to 31.1%). The basicity plays a key role in the reaction control, preventing the oligomerization and other possible secondary reactions, obtaining very high carbon balances (>95%).

Although all reactions start at pH 14, the production of different acids affects the pH, particularly in reactions with lower NaOH concentrations (0.02M and 0.03M). For instance, the 1:1:2 NaOH:HMF:FFL ratio reaches neutral pH after 1 h and continues to decrease to 6 after 8 h. The same pH is obtained when working with other aldehydes ratios, observing a softer decrease as the relative weight of HMF increases (FCA being the main responsible of this decrease). In reactions with 0.03M NaOH, the pH stabilizes after 6 hours at 7, with almost negligible effect of HMF:FFL ratio. In contrast, reactions with a higher NaOH concentration (0.04M) maintain a constant pH of 14 during all reaction time, nevertheless the aldehydes ratio used.

Considering all these aspects, the optimum configuration proposed for the simultaneous partial oxidation of HMF and FFL is 4:1:2, working with 0.04 M of NaOH, and an HMF:FFL ratio of 1:2. At these conditions, complete conversion of both reactants is achieved, yielding a high selectivity of 99.6% for FCA and 31.1% for FDCA. Humins formation is also

minimized, particularly in the C₅ pathway (99.6% carbon balance) and achieving an 88.5% carbon balance for C₆ pathway.

4.6.3. Reaction mechanism and kinetic modeling

Based on the experimental results, a reaction mechanism that evaluates the simultaneous oxidation of both biomass-derived aldehydes is proposed, fitting the experimental data to the corresponding kinetic model. According to temporal profiles obtained at different conditions, two parallel oxidations are considered as the main routes. HMF is oxidated in two consecutive steps, yielding HMFCa as intermediate and the target FDCA as the final product. On the other hand, FFL is converted to FOH and FCA by Cannizzaro reaction. Both aldehydes are humins precursors, whereas furfuryl alcohol is a quite instable compound that suffers oligomerization and can be reoxidized, yielding furfural.

In the particular case of 1:1 reaction, individual oxidations compete with rearrangement reactions by MPV-O mechanism, yielding furfuryl alcohol and DFF. This last compound suffers oxidative decarbonylation, yielding furoic acid (increase of C₅ compounds from C₆ decomposition), releasing CO₂. This reaction is only considered for reactions 1:1 because it requires a strong balance between furfural and HMF adsorption, being a negligible route in case of having excess of any of these aldehydes. This complex mechanism is illustrated in **Figure 4.88**.

The proposed mechanism is validated by fitting the temporal evolution of all compounds involved in the oxidation of mixtures under different NaOH concentrations to the corresponding mass balances (**Eq.3.39 – 44**). Since the experiments were conducted with a large excess of oxygen in the reactor (30 bar, concentration two orders of magnitude higher than the theoretical one required to complete oxidation). This excess in the gas phase as well as the strong stirring allows suggesting a continuous diffusion to the liquid phase, having a constant concentration of $3.7 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. Therefore, all the constants in the model are considered apparent constants that implicitly include the dependence on oxygen concentration.

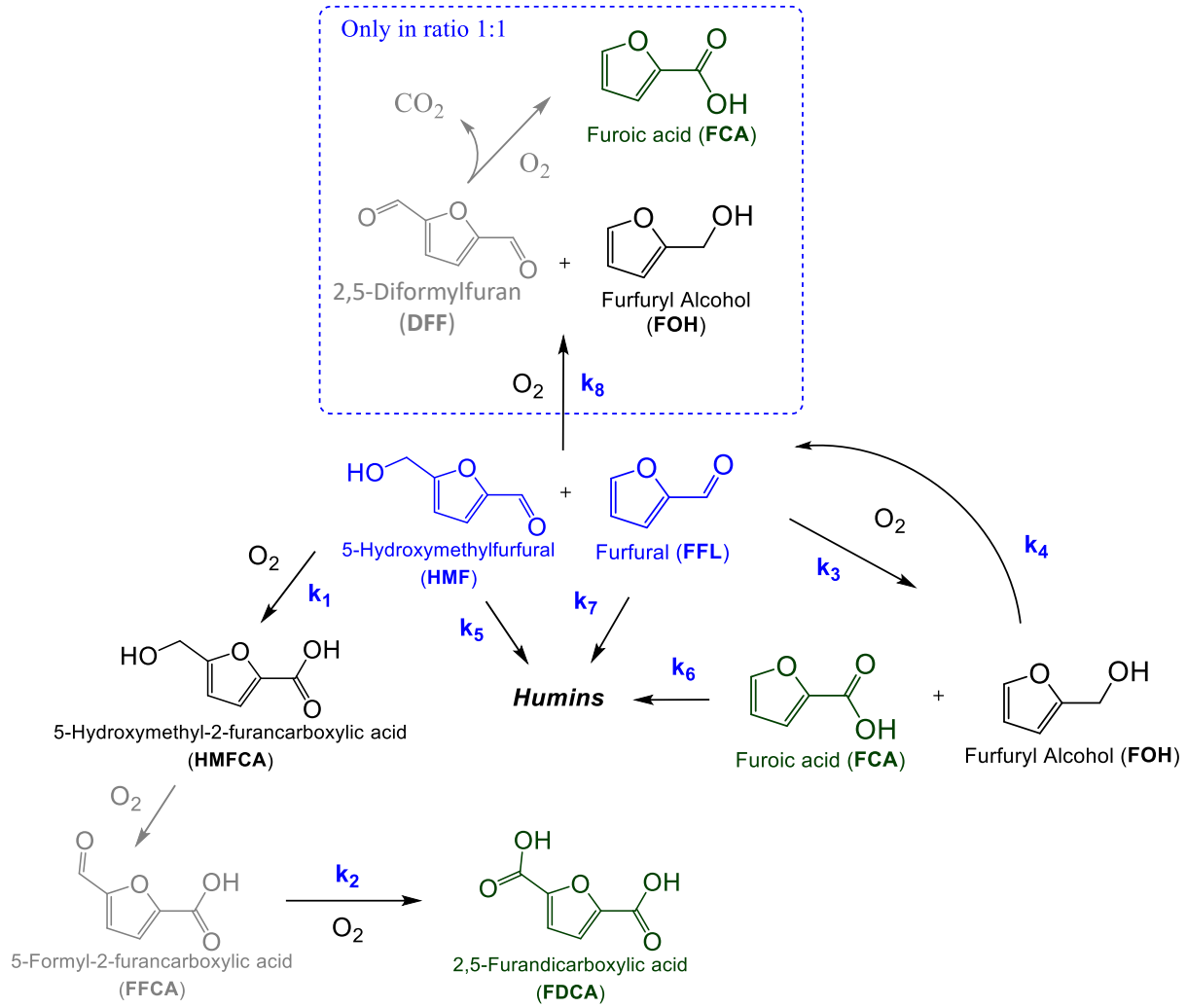


Figure 4.88. Scheme of reaction pathway for HMF and FFL mixtures oxidation in basic media.

Legend: (blue) reactants, (green) target products

$$\frac{dC_{HMF}}{dt} = -\frac{k_1 \cdot C_{HMF}}{1 + K_{FFL} \cdot C_{FFL}} - k_5 \cdot C_{HMF}^2 - \frac{k_8 \cdot C_{HMF} \cdot C_{FFL}}{1 + K_{FFL} \cdot C_{FFL}} \quad [4.39]$$

$$\frac{dC_{FFL}}{dt} = -k_3 \cdot C_{FFL}^2 + \frac{k_4 \cdot C_{FOH}}{1 + K_{FFL} \cdot C_{FFL}} - k_7 \cdot C_{FFL} - \frac{k_8 \cdot C_{HMF} \cdot C_{FFL}}{1 + K_{FFL} \cdot C_{FFL}} \quad [4.40]$$

$$\frac{dC_{HMFCA}}{dt} = \frac{k_1 \cdot C_{HMF}}{1 + K_{FFL} \cdot C_{FFL}} - \frac{k_2 \cdot C_{HMFCA}}{1 + K_{FFL} \cdot C_{FFL}} \quad [4.41]$$

$$\frac{dC_{FDCA}}{dt} = \frac{k_2 \cdot C_{HMFCA}}{1 + K_{FFL} \cdot C_{FFL}} \quad [4.42]$$

$$\frac{dC_{FOH}}{dt} = k_3 \cdot C_{FFL}^2 + \frac{k_8 \cdot C_{HMF} \cdot C_{FFL}}{1 + K_{FFL} \cdot C_{FFL}} - \frac{k_4 \cdot C_{FOH}}{1 + K_{FFL} \cdot C_{FFL}} - k_6 \cdot C_{FOH} \quad [4.43]$$

$$\frac{dC_{FCA}}{dt} = k_3 \cdot C_{FFL}^2 + \frac{k_8 \cdot C_{HMF} \cdot C_{FFL}}{1 + K_{FFL} \cdot C_{FFL}} \quad [4.44]$$

The C6-compounds mass balances are conditioned by two different catalytic reactions, the two-step HMF oxidations (k_1 and k_2) and, in case of 1:1 experiments, the simultaneous oxidation of both aldehydes (k_8). These three reactions have a first-order dependence with respect to the aldehyde. As to furfural conversion, Cannizzaro reaction follows a biomolecular mechanism, requiring two furfural molecules to produce the disproportionation. Based on this hypothesis, and according to the literature [98], a second order was considered for this step (k_3). The mass balance applied to furfuryl alcohol includes the two reactions that produce this compound (k_3 and k_8) as well as the two reactions that consume this alcohol, including its reoxidation (k_4) and oligomerization (k_6).

In all cases, first kinetic orders are proposed. The oligomerization of both aldehydes is also considered. Based on experimental results with individual compounds, a first order was proposed for the furfural oligomerization (k_7) and second order for the HMF one (k_5). FFL adsorption on metal active sites has been considered for all oxidation steps (K_{FFL}). As for Cannizzaro reaction, a disproportionation reaction that does not require oxygen and, subsequently, is not catalyzed by metal active sites, this inhibition effect by furfural adsorption is not considered. Instead, it must be conditioned by the interaction with the support (TiO_2) and the homogeneous contribution of NaOH [98]. Also, oligomerizations are not affected by FFL adsorption because they can be non-catalytic.

These orders are proposed based on the literature, previous conclusions obtained in experiments with furfural or HMF and after testing other possibilities, choosing the simplest mechanism that allow obtaining good correlations and robust kinetic rates values. **Figures 4.89-90** illustrate the temporal profiles obtained (symbols) as well as the fitted values once applying the kinetic model (dashed lines) for all conditions tested (different aldehydes ratios and different basicity).

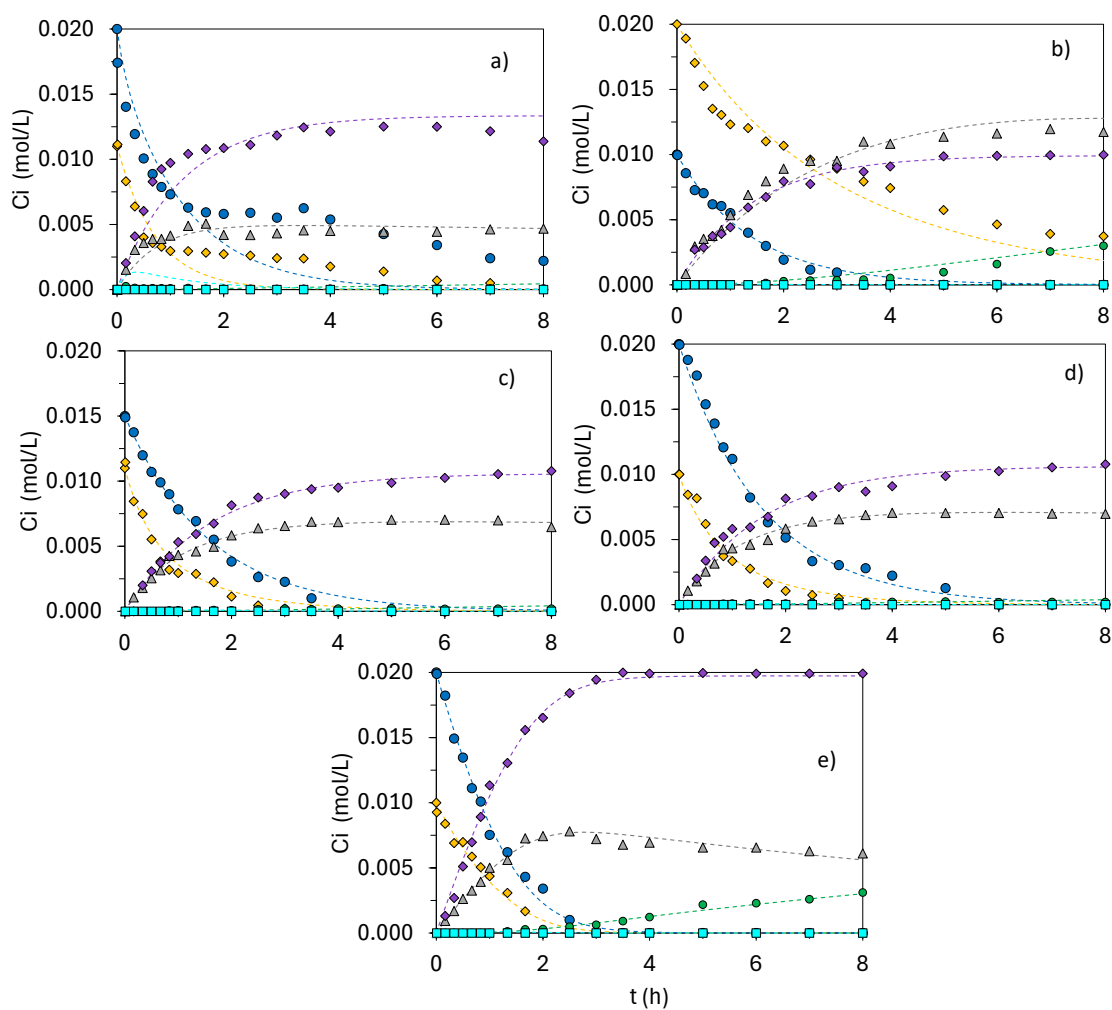


Figure 4.89. Comparison between experimental (symbols) and fit values (dashed lines) of all the compounds involved in the oxidation of mixtures as a function of reactants ratio and NaOH concentration at 80°C and 30 bar O_2 over Au/TiO_2 ($2 \text{ g} \cdot \text{L}^{-1}$). Legend HMF:FLL:NaOH: (a) 1:2:2, (b) 2:1:3, (c) 1:1.5:3, (d) 1:2:3, and (e) 1:2:4. Symbols: HMF (◆), HMFCFA (▲), FDCA (●), FFL (●), FCA (◆), and FOH (■)

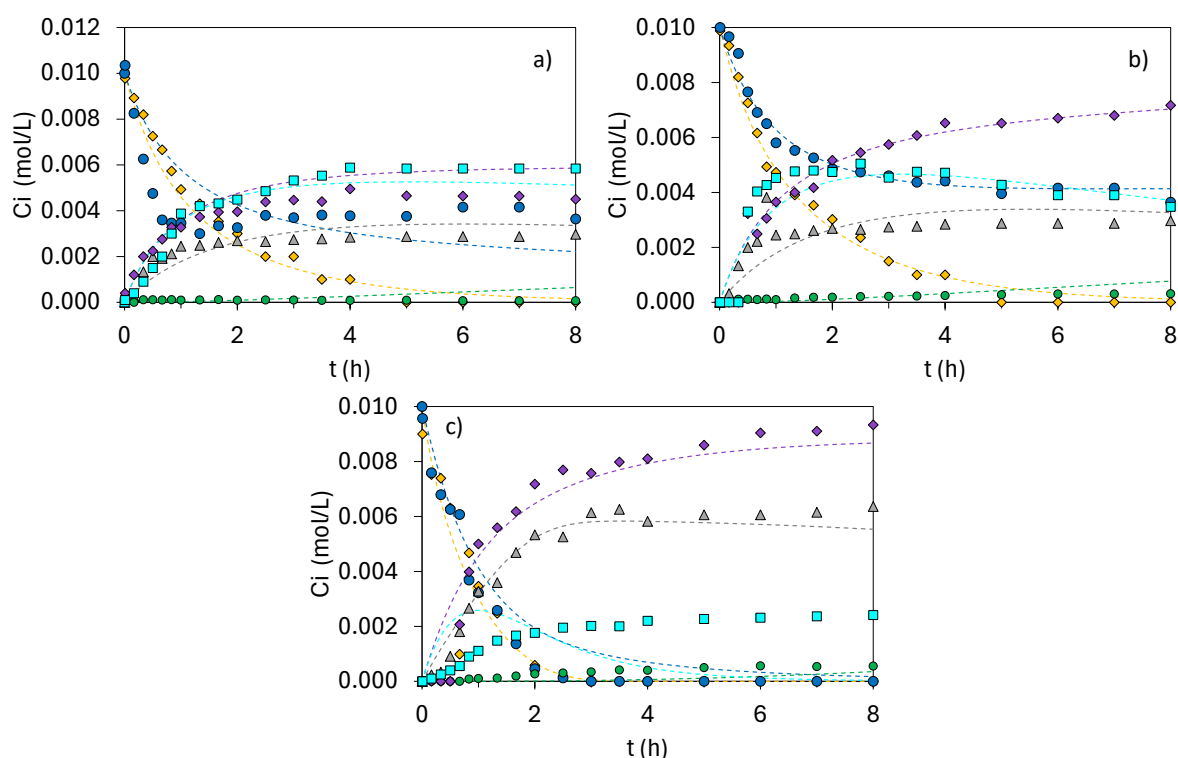


Figure 4.90. Comparison between experimental (symbols) and fit values (dashed lines) of all the compounds involved in the oxidation of equimolar mixtures as a function of reactants ratio and NaOH concentration at 80°C and 30 bar O₂ over Au/TiO₂ (2 g·L⁻¹). Legend HMF:FFL:NaOH: (a) 1:1:2, (b) 1:1:3, and (c) 1:1:4. Symbols: HMF (◆), HMFA (▲), FDCA (●), FFL (●), FCA (◆), and FOH (■)

Table 4.24 summarizes the apparent kinetic rate constants obtained as well as the corresponding regression coefficients for reactions in excess of one of the aldehydes (MPV-O mechanism not considered). The high values obtained (>0.9 in all cases) indicate good correspondence between the theoretical model proposed and the experimental data.

Results obtained when working in excess of furfural support the proposed mechanism, obtaining congruent kinetic rate values that follow an increasing trend with basicity. The goodness of this model is also verified by the close values obtained for all kinetic rate constants when, with the same basicity, different furfural excesses were tested. The 2:1 ratio is an exception to this discussion. The relevant discrepancies with respect to other reactions suggest that the MPV-O mechanism initially proposed only when working at equimolar conditions also affects this configuration.

Table 4.24. Apparent kinetic and adsorption constants for oxidation of HMF and FFL mixtures using Au/TiO₂ as a catalyst as a function of NaOH concentration

C _{NaOH} (M)	HMF: FFL	k ₁ (h ⁻¹)	k ₂ (h ⁻¹)	k ₃ (M ⁻¹ h ⁻¹)	k ₄ (h ⁻¹)	K ₅ (M ⁻¹)	k ₆ (M ⁻¹ h ⁻¹)	k ₇ (h ⁻¹)	k ₈ (h ⁻¹)	r ²
0.02	1:2	0.59	0.02	31.9	<10 ⁻⁴	<10 ⁻⁴	12.5	10.1	0.2	0.95
	2:1	0.34	0.06	114.3	37.6	<10 ⁻⁴	6.4	34.6	0.3	0.96
0.03	1:1.5	0.75	0.01	48.1	93.6	0.03	27.6	14.4	0.5	0.98
	1:2	0.70	0.01	51.9	99.2	0.01	23.4	15.7	0.5	0.99
0.04	1:2	0.82	0.06	67.3	175.5	0.08	39.6	19.6	0.6	0.99

Basicity affects not only the oxidation steps but also the furfural adsorption (strongly promoted by basicity) and oligomerization steps (k₅, k₆ and k₇). In general, the increase in the oxidation steps is more marked, which is congruent with the high yield of FCA and FDCA obtained with these configurations. The data for equimolar ratios and 2:1 (in this case considering the MPV-O mechanism, k₈) are included in **Table 4.25**.

Table 4.25. Apparent kinetic and adsorption constants for oxidation of HMF and FFL equimolar mixtures using Au/TiO₂ as a catalyst as a function of NaOH concentration

C _{NaOH} (M)	k ₁ (h ⁻¹)	k ₂ (h ⁻¹)	k ₃ (M ⁻¹ h ⁻¹)	k ₄ (h ⁻¹)	K ₅ (M ⁻¹)	k ₆ (M ⁻¹ h ⁻¹)	k ₇ (h ⁻¹)	k ₈ (h ⁻¹)	k ₉ (M ⁻¹ h ⁻¹)	r ²
0.02	0.17	0.03	0.06	0.02	0.01	1.27	<10 ⁻⁴	0.09	68.2	0.89
0.03	0.24*	0.05*	7.7*	15.4*	11.7*	1.47*	0.01*	0.02*	37.6*	0.90
	0.28	0.04	6.01	10.1	9.98	1.10	0.05	0.02	34.1	0.97
0.04	1.76	0.07	114.7	20.2	304.6	82.2	0.95	0.13	21.8	0.91

*Values obtained for 2:1 reaction

As observed in Table 4.25 and Figure 4.92, the comprehensive model considering the coexistence of two different routes to obtain furoic acid matches with experimental data with quite high regression coefficients and congruent kinetic rate values. As hypothesized before, the 2:1 ratio also corresponds to this model, suggesting that the MPV-O is relevant when working with high HMF concentrations. Comparing these results with the previous ones obtained with the simplified model, the kinetic rate for HMF oxidation (k_1) decreases and most of the HMF is consumed by the MPV-O route (two orders of magnitude higher). The effect in the FFL oxidation step by Cannizzaro mechanism as well as in the furfuryl alcohol reoxidation are less marked but follow the same trend, whereas the HMFCA oxidation into FDCA (k_2) have very similar values considering both mechanisms. This is explained since this step is the only independent one in the second model.

Based on these studies, a ratio 4:1:2 (NaOH:HMF:FFL) is defined as the optimum conditions to perform the oxidation of HMF and FFL mixtures. Despite the selectivities are lower than those obtained with isolate aldehydes (individual optimization), results are promising enough to consider this alternative, which could imply a relevant reduction in purification costs.

4.6.4. Carboxylation of furoic acid to 2,5-furandicarboxylic acid

The last step in the process to obtain FDCA from lignocellulose biomass concerns the furoic acid carboxylation. It should be highlighted that FDCA is directly obtained by HMF oxidation, but in the case of FFL precursor, the oxidized product needs to incorporate an extra carbon. Despite the increase in complexity that the route from furfural could need, this last step implies the incorporation of a CO_2 molecule. Thus, this step could contribute to the depletion of atmospheric CO_2 , obtaining a process based on biomass with negative CO_2 emission. In addition, obtaining furfural from biomass is a more controlled process than obtaining HMF due to the higher stability of this aldehyde. Thus, this route cannot be discarded.

Considering the deep analysis of the state-of-the-art of this reaction, see introduction section, carboxylation is still far from being a realistic option in most cases, including the FDCA production. The main drawbacks of this reaction include the challenges associated with carbon capture and utilization (CCU) methods, primarily due to the high CO_2 pressure used in

most of these studies. These works use pure CO₂ in conditions difficult and expensive to obtain with atmospheric CO₂. Another issue is related to the solid-gas configuration and the elevated cost of cesium, which is required to form a molten salt during the reaction, enabling ion mobility. Based on these preliminary results already published in the literature, the experimental effort was focused on two different approaches to this step: (1) optimizing the solid-gas reaction trying to reduce the severe conditions proposed in the literature, and (2) proposing an alternative configuration in the liquid phase.

As mentioned in the introduction section, the formation of FDCA by carboxylation with CO₂ is thermodynamically unfavorable. This challenge is addressed by first forming a metal furoate through the reaction of furoic acid with an alkaline salt. These solids need to be melted to allow the necessary ionic mobility for proper interaction between the involved ions. Therefore, knowing the thermal stability of the salt used is crucial to define the working range between the melting point and the decomposition temperature of this salt. In this context, Cs₂CO₃ the best option because of its melting point (195°C) significantly lower than the corresponding ones of other alkaline salts (>300°C). This allows defining a temperature range for performing the carboxylation that could be more sustainable. Based on this premise, to identify the range of temperatures that could be evaluated, understanding of the thermal stability and decomposition behavior of cesium furoate is crucial. The thermogravimetric decomposition of cesium furoate is illustrated in **Figure 4.91**.

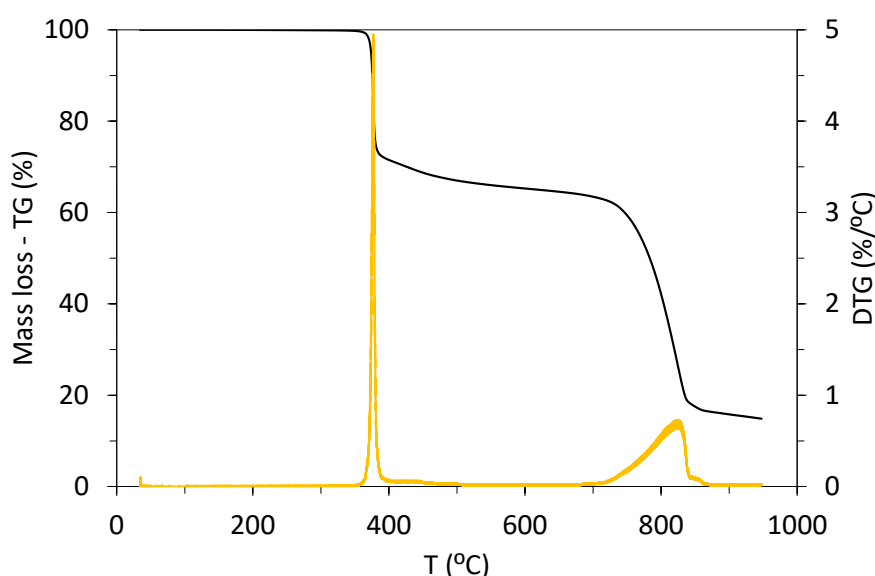


Figure 4.91. TG (black) and DTG (yellow) curves of F-Cs. DGT curve corresponds to secondary axis

The decomposition of cesium furoate under a nitrogen atmosphere reveals two significant mass loss events. The initial mass loss of 27.3% occurs at approximately 390 °C, indicating the possible release of a volatile component or a partial decomposition. This is followed by a substantial mass loss of 55.2% at a final temperature of 850 °C, ultimately leading to the formation of 17.5% of cesium oxide as residue. Therefore, the operating temperature for the proposed experiments is constrained by thermal stability, prompting the design of experiments at temperatures below this threshold of 390°C. To ensure good contact between O₂ and the salt, this last must be melted. This fact introduces a minimum requirement in terms of temperature, and the carboxylation must be studied over 190°C to ensure the melting state of cesium furoate. The theoretical range (190-390°C) can be reduced also considering sustainability aspects, trying to prevent harsh conditions that could imply too high energy consumption.

Based on these premises, the solid-gas carboxylation was studied in a temperature range 200-260°C, working at 10 bar of CO₂ (typical experiments consider pressures up to 60 bar). In these experiments, cesium furoate (F-Cs) was used as a reactant since this salt is the only one melted at the temperature range studied. Main results obtained are summarized in **Table 4.26** considering only the final point (6h) because working in absence of a solvent hinders sampling to determine the temporal evolution.

Table 4.26. Influence of reaction conditions on the conversion of F-Cs into FDCA after 6h reaction in gas-solid configuration

T(°C)	m _o (mol)	m Cs ₂ CO ₃ (mol)	FDCA Yield (%)
200	0.05	0.05	0.6
230	0.05	0.05	1.7
260	0.1	0.1	7

After 6 hours, a maximum 7% yield to FDCA was reached at 260°C, whereas almost no reaction is observed at lower temperatures. This quite low selectivity is explained by two concomitant effects: on the one hand, the lower pressure, with the subsequent diffusional limitations; and, on the other hand, a possible reactant decomposition due to the heater system. This second cause is suggested based on the appearance of a black solid inside the

reactor. This black solid is the reason why higher temperatures were not considered for this configuration.

Trying to prevent this decomposition and facilitate CO₂ diffusion, new experiments were performed in a liquid phase configuration. In the liquid phase, the reactant has a higher dispersion, allowing it to be more accessible to CO₂, which helps mitigate diffusion-related issues. Additionally, the presence of a solvent ensures uniform heat transfer throughout the medium, preventing the formation of localized "hot spots" that can lead to unwanted decomposition reactants. This uniform heat distribution is crucial for maintaining reaction stability and optimizing product selectivity. Working in a liquid phase configuration removes the minimum temperature limitation due to the melting salt, allowing working in more sustainable conditions.

The selection of solvents for carboxylation, specifically DMSO, is based on its ability to ensure high solubility for FDCA and its thermal stability (corroborated by the absence of decomposition signals in the GC). Additionally, water is used in binary systems as it enhances the solubility of cesium furoate, thereby ensuring that the main compounds remain soluble throughout the process. This combination of DMSO and water thus supports both the thermal and solubility requirements necessary for effective carboxylation reactions. Main experimental results are summarized in **Table 4.27**.

Table 4.27. Influence of reaction conditions on FDCA yield after 6h reaction in liquid phase reactions

Reactant	Solvent	T(°C)	Co (mol/L)	C Cs ₂ CO ₃ (mol/L)	FDCA Yield (%)
FCA	DMSO/H ₂ O	170	0.2	0.4	0
F-Cs	DMSO/H ₂ O	170	0.2	0.2	1.4
Cu(F) ₂	DMSO/H ₂ O	170	0.2	0.4	0
F-Cs	DMSO	170	0.2	0.2	0
F-Cs	DMSO	200	0.2	0.2	0

An initial experiment was proposed using FCA as the reactant and cesium carbonate in a 1:2 ratio. This configuration is justified since the melting salt (F-Cs) is expected to be not needed since in the aqueous phase the FCA will be always as a furoate. Experimental results discard this approach, not observing any FDCA after 6 h at 170°C, and demonstrate the crucial role of the alkaline metal in this process, previously suggested in the literature for solid-gas configurations, where Cs is identified as essential to activate the CO₂ and stabilize the reaction intermediates [99]. A second approach considered the same system but using F-Cs as a reactant. Results after 6h demonstrate a low but quantifiable activity, with 1.4% of FDCA yield. Trying to reduce the Cs consumption (very expensive reactant), a new approach considering the copper salt (Cu(F)₂) but keeping the Cs₂CO₃ in the medium was performed, but no FDCA was produced. The higher activity of Cs over the Cu one was demonstrated, concluding that, at least at working conditions, doing without Cs is not viable.

The literature also suggests that water can play a negative role in carboxylations. Next studies were focused on analyzing the behavior of DMSO without the aqueous solvent. As in previous cases, no quantitative results were obtained, in this case being assumed to be due to the low solubility of FCA in the solvent. To increase FCA solubility in the medium, binary systems were tested, replacing water with ethanol, an organic solvent with similar properties in terms of polarity. However, the amount of FDCA generated remained negligible, below the quantification limit even low (10 bar) or high (30 bar) CO₂ pressure. Moreover, the solubility of Cs₂CO₃ in any organic solvent is much more limited, making it difficult to achieve equimolar concentrations of F-Cs and Cs₂CO₃ in any case. Thus, this configuration was not considered for future experiments.

These preliminary results are far from being optimized and indicate that there is a big space for studying and improving in this step of the process. Results obtained in the solid-gas phase configuration are aligned with the literature (considering the lower pressure and temperatures used in this work) but the liquid phase configuration requires deeper analysis and more research. Results obtained with F-Cs and the binary system DMSO/water at 170°C suggest that this configuration is feasible. However, these results indicate that the thermochemical pathway in the liquid phase for carboxylation of furoic acid to FDCA is significantly limited and has not yielded promising results. This does not mean the possibility that alternative approaches, such as enzymatic or electrochemical routes, could facilitate the

carboxylation of furoic acid to FDCA allowing a full biomass conversion into FDCA in liquid phase. Notably, the thermocatalytic oxidation pathway of HMF stands out as a much simpler route for obtaining FDCA, offering a more feasible and efficient approach to achieve the desired plastic monomer.

4.7. REFERENCES

- [1] D. Garcés, L. Faba, E. Díaz, S. Ordóñez, Aqueous-Phase Transformation of Glucose into Hydroxymethylfurfural and Levulinic Acid by Combining Homogeneous and Heterogeneous Catalysis. *ChemSusChem* **2019** (12) 924-934. <https://doi.org/10.1002/cssc.201802315>
- [2] L. Faba, D. Garcés, E. Díaz, S. Ordóñez, Carbon Materials as Phase-Transfer Promoters for Obtaining 5-Hydroxymethylfurfural from Cellulose in a Biphasic System. *ChemSusChem* **2019** (12) 3769-3777. <https://doi.org/10.1002/cssc.201901264>
- [3] A. Toftgaard Pedersen, R. Ringborg, T. Grotkjær, S. Pedersen, J.M. Woodley, Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose–fructose mixtures. *Chemical Engineering Journal* **2015** (273) 455-464. <https://doi.org/10.1016/j.cej.2015.03.094>
- [4] D. Garcés, E. Díaz, S. Ordóñez, Aqueous Phase Conversion of Hexoses into 5-Hydroxymethylfurfural and Levulinic Acid in the Presence of Hydrochloric Acid: Mechanism and Kinetics. *Industrial & Engineering Chemistry Research* **2017** (56) 5221-5230. <https://doi.org/10.1021/acs.iecr.7b00952>
- [5] M. Ohara, A. Takagaki, S. Nishimura, K. Ebitani, Syntheses of 5-hydroxymethylfurfural and levoglucosan by selective dehydration of glucose using solid acid and base catalysts. *Applied Catalysis A: General* **2010** (383) 149-155. <https://doi.org/10.1016/j.apcata.2010.05.040>
- [6] V. Choudhary, R.I. Burnett, D.G. Vlachos, S.I. Sandler, Dehydration of Glucose to 5-(Hydroxymethyl)furfural and Anhydroglucose: Thermodynamic Insights. *The Journal of Physical Chemistry C* **2012** (116) 5116-5120. <https://doi.org/10.1021/jp2113895>
- [7] B. Girisuta, L.P.B.M. Janssen, H.J. Heeres, Kinetic Study on the Acid-Catalyzed Hydrolysis of Cellulose to Levulinic Acid. *Industrial & Engineering Chemistry Research* **2007** (46) 1696-1708. <https://doi.org/10.1021/ieo61186z>
- [8] J. Fan, M. De bruyn, V.L. Budarin, M.J. Gronnow, P.S. Shuttleworth, S. Breeden, D.J. Macquarrie, J.H. Clark, Direct Microwave-Assisted Hydrothermal Depolymerization of Cellulose. *Journal of the American Chemical Society* **2013** (135) 11728-11731. <https://doi.org/10.1021/ja4056273>
- [9] S.S. Chen, I.K.M. Yu, D.C.W. Tsang, A.C.K. Yip, E. Khan, L. Wang, Y.S. Ok, C.S. Poon, Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous Brønsted

- acids: Temperature and solvent effects. *Chemical Engineering Journal* **2017** (327) 328-335. <https://doi.org/10.1016/j.cej.2017.06.108>
- [10] D.H. Fockink, J.H. Sánchez, L.P. Ramos, Comprehensive analysis of sugarcane bagasse steam explosion using autocatalysis and dilute acid hydrolysis (H_3PO_4 and H_2SO_4) at equivalent combined severity factors. *Industrial Crops and Products* **2018** (123) 563-572. <https://doi.org/10.1016/j.indcrop.2018.07.017>
- [11] G. Gliozzi, A. Innorta, A. Mancini, R. Bortolo, C. Perego, M. Ricci, F. Cavani, Zr/P/O catalyst for the direct acid chemo-hydrolysis of non-pretreated microcrystalline cellulose and softwood sawdust. *Applied Catalysis B: Environmental* **2014** (145) 24-33. <https://doi.org/10.1016/j.apcatb.2012.12.035>
- [12] Z. Wen, L. Yu, F. Mai, Z. Ma, H. Chen, Y. Li, Catalytic Conversion of Microcrystalline Cellulose to Glucose and 5-Hydroxymethylfurfural over a Niobic Acid Catalyst. *Industrial & Engineering Chemistry Research* **2019** (58) 17675-17681. <https://doi.org/10.1021/acs.iecr.9b03824>
- [13] N.V. Gromov, O.L. Ogorodnikova, T.B. Medvedeva, V.N. Panchenko, I.S. Yakovleva, L.A. Isupova, M.N. Timofeeva, O.P. Taran, C. Aymonier, V.N. Parmon, Hydrolysis–Dehydration of Cellulose: Efficiency of NbZr Catalysts under Batch and Flow Conditions. *Catalysts* **2023** (13) 9. <https://doi.org/10.3390/catal13091298>
- [14] A.D. French, Idealized powder diffraction patterns for cellulose polymorphs. *Cellulose* **2014** (21) 885-896. <https://doi.org/10.1007/s10570-013-0030-4>
- [15] L. Zhang, G. Xi, Z. Chen, D. Jiang, H. Yu, X. Wang, Highly selective conversion of glucose into furfural over modified zeolites. *Chemical Engineering Journal* **2017** (307) 868-876. <https://doi.org/10.1016/j.cej.2016.09.001>
- [16] T. Istasse, A. Richel, Mechanistic aspects of saccharide dehydration to furan derivatives for reaction media design. *RSC Advances* **2020** (10) 23720-23742. <https://doi.org/10.1039/D0RA03892J>
- [17] J. Gong, J. Li, J. Xu, Z. Xiang, L. Mo, Research on cellulose nanocrystals produced from cellulose sources with various polymorphs. *RSC Advances* **2017** (7) 33486-33493. <https://doi.org/10.1039/C7RA06222B>
- [18] Y. Yao, S. Chen, M. Zhang, Sustainable Approaches to Selective Conversion of Cellulose Into 5-Hydroxymethylfurfural Promoted by Heterogeneous Acid Catalysts: A Review. *Frontiers in Chemistry* **2022** (10). <https://doi.org/10.3389/fchem.2022.880603>
- [19] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chemistry* **2011** (13) 754-793. <https://doi.org/10.1039/C0GC00401D>
- [20] S.S. Chen, L. Wang, I.K.M. Yu, D.C.W. Tsang, A.J. Hunt, F. Jérôme, S. Zhang, Y.S. Ok, C.S. Poon, Valorization of lignocellulosic fibres of paper waste into levulinic acid using solid and aqueous Brønsted acid. *Bioresource Technology* **2018** (247) 387-394. <https://doi.org/10.1016/j.biortech.2017.09.110>
- [21] J. Kluska, M. Ochnio, D. Kardaś, Ł. Heda, The influence of temperature on the physicochemical properties of products of pyrolysis of leather-tannery waste. *Waste Management* **2019** (88) 248-256. <https://doi.org/10.1016/j.wasman.2019.03.046>
- [22] K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, H. Schnitzer, Conversion of rapeseed cake into bio-fuel in a batch reactor: Effect of catalytic vapor upgrading. *Microporous and Mesoporous Materials* **2010** (128) 126-135. <https://doi.org/10.1016/j.micromeso.2009.08.022>

-
- [23] F. Cotana, G. Cavalaglio, M. Gelosia, A. Nicolini, V. Coccia, A. Petrozzi, Production of bioethanol in a second generation prototype from pine wood chips. *Energy Procedia* **2014** (45) 42-51. <https://doi.org/10.1016/j.egypro.2014.01.006>
- [24] P.N. Trisant, I. Gunardi, Sumarno, The Influence of Hydrolysis Time in Hydrothermal Process of Cellulose from Sengon Wood Sawdust. *Macromol. Symp.* **2020** (391) 2000016. <https://doi.org/10.1002/masy.202000016>
- [25] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S.F. Koelewijn, T. Renders, B. De Meester, W.J.J. Huijgen, W. Dehaen, C.M. Courtin, B. Lagrain, W. Boerjan, B.F. Sels, Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. *Energy & Environmental Science* **2015** (8) 1748-1763. <https://doi.org/10.1039/C5EE00204D>
- [26] C.A. Hubbell, A.J. Ragauskas, Effect of acid-chlorite delignification on cellulose degree of polymerization. *Bioresource Technology* **2010** (101) 7410-7415. <https://doi.org/10.1016/j.biortech.2010.04.029>
- [27] J. Shen, S. Zhu, X. Liu, H. Zhang, J. Tan, The prediction of elemental composition of biomass based on proximate analysis. *Energy Conversion and Management* **2010** (51) 983-987. <https://doi.org/10.1016/j.enconman.2009.11.039>
- [28] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A.A. Lappas, Effect of Lewis and Brønsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media. *Applied Catalysis A: General* **2018** (555) 75-87. <https://doi.org/10.1016/j.apcata.2018.01.029>
- [29] G. Yang, E.A. Pidko, E.J.M. Hensen, Mechanism of Brønsted acid-catalyzed conversion of carbohydrates. *Journal of Catalysis* **2012** (295) 122-132. <https://doi.org/10.1016/j.jcat.2012.08.002>
- [30] M. Sarno, M. Iuliano, S. De Pasquale, E. Ponticorvo, A new nano-catalyst for sawdust hydrolysis. *Applied Catalysis A: General* **2020** (602) 117686. <https://doi.org/10.1016/j.apcata.2020.117686>
- [31] N.M. Clauser, F.E. Felissia, M.C. Area, M.E. Vallejos, S. Gutiérrez, An energy-saving re-use strategy for the treatment of lignocellulosic biomass applied to the production of levulinic acid. *Journal of Cleaner Production* **2020** (257) 120549. <https://doi.org/10.1016/j.jclepro.2020.120549>
- [32] A. Kruse, A. Gawlik, Biomass Conversion in Water at 330–410 °C and 30–50 MPa. Identification of Key Compounds for Indicating Different Chemical Reaction Pathways. *Industrial & Engineering Chemistry Research* **2003** (42) 267-279. <https://doi.org/10.1021/ie0202773>
- [33] S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* **2011** (36) 2328-2342. <https://doi.org/10.1016/j.energy.2011.03.013>
- [34] I. Van Zandvoort, Y. Wang, C.B. Rasrendra, E.R.H. van Eck, P.C.A. Bruijninx, H.J. Heeres, B.M. Weckhuysen, Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem* **2013** (6) 1745-1758. <https://doi.org/10.1002/cssc.201300332>
- [35] S.K.R. Patil, J. Heltzel, C.R.F. Lund, Comparison of Structural Features of Humins Formed Catalytically from Glucose, Fructose, and 5-Hydroxymethylfurfuraldehyde. *Energy & Fuels* **2012** (26) 5281-5293. <https://doi.org/10.1021/ef3007454>
-

- [36] T. Rogalinski, T. Ingram, G. Brunner, Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. *The Journal of Supercritical Fluids* **2008** (47) 54-63. <https://doi.org/10.1016/j.supflu.2008.05.003>
- [37] J.-W. Lee, T.W. Jeffries, Efficiencies of acid catalysts in the hydrolysis of lignocellulosic biomass over a range of combined severity factors. *Bioresource Technology* **2011** (102) 5884-5890. <https://doi.org/10.1016/j.biortech.2011.02.048>
- [38] A. Rodríguez-Chong, J. Alberto Ramírez, G. Garrote, M. Vázquez, Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment. *Journal of Food Engineering* **2004** (61) 143-152. [https://doi.org/10.1016/S0260-8774\(03\)00080-3](https://doi.org/10.1016/S0260-8774(03)00080-3)
- [39] T. Tsoutsos, D. Bethanis, Optimization of the dilute acid hydrolyzator for cellulose-to-bioethanol saccharification. *Energies* **2011** (4) 1601-1623. <https://doi.org/10.3390/en4101601>
- [40] X. Li, X. Lan, T. Wang, Selective oxidation of furfural in a bi-phasic system with homogeneous acid catalyst. *Catalysis Today* **2016** (276) 97-104. <https://doi.org/10.1016/j.cattod.2015.11.036>
- [41] C.M. Pichler, M.G. Al-Shaal, D. Gu, H. Joshi, W. Ciptonugroho, F. Schüth, Ruthenium Supported on High-Surface-Area Zirconia as an Efficient Catalyst for the Base-Free Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid. *ChemSusChem* **2018** (11) 2083-2090. <https://doi.org/10.1002/cssc.201800448>
- [42] N. Alonso-Fagúndez, I. Agirrezabal-Telleria, P.L. Arias, J.L.G. Fierro, R. Mariscal, M.L. Granados, Aqueous-phase catalytic oxidation of furfural with H₂O₂: high yield of maleic acid by using titanium silicalite-1. *RSC Advances* **2014** (4) 54960-54972. <https://doi.org/10.1039/C4RA11563E>
- [43] M.A. Hasnat, M.M. Rahman, S.M. Borhanuddin, A. Siddiqua, N.M. Bahadur, M.R. Karim, Efficient hydrogen peroxide decomposition on bimetallic Pt–Pd surfaces. *Catalysis Communications* **2010** (12) 286-291. <https://doi.org/10.1016/j.catcom.2010.10.001>
- [44] H. Yang, T. Zhang, H. Tian, J. Tang, D. Xu, W. Yang, L. Lin, Effect of Sr Substitution on Catalytic Activity of La_{1-x}Sr_xMnO₃ (0 ≤ x ≤ 0.8) Perovskite-Type Oxides for Catalytic Decomposition of Hydrogen Peroxide. *Reaction Kinetics and Catalysis Letters* **2001** (73) 311-316. <https://doi.org/10.1023/A:1014115508872>
- [45] B. Geng, S. Zhang, X. Yang, W. Shi, P. Li, D. Pan, L. Shen, Cu_{2-x}O@TiO_{2-y} Z-scheme heterojunctions for sonodynamic-chemodynamic combined tumor eradication. *Chemical Engineering Journal* **2022** (435) 134777. <https://doi.org/10.1016/j.cej.2022.134777>
- [46] C.P. Ferraz, S. Navarro-Jaén, L.M. Rossi, F. Dumeignil, M.N. Ghazzal, R. Wojcieszak, Enhancing the activity of gold supported catalysts by oxide coating: towards efficient oxidations. *Green Chemistry* **2021** (23) 8453-8457. <https://doi.org/10.1039/D1GC02889H>
- [47] G. Chen, D. Hong, H. Xia, W. Sun, S. Shao, B. Gong, S. Wang, J. Wu, X. Wang, Q. Dai, Amorphous and homogeneously Zr-doped MnO_x with enhanced acid and redox properties for catalytic oxidation of 1,2-Dichloroethane. *Chemical Engineering Journal* **2022** (428) 131067. <https://doi.org/10.1016/j.cej.2021.131067>
- [48] C. Jiménez-Sanchidrián, J.R. Ruiz, The Baeyer–Villiger reaction on heterogeneous catalysts. *Tetrahedron* **2008** (64) 2011-2026. <https://doi.org/10.1016/j.tet.2007.11.024>
- [49] D. Zhao, T. Su, Y. Wang, R.S. Varma, C. Len, Recent advances in catalytic oxidation of 5-hydroxymethylfurfural. *Molecular Catalysis* **2020** (495) 111133. <https://doi.org/10.1016/j.mcat.2020.111133>

- [50] G. Papanikolaou, P. Lanzafame, S. Perathoner, G. Centi, D. Cozza, G. Giorgianni, M. Migliori, G. Giordano, High performance of Au/ZTC based catalysts for the selective oxidation of bio-derivative furfural to 2-furoic acid¹¹This paper in honor of Professor James G. Goodwin, Jr., in the occasion of his 75th birthday, to celebrate his outstanding contribution to catalysis sciences and technology. *Catalysis Communications* **2021** (149) 106234. <https://doi.org/10.1016/j.catcom.2020.106234>
- [51] R. Ciriminna, L. Albanese, F. Meneguzzo, M. Pagliaro, Hydrogen Peroxide: A Key Chemical for Today's Sustainable Development. *ChemSusChem* **2016** (9) 3374-3381. <https://doi.org/10.1002/cssc.201600895>
- [52] D.Y. Murzin, E. Bertrand, P. Tolvanen, S. Devyatkov, J. Rahkila, K. Eränen, J. Wärnå, T. Salmi, Heterogeneous Catalytic Oxidation of Furfural with Hydrogen Peroxide over Sulfated Zirconia. *Industrial & Engineering Chemistry Research* **2020** (59) 13516-13527. <https://doi.org/10.1021/acs.iecr.0c02566>
- [53] F. Saleem, P. Müller, K. Eränen, J. Wärnå, D. Yu Murzin, T. Salmi, Kinetics and modelling of furfural oxidation with hydrogen peroxide over a fibrous heterogeneous catalyst: effect of reaction parameters on yields of succinic acid. *Journal of Chemical Technology & Biotechnology* **2017** (92) 2206-2220. <https://doi.org/10.1002/jctb.5248>
- [54] H. Kumar, M.W. Fraaije, Conversion of Furans by Baeyer-Villiger Monooxygenases. *Catalysts* **2017** (7) 6. <https://doi.org/10.3390/catal7060179>
- [55] J. Luo, H. Yuan, H. Liu, J. Li, Y. Wang, Y. Wang, J. Yao, H. Li, One-pot Baeyer–Villiger oxidation of cyclohexanone with in situ generated hydrogen peroxide over Sn-Beta zeolites. *Green Chemical Engineering* **2021** (2) 294-300. <https://doi.org/10.1016/j.gce.2021.03.003>
- [56] M. Douthwaite, X. Huang, S. Iqbal, P.J. Miedziak, G.L. Brett, S.A. Kondrat, J.K. Edwards, M. Sankar, D.W. Knight, D. Bethell, G.J. Hutchings, The controlled catalytic oxidation of furfural to furoic acid using AuPd/Mg(OH)₂. *Catalysis Science & Technology* **2017** (7) 5284-5293. <https://doi.org/10.1039/C7CY01025G>
- [57] C. Jiménez-Sanchidrián, J.M. Hidalgo, R. Llamas, J.R. Ruiz, Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide/benzonitrile over hydrotalcites as catalysts. *Applied Catalysis A: General* **2006** (312) 86-94. <https://doi.org/10.1016/j.apcata.2006.06.031>
- [58] E. Kertalli, J.C. Schouten, T.A. Nijhuis, Effect of hydrogen and propylene on the hydrogen peroxide decomposition over Pt, PtO and Au catalysts. *Applied Catalysis A: General* **2017** (538) 131-138. <https://doi.org/10.1016/j.apcata.2017.03.023>
- [59] L.A. García-Contreras, J.O. Flores-Flores, J.Á. Arenas-Alatorre, J.Á. Chávez-Carvayar, Synthesis, characterization and study of the structural change of nanobelts of TiO₂ (H₂Ti₃O₇) to nanobelts with anatase, brookite and rutile phases. *Journal of Alloys and Compounds* **2022** (923) 166236. <https://doi.org/10.1016/j.jallcom.2022.166236>
- [60] V. Collins-Martínez, A. López Ortiz, A. Aguilar Elguézabal, Influence of the Anatase/Rutile Ratio on the TiO₂ Photocatalytic Activity for the Photodegradation of Light Hydrocarbons. *International Journal of Chemical Reactor Engineering* **2007** (5). <https://doi.org/10.2202/1542-6580.1613>
- [61] A.G. Ilie, M. Scarisoareanu, I. Morjan, E. Dutu, M. Badiceanu, I. Mihailescu, Principal component analysis of Raman spectra for TiO₂ nanoparticle characterization. *Applied Surface Science* **2017** (417) 93-103. <https://doi.org/10.1016/j.apsusc.2017.01.193>
- [62] A. Banerjee, G.R. Dick, T. Yoshino, M.W. Kanan, Carbon dioxide utilization via carbonate-promoted C–H carboxylation. *Nature* **2016** (531) 215-219. <https://doi.org/10.1038/nature17185>

- [63] J.-D. Grunwaldt, M. Maciejewski, O.S. Becker, P. Fabrizioli, A. Baiker, Comparative Study of Au/TiO₂ and Au/ZrO₂ Catalysts for Low-Temperature CO Oxidation. *Journal of Catalysis* **1999** (186) 458-469. <https://doi.org/10.1006/jcat.1999.2564>
- [64] Y. Wang, D. Widmann, M. Heenemann, T. Diemant, J. Biskupek, R. Schlögl, R.J. Behm, The role of electronic metal-support interactions and its temperature dependence: CO adsorption and CO oxidation on Au/TiO₂ catalysts in the presence of TiO₂ bulk defects. *Journal of Catalysis* **2017** (354) 46-60. <https://doi.org/10.1016/j.jcat.2017.07.029>
- [65] Z. Ren, Y. Yang, S. Wang, X. Li, H. Feng, L. Wang, Y. Li, X. Zhang, M. Wei, Pt atomic clusters catalysts with local charge transfer towards selective oxidation of furfural. *Applied Catalysis B: Environmental* **2021** (295) 120290. <https://doi.org/10.1016/j.apcatb.2021.120290>
- [66] A.S.K. Hashmi, Gold-Catalyzed Organic Reactions. *Chemical Reviews* **2007** (107) 3180-3211. <https://doi.org/10.1021/cr000436x>
- [67] A. Sadier, S. Paul, R. Wojcieszak, Selective Oxidation of Furfural at Room Temperature on a TiO₂-Supported Ag Catalyst. *Catalysts* **2022** (12) 8. <https://doi.org/10.3390/catal12080805>
- [68] C.P. Ferraz, M.A.S. Garcia, É. Teixeira-Neto, L.M. Rossi, Oxidation of benzyl alcohol catalyzed by gold nanoparticles under alkaline conditions: weak vs. strong bases. *RSC Advances* **2016** (6) 25279-25285. <https://doi.org/10.1039/C6RA01795A>
- [69] F. Nocito, N. Ditaranto, D. Linsalata, M. Naschetti, R. Comparelli, M. Aresta, A. Dibenedetto, Selective Aerobic Oxidation of Furfural into Furoic Acid over a Highly Recyclable MnO₂@CeO₂ Core-Shell Oxide: The Role of the Morphology of the Catalyst. *ACS Sustainable Chemistry & Engineering* **2022** (10) 8615-8623. <https://doi.org/10.1021/acssuschemeng.2c02341>
- [70] A. Roselli, Y. Carvalho, F. Dumeignil, F. Cavani, S. Paul, R. Wojcieszak, Liquid Phase Furfural Oxidation under Uncontrolled pH in Batch and Flow Conditions: The Role of In Situ Formed Base. *Catalysts* **2020** (10) 1. <https://doi.org/10.3390/catal10010073>
- [71] C.P. Ferraz, M. Zieliński, M. Pietrowski, S. Heyte, F. Dumeignil, L.M. Rossi, R. Wojcieszak, Influence of Support Basic Sites in Green Oxidation of Biobased Substrates Using Au-Promoted Catalysts. *ACS Sustainable Chemistry & Engineering* **2018** (6) 16332-16340. <https://doi.org/10.1021/acssuschemeng.8b03330>
- [72] C. P. Ferraz, N.J.S. Costa, E. Teixeira-Neto, Â.A. Teixeira-Neto, C.W. Liria, J. Thuriot-Roukos, M.T. Machini, R. Froidevaux, F. Dumeignil, L.M. Rossi, R. Wojcieszak, 5-Hydroxymethylfurfural and Furfural Base-Free Oxidation over AuPd Embedded Bimetallic Nanoparticles. *Catalysts* **2020** (10) 1. <https://doi.org/10.3390/catal10010075>
- [73] V.P. Santos, S.A.C. Carabineiro, P.B. Tavares, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, Oxidation of CO, ethanol and toluene over TiO₂ supported noble metal catalysts. *Applied Catalysis B: Environmental* **2010** (99) 198-205. <https://doi.org/10.1016/j.apcatb.2010.06.020>
- [74] H. Shen, H. Shan, L. Liu, Evolution Process and Controlled Synthesis of Humins with 5-Hydroxymethylfurfural (HMF) as Model Molecule. *ChemSusChem* **2020** (13) 513-519. <https://doi.org/10.1002/cssc.201902799>
- [75] S. Liu, Y. Zhu, Y. Liao, H. Wang, Q. Liu, L. Ma, C. Wang, Advances in understanding the humins: Formation , prevention and application. *Applications in Energy and Combustion Science* **2022** (10) 100062. <https://doi.org/10.1016/j.jaecs.2022.100062>
- [76] L. Filiciotto, A.M. Balu, J.C. Van der Waal, R. Luque, Catalytic insights into the production of biomass-derived side products methyl levulinate, furfural and humins. *Catalysis Today* **2018** (302) 2-15. <https://doi.org/10.1016/j.cattod.2017.03.008>

- [77] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, How Catalysts and Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5-Hydroxymethylfurfural. *Chemical Reviews* **2018** (118) 11023-11117. <https://doi.org/10.1021/acs.chemrev.8b00134>
- [78] M. Lin, C. Mochizuki, T. Ishida, Y. Zhang, M. Haruta, T. Murayama, Effect of poly(N-vinylpyrrolidone) ligand on catalytic activities of Au nanoparticles supported on Nb₂O₅ for CO oxidation and furfural oxidation. *Catalysis Today* **2023** (410) 143-149. <https://doi.org/10.1016/j.cattod.2022.03.034>
- [79] D. Yan, J. Xin, Q. Zhao, K. Gao, X. Lu, G. Wang, S. Zhang, Fe–Zr–O catalyzed base-free aerobic oxidation of 5-HMF to 2,5-FDCA as a bio-based polyester monomer. *Catalysis Science & Technology* **2018** (8) 164-175. <https://doi.org/10.1039/C7CY01704A>
- [80] W. Wei, G. Lyu, W. Jiang, Z. Chen, S. Wu, High-efficiency synthesis of 5-hydroxymethylfurfural and 2,5-diformylfuran from fructose over magnetic separable catalysts. *Journal of Colloid and Interface Science* **2021** (602) 146-158. <https://doi.org/10.1016/j.jcis.2021.05.161>
- [81] T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J.A. Lopez-Sanchez, M. Sankar, Q. He, C.J. Kiely, G.J. Hutchings, F. Cavani, Selective oxidation of 5-hydroxymethyl-2-furfural using supported gold–copper nanoparticles. *Green Chemistry* **2011** (13) 2091-2099. <https://doi.org/10.1039/C1GC15355B>
- [82] A. Piccolo, P. Conte, A. Cozzolino, Effects of mineral and monocarboxylic acids on the molecular association of dissolved humic substances. *European Journal of Soil Science* **1999** (50) 687-694. <https://doi.org/10.1046/j.1365-2389.1999.00276.x>
- [83] S.E. Davis, L.R. Houk, E.C. Tamargo, A.K. Datye, R.J. Davis, Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts. *Catalysis Today* **2011** (160) 55-60. <https://doi.org/10.1016/j.cattod.2010.06.004>
- [84] S.G. Maerten, D. Voß, M.A. Liauw, J. Albert, Selective Catalytic Oxidation of Humins to Low-Chain Carboxylic Acids with Tailor-Made Polyoxometalate Catalysts. *ChemistrySelect* **2017** (2) 7296-7302. <https://doi.org/10.1002/slct.201701553>
- [85] H. Cong, H. Yuan, Z. Tao, H. Bao, Z. Zhang, Y. Jiang, D. Huang, H. Liu, T. Wang, Recent Advances in Catalytic Conversion of Biomass to 2,5-Furandicarboxylic Acid. *Catalysts* **2021** (11) 9. <https://doi.org/10.3390/catal11091113>
- [86] F. Neațu, R.S. Marin, M. Florea, N. Petrea, O.D. Pavel, V.I. Pârvulescu, Selective oxidation of 5-hydroxymethyl furfural over non-precious metal heterogeneous catalysts. *Applied Catalysis B: Environmental* **2016** (180) 751-757. <https://doi.org/10.1016/j.apcatb.2015.07.043>
- [87] X. Liu, D.C.Y. Leong, Y. Sun, The production of valuable biopolymer precursors from fructose. *Green Chemistry* **2020** (22) 6531-6539. <https://doi.org/10.1039/DoGC02315A>
- [88] S. Albonetti, A. Lolli, V. Morandi, A. Migliori, C. Lucarelli, F. Cavani, Conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Au-based catalysts: Optimization of active phase and metal–support interaction. *Applied Catalysis B: Environmental* **2015** (163) 520-530. <https://doi.org/10.1016/j.apcatb.2014.08.026>
- [89] Y. Yang, C.-W. Hu, M.M. Abu-Omar, Synthesis of Furfural from Xylose, Xylan, and Biomass Using AlCl₃·6 H₂O in Biphasic Media via Xylose Isomerization to Xylulose. *ChemSusChem* **2012** (5) 405-410. <https://doi.org/10.1002/cssc.201100688>

- [90] L. Zhang, H. Yu, P. Wang, H. Dong, X. Peng, Conversion of xylan, d-xylose and lignocellulosic biomass into furfural using AlCl_3 as catalyst in ionic liquid. *Bioresource Technology* **2013** (130) 110-116. <https://doi.org/10.1016/j.biortech.2012.12.018>
- [91] Y. Zhao, K. Lu, H. Xu, L. Zhu, S. Wang, A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion. *Renewable and Sustainable Energy Reviews* **2021** (139) 110706. <https://doi.org/10.1016/j.rser.2021.110706>
- [92] M. Douthwaite, X. Huang, S. Iqbal, P.J. Miedziak, G.L. Brett, S.A. Kondrat, J.K. Edwards, M. Sankar, D.W. Knight, D. Bethell, The controlled catalytic oxidation of furfural to furoic acid using $\text{AuPd/Mg}(\text{OH})_2$. *Catalysis Science & Technology* **2017** (7) 5284-5293. <https://doi.org/10.1039/C7CY01025G>
- [93] F. D'Amico, M.E. Musso, R.J.F. Berger, N. Cefarin, G. Birarda, G. Tondi, D. Bertoldo Menezes, A. Reyer, L. Scarabattoli, T. Sepperer, T. Schnabel, L. Vaccari, Chemical constitution of polyfurfuryl alcohol investigated by FTIR and Resonant Raman spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2021** (262) 120090. <https://doi.org/10.1016/j.saa.2021.120090>
- [94] A.O.C. Iroegbu, S.S. Ray, On the chemistry of furfuryl alcohol polymerization: A review. *Journal of Polymer Science* **2024** (62) 1044-1060. <https://doi.org/10.1002/pol.20230708>
- [95] C.F. de Graauw, J.A. Peters, H. van Bekkum, J. Huskens, Meerwein-Ponndorf-Verley Reductions and Oppenauer Oxidations: An Integrated Approach. *Synthesis* **1994** (10) 1007-1017. <https://doi.org/10.1055/s-1994-25625>
- [96] A. Choplin, B. Coutant, C. Dubuisson, P. Leyrit, C. McGill, F. Quignard, R. Teisser, Heterogeneous catalysts from organometallic precursors: how to design isolated, stable and active sites. Applications to zirconium catalyzed organic reactions. Heterogeneous catalysts from organometallic precursors: how to design isolated, stable and active sites. Applications to zirconium catalyzed organic reactions. *Studies in Surface and Catalysis* **1997** (108) 353-360. [https://doi.org/10.1016/S0167-2991\(97\)80924-X](https://doi.org/10.1016/S0167-2991(97)80924-X)
- [97] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, F.J. Romero, The Meerwein-Ponndorf-Verley-Oppenauer reaction between 2-hexanol and cyclohexanone on magnesium phosphates. *Catalysis Letters* **1999** (58) 53-58. <https://doi.org/10.1023/A:1019088708653>
- [98] D. Tang, Ma B., R. Liu, J. Tian, and C. Zhao, One-Pot Solvent-Free Conversion of Furfural and CO_2 into 2,5-Furandicarboxylic Acid. *ACS Sustainable Chemistry & Engineering* **2024** 12 (42), 15752-15761 <https://doi.org/10.1021/acssuschemeng.4c07106>
- [99] G.R. Dick, A.D. Frankhouser, A. Banerjee, M.W. Kanan, A scalable carboxylation route to furan-2,5-dicarboxylic acid, *Green Chemistry* **2017** (19) 2966-2972. <https://doi.org/10.1039/C7GC01059A>



5. CONCLUSIONES



La presente Tesis Doctoral explora una vía sostenible para la producción de monómeros renovables a partir de biomasa, proceso propuesto en tres etapas de condiciones de operación muy diferentes: hidrólisis ácida, oxidación y carboxilación. Dada la extensión y diversidad de las reacciones estudiadas, las conclusiones se organizan en conclusiones parciales derivadas del estudio de cada etapa. Estos apartados abarcan desde la producción de 5-hidroximetilfurfural (HMF) y furfural (FFL) mediante la hidrólisis de celulosas pretratadas y serrín de pino, hasta la oxidación catalítica del FFL para la producción de ácido furoico (FCA), y el desarrollo de procesos de carboxilación en fase líquida para sintetizar ácido 2,5-furandicarboxílico (FDCA) a partir de fuentes renovables. En cada etapa se señalan las condiciones óptimas y las posibles aplicaciones industriales de estas reacciones.

Producción de 5-hidroximetilfurfural mediante hidrólisis de celulosas pretratadas

Se ha verificado la eficacia del sistema bicatalítico (HCl y beta zeolita) en la hidrólisis de celulosa microcristalina. Como resultado, se produce HMF debido a la sinergia entre los centros de Brønsted (que favorecen la hidrólisis) y los centros de Lewis (que facilitan la deshidratación de azúcares a través de la isomerización previa de glucosa a fructosa).

El análisis en términos de severidad (CSF) descarta un efecto preferente de la temperatura, el tiempo de reacción o la concentración de ácido, obteniéndose selectividades similares para factores de severidad combinada iguales. Basado en este análisis, se definen 140 °C y 0,02% de HCl como los parámetros óptimos para maximizar la producción de HMF

(19% de selectividad). Sin embargo, estos resultados están limitados por la baja reactividad de la celulosa (carácter recalcitrante). Debido a esto, la obtención de HMF requiere altas temperaturas y tiempos de reacción tan prolongados que el control de la reacción es deficiente y se obtiene una concentración relevante de ácidos (degradación de HMF).

Se propusieron tres pretratamientos químicos (HCl , H_2O_2 y HNO_3) para resolver este inconveniente. La suavidad de estos pretratamientos (a temperatura ambiente) no permite una alteración completa de la estructura cristalina, pero genera una superficie más reactiva (principalmente después del tratamiento con HNO_3) que produce un aumento significativo en la producción de HMF, logrando selectividades de HMF superiores al 50%.

Las pruebas de reutilización indican que la zeolita permanece activa una vez que la celulosa no reaccionada se elimina por calcinación, obteniéndose una correspondencia perfecta en conversión y distribución de productos (49% de conversión de celulosa, >44% de selectividad de HMF).

Producción de 5-hidroximetilfurfural y furfural mediante hidrólisis de serrín de pino

La lignina limita fuertemente la hidrólisis del serrín de pino, requiriendo condiciones tan fuertes que la producción de huminas restringe el proceso. Las deslignificaciones reductiva y oxidativa producen un efecto positivo, marcado por una productividad de TRS 140 veces mayor que con el serrín fresco y una disminución relevante en la producción de huminas. Los mejores resultados obtenidos son 3.2 g/L de ácido levulínico con una selectividad del 86% después de 7 h de reacción a 220 °C y 1000 ppm de HCl aplicando el pretratamiento oxidativo, y 1.2 g/L de aldehídos (selectividad del 35.4 %) en menos de 1 h, con el pretratamiento reductivo.

Producción de ácido furoico mediante oxidación catalítica de furfural con H_2O_2

La oxidación parcial del FFL utilizando H_2O_2 es una reacción compleja en la que la conversión y las selectividades están definidas por una combinación de contribuciones homogéneas y heterogéneas, incluyendo acidez (para promover la oxidación), basicidad (para estabilizar los ácidos orgánicos evitando su descomposición total en CO_2), la actividad

particular de cada metal utilizado (Pd, Pt o Au) y un efecto sinérgico entre el metal y el soporte, principalmente cuando el soporte tiene propiedades redox.

La máxima selectividad hacia ácido furoico se obtiene con Au/TiO₂ (42%). En términos de rendimiento del producto, Au/MgAl (8.5%) también es un buen candidato para su producción. La hipótesis de que la producción del ácido furoico está favorecida por el Au con un papel secundario del soporte fue corroborada, definiendo un tamaño de partícula óptimo de 5-7 nm. Este tamaño promueve la quimisorción necesaria de FFL y peróxido de hidrógeno en las partículas metálicas, reduciendo la relevancia de las reacciones paralelas (el mecanismo de B-V).

Producción de ácido furoico mediante oxidación catalítica de furfural con O₂

Se propone un nuevo enfoque para obtener ácido furoico mediante oxidación parcial en fase acuosa de FFL trabajando con una solución tampón a pH controlado = 8 y utilizando una baja carga catalítica. Se probaron diferentes catalizadores, involucrando soportes (TiO₂, MgAl y CeO₂) y metales activos (Au, Pd, Pt), con un cribado de las condiciones de reacción. Los resultados experimentales demuestran la alta actividad oxidante del Au, así como un efecto sinérgico con TiO₂ para activar el oxígeno, obteniéndose los resultados más prometedores al trabajar a 100 °C y 20 bares: 100% de selectividad de ácido furoico en fase líquida, 16% de conversión de FFL, y 35,8% de selectividad total de ácido furoico, reduciendo la producción de huminas. Se propone un mecanismo común de reacción condicionado por la adsorción de FFL, concluyendo que la temperatura y las propiedades del soporte juegan un papel clave en la producción de ácido furoico.

Este estudio introduce un camino para obtener precursores poliméricos por una vía sostenible, obteniendo un buen equilibrio entre las ventajas de las configuraciones anteriores propuestas en la literatura (pH fuerte usando NaOH y pH no controlado) y reduciendo los inconvenientes de ambos procedimientos. Así, el ácido furoico se puede producir selectivamente en condiciones suaves (una mejora clara respecto al mecanismo de Cannizzaro obtenido al trabajar a pH 14), se reduce significativamente la relevancia de la producción de huminas y se obtienen resultados muy interesantes en términos de estabilidad catalítica (un inconveniente muy relevante de la configuración de base libre).

Producción de ácido 2,5-furandicarboxílico mediante oxidación de 5-hidroximetilfurfural y fructosa

Este estudio demuestra la influencia crítica de las condiciones de reacción en la síntesis catalítica de FDCA a partir de HMF. La temperatura influye significativamente en la cinética de la reacción, principalmente en el segundo paso de oxidación, que requiere un mínimo de 80°C para obtener el FDCA en cantidades significativas. Esta selectividad aumenta con la temperatura, pero la formación de huminas prevalece sobre la ruta oxidativa, requiriendo de un equilibrio. Los estudios a diferentes presiones demuestran que un exceso de presión de O₂ sobre las condiciones estequiométricas garantiza la adsorción disociativa de oxígeno en la superficie de las nanopartículas de Au, activando la carboxilación y, consecuentemente, reduciendo la formación de huminas.

Las huminas se producen principalmente a través de una ruta catalítica homogénea, reduciendo la concentración inicial de HMF disponible para la oxidación. Trabajar con un bajo exceso de NaOH es crucial para reducir su relevancia y aumentar el carácter sostenible de esta ruta. A 80 °C, utilizando una proporción de NaOH de 2:1 y una presión de oxígeno de 25 bares, la selectividad de FDCA alcanzó el 87% después de 8 horas, con una formación de huminas despreciable, como lo confirmó el análisis del balance de carbono.

Además, el estudio exploró un proceso de un solo paso que integra la hidrólisis de fructosa y la oxidación de HMF, mostrando viabilidad (14% de FDCA obtenido después de 9 horas de reacción), pero destacando los desafíos en la prevención de la degradación del HMF.

Oxidación de mezclas de furfural/5-hidroximetilfurfural a ácidos furánicos sobre Au/TiO₂ y carboxilación de ácido furoico

Estudios preliminares comparando la evolución de la oxidación de HMF con la oxidación conjunta de furfural y HMF en condiciones de elevada basicidad (0.03 M de NaOH) demuestran un claro efecto inhibitorio del furfural debido a una adsorción competitiva sobre los centros metálicos del catalizador. Esta conclusión inicial propició nuevos estudios de optimización paramétrica, definiendo la proporción 4:1:2 (NaOH:HMF:FFL) como las condiciones óptimas, obteniendo una selectividad global del 10.4% de FDCA y del 66.4% de

FCA. Estos valores se corresponden con selectividades parciales (considerando las familias de compuestos independientemente) de 31.1% y 99.6%, respectivamente.

Los diferentes perfiles temporales obtenidos indican un mecanismo común para las reacciones en exceso de furfural, en las que ambos aldehídos se oxidan de forma independiente, detectándose el HMFCa como intermedio de oxidación del HMF, y mediante un mecanismo de Cannizzaro con reoxidación del alcohol furfurílico en el caso del furfural. En estas reacciones, el mecanismo principal compite con la formación de huminas por la oligomerización de ambos reactivos y del alcohol. El modelo cinético demuestra que la adsorción de furfural inhibe la ruta del HMF, mientras que la del furfural no se ve afectada por la presencia del HMF ya que no ocurre sobre los centros metálicos. Por el contrario, en condiciones equimolares de ambos reactivos o en exceso de HMF, las oxidaciones individuales conviven con una reacción simultánea de ambos aldehídos mediante un mecanismo MPV-O (oxidación-reducción) con descarboxilación oxidativa del compuesto de seis carbonos, generando un medio enriquecido en compuestos de cinco carbonos y mayor FCA del esperado por estequiometría del proceso.

Respecto a las reacciones de carboxilación de FCA, los ensayos termocatalíticos de carboxilación de FCA en fase líquida muestran una selectividad limitada hacia FDCA (1.4% tras 6 horas a 170°C), no siendo posible mejorar los resultados preexistentes en configuración sólido-gas. Estos resultados evidencian las limitaciones de la ruta termoquímica en fase líquida, destacando la oxidación de HMF como una vía más prometedora para obtener FDCA. Sin embargo, esto no descarta el potencial de otras rutas, como la enzimática o electroquímica, para desarrollar procesos de conversión de biomasa a monómeros renovables completamente en fase líquida.



6. CONCLUSIONS

This PhD Thesis explores a sustainable pathway to produce renewable monomers from biomass, with a proposed process consisting of three stages with different operating conditions: acid hydrolysis, oxidation, and carboxylation. Given the scope and diversity of the reactions studied, the conclusions are organized into partial conclusions derived from the study of each stage. These sections cover diverse topics, from the production of 5-hydroxymethylfurfural (HMF) and furfural (FFL) through hydrolysis of pretreated celluloses and pine sawdust, to the catalytic oxidation of FFL for furoic acid production, and the development of liquid-phase carboxylation processes to synthesize 2,5-furandicarboxylic acid (FDCA) from renewable sources. Each segment provides insights into the optimal conditions.

Production of 5-hydroxymethylfurfural by pretreated celluloses hydrolysis

The effectiveness of the bicatalytic system (HCl and beta zeolite) in the hydrolysis of microcrystalline cotton cellulose has been verified. As a result, HMF is produced due to the synergy between Bronsted centers (favoring hydrolysis) and Lewis centers (facilitating sugar dehydration through prior isomerization of glucose into fructose).

Analysis in terms of severity (CSF) rules out a preferential effect of temperature, reaction time, or acid concentration, yielding similar selectivities for equal combined severity factors. Based on this analysis, 140 °C and 0.02% of HCl are defined as the optimal

parameters to maximize HMF production (19% of selectivity). However, these results are limited by the low reactivity of the cellulose (recalcitrant character). Due to this, obtaining HMF requires high temperatures and reaction times so long that the control of the reaction is poor, and a relevant concentration of acids is obtained (HMF degradation).

Three chemical pretreatments (HCl, H_2O_2 , and HNO_3) were proposed to solve this drawback. The mildness of these pretreatments (room temperature) does not allow for complete alteration of the crystalline structure but generates a more reactive surface (mainly after treatment with HNO_3) that produces a significant increase in HMF production, achieving HMF selectivities higher than 50%.

Reusability tests indicate that the zeolite remains active once the unreacted cellulose is removed by calcination, obtaining a perfect correspondence in conversion and product distribution (49% of cellulose conversion, >44% of HMF selectivity).

Production of 5-hydroxymethylfurfural and furfural by pine sawdust hydrolysis

Lignin strongly limits the hydrolysis of pine sawdust requiring so strong conditions that humins production restricts the process. Reductive and oxidative delignifications produce a positive effect, marked by a productivity of TRS 140 times higher than with the fresh sawdust and a relevant decrease in humins production. The best results obtained are 3.2 g/L of levulinic acid with a selectivity of 86% after 7 h of reaction at 220 °C and 1000 ppm of HCl applying the oxidative pretreatment, and 1.2 g/L of aldehydes (selectivity of 35.4 %) in less than 1 h, with the reductive pretreatment.

Furoic acid production by catalytic oxidation of furfural with H_2O_2

The partial oxidation of FFL using H_2O_2 is a complex reaction in which the conversion and the selectivities are defined by a combination of homogeneous and heterogeneous contributions, including acidity (to promote the oxidation), basicity (to stabilize the organic acids preventing their total decomposition into CO_2), the particular activity of each metal

used (Pd, Pt or Au) and a synergetic effect between the metal and the support, mainly when the support has redox properties.

As to furoic acid, the maximum selectivity is obtained with Au/TiO₂ (42%). In terms of product yields, Au/MgAl (8.5%) is also a good candidate for its production. The hypothesis that furoic acid is promoted by Au with a secondary role of the support was corroborated, defining an optimum particulate size of 5-7 nm. This size promotes the required chemisorption of FFL and hydrogen peroxide on the metal particles, reducing the relevance of the parallel reactions (the B-V mechanism).

Furoic acid production by catalytic oxidation of furfural with O₂

We propose a new approach for obtaining furoic acid by aqueous-phase partial oxidation of FFL working with a buffer solution at controlled pH = 8 and using a low catalytic loading. Different catalysts were tested, involving supports (TiO₂, MgAl, and CeO₂) and active metals (Au, Pd, Pt), with a thorough screening of reaction conditions. Experimental results demonstrate the high oxidation activity of Au, as well as a synergetic effect with TiO₂ to activate the oxygen, obtaining the most promising results when working at 100 °C and 20 bar: 100% of furoic acid selectivity in the liquid phase, 16% of FFL conversion, and 35.8% of furoic acid total selectivity, reducing the humins production. All these results were fit to a common reaction mechanism conditioned by FFL adsorption, concluding that temperature and the support properties play a key role in furoic acid production.

This study introduces a very promising path to obtain polymer precursors by a sustainable route, obtaining a good equilibrium between the advantages of the previous configurations proposed in the literature (strong pH using NaOH and uncontrolled pH) and reducing the drawbacks of both procedures. Thus, furoic acid can be selectively produced at mild conditions (a clear improvement with respect to the Cannizzaro mechanism obtained when working at pH 14), the relevance of humins production is significantly reduced, and very interesting results in terms of catalytic stability are obtained (a very relevant drawback of the free-base configuration).

Production of 2,5-furandicarboxylic acid by oxidation of 5-hydroxymethylfurfural and fructose

This study demonstrates the critical influence of reaction conditions on the catalytic synthesis of FDCA from HMF. Temperature significantly influences the reaction kinetics, mainly the second oxidation step, requiring a minimum of 80 °C to obtain FDCA as the main product. This selectivity increases with the temperature, but the humins formation prevails over the oxidizing route. A high excess of O₂ pressure is required to guarantee the oxygen dissociative adsorption on the total amount of Au nanoparticles, a fact which reduces the humins formation enhancing the oxidation. Humins are mainly produced by a homogeneous catalytic route, reducing the HMF initial concentration. Working with a low NaOH excess is crucial to reduce their relevance and to increase the sustainability character of this route. At 80 °C, using a NaOH:HMF ratio of 2:1 and 25 bar oxygen pressure, FDCA selectivity reached 87% after 8 hours, with negligible humins formation, as confirmed by carbon balance analysis. Furthermore, the study explored a one-pot process integrating fructose hydrolysis and HMF oxidation, showing feasibility (14% of FDCA obtained after 9 h of reaction) but highlighting challenges in preventing HMF degradation.

Oxidation of furfural/5-hydroxymethylfurfural mixtures to furanic acids over Au/TiO₂ and carboxylation of furoic acid

Preliminary studies comparing the oxidation of HMF with the co-oxidation of furfural and HMF under highly basic conditions (0.03 M NaOH) demonstrate a clear inhibitory effect of furfural due to competitive adsorption on the metallic sites of the catalyst. This initial conclusion prompted further parametric optimization studies, identifying the ratio 4:1:2 (NaOH:HMF) as the optimal conditions for oxidizing HMF and FFL mixtures, achieving an overall selectivity of 10.4% for FDCA and 66.4% for FCA. These values correspond to partial selectivities (considering compound families independently) of 31.1% and 99.6%, respectively.

The different temporal profiles obtained suggest a common mechanism for reactions with an excess of furfural, where both aldehydes are oxidized independently. HMFCFA is

identified as an intermediate in the oxidation of HMF, while furfural undergoes a Cannizzaro mechanism followed by reoxidation of furfuryl alcohol. In these reactions, the primary mechanism competes with humin formation through oligomerization of both reactants and the alcohol. The kinetic model shows that furfural adsorption inhibits the HMF pathway, while furfural oxidation is unaffected by the presence of HMF since it does not occur on the metallic sites. Conversely, under equimolar conditions or in excess of HMF, individual oxidations coexist with a simultaneous reaction of both aldehydes through an MPV-O mechanism (oxidation-reduction) involving oxidative decarbonylation of the C6-derived intermediate. This results in a medium enriched in five-carbon compounds and higher FCA yields than expected from the stoichiometry of the process.

Regarding the carboxylation of FCA, thermocatalytic carboxylation tests of FCA in the liquid phase show limited selectivity toward FDCA (1.4% after 6 hours at 170°C), being not possible to improve the preexistent results in the gas-solid configuration. These results highlight the limitations of the thermochemical route in the liquid phase, emphasizing HMF oxidation as a more promising pathway to produce FDCA. However, this does not discard the potential of other routes, such as enzymatic or electrochemical approaches, to develop fully liquid-phase biomass conversion processes for renewable monomers.



7. ANEXOS

LISTA DE ABREVIATURAS

List of abbreviations

AB	Acrilonitrilo butadieno
AHG	Anhydroglucose
ALD	Aldehydes
ASA	Acrilonitrilo estireno acrilato
BEI	Backscattered Electron Image
BET	Brunauer, Emmet y Teller
BFA	Ácido β -formilacrílico
BJH	Barret, Joyner y Halenda
B-V	Baeyer-Villiger
CB	Carbon balance
CCU	Procesos de captura y utilización de CO ₂
CMNUCC	Convención Marco de las Naciones Unidas sobre el Cambio Climático
COP	Conferencia de las partes
CSF	Combined severity factor
Cu(F)₂	Difuroato de cobre
DAD	Detector de absorción a diferentes longitudes de onda
DFF	2,5-Diformilfurano
DME	Dimetil éter
DMSO	Dimethildulfoxide
DRIFT	Espectroscopía infrarroja de reflexión difusa por transformada de Fourier
DRX	Difracción de Rayos X
DP	Grado de polimerización
EDS	Energy Dispersive Spectrometer
FA	Ácido fórmico
FCA	Ácido Furoico

F-Cs	Furoato de cesio
FDCA	Ácido 2,5-furandicarboxílico
FFL	Furfural
FN	2-(5H)-furanona
FOH	Furfuryl alcohol
FTIR	Espectroscopía Infrarroja por Transformada de Fourier
FTIR	Fourier transform infrared
FUM	Ácido fumarico
GC	Cromatografía de gases
GC-MS	Cromatografía de gases acoplada a espectrometría de masas
GEI	Gases de efecto Invernadero
HDPE	Polietileno de alta densidad
HF	2-hidroxifurano
HFN	5-hidroxi-2(5H)-furanona
HMF	5-Hidroximetilfurfural
HMFA	Ácido 5-hidroximetil-2-furancarboxílico
HPLC	Cromatografía líquida de alta eficiencia
ICP-MS	Espectrometría de masas con plasma acoplado inductivamente
LA	Ácido levulínico
LDPE	Polietileno de baja densidad
MA	Ácido maleico
MAL	Ácido málico
MCC	Celulosa microcristalina
MCT	Mercury-Cadmium-Telluride detector
MS	Espectrometría de masas
MPV-O	Meerweing-Ponndorf-Verley & Oppenauer
ODEs	Ecuaciones diferenciales ordinarias
ODS	Objetivos de Desarrollo Sostenible

ONU	Organización de las Naciones Unidas
PE	Polietileno
PEF	Furanoato de polietileno
PET	Tereftalato de polietileno
PP	Polipropileno
PS	Poliestireno
PTA	Ácido tereftálico
PUR	Poliuretano
PVC	Cloruro de polivinilo
RID	Detector de índice de refracción
SEI	Secondary Electron Image
SEM	Microscopía electrónica de barrido
TCD	Detector de conductividad térmica
TEM	Microscopía electrónica de transmisión
TGA	Thermal gravimetric analyzer
TPD	Desorción a temperatura programada
TPO	Oxidación a temperatura programada
TPR	Reducción a temperatura programada
TRS	Total reduced sugars
XPS	Espectroscopía electrónica de rayos X

LISTA DE SÍMBOLOS

List of symbols

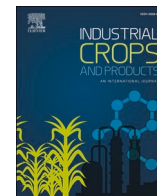
β	Anchura a media altura del pico (radianes)
γ	Dispersión metálica (%)
η	Rendimiento
θ	Ángulo de difracción o ángulo de Bragg
λ	Longitud de onda de la radiación incidente (nm)
$h\nu$	Energía de fotones
ρ	Densidad del metal
%C	Mass percentage of carbon in the sawdust
A_{sm}	Área activa por gramo de metal puro
C_{ac}	Amount of formic and levulinic acid (g/L)
C_{adl}	Sum of HMF and FFL (g/L)
C_D	Dimer concentration detected in liquid phase (g/L)
$C_{FFL,0}$	Concentración de furfural a $t=0$
$C_{FFL,t}$	Concentración de furfural a tiempo t
$C_{H_2O_2,0}$	Concentración de H_2O_2 a $t=0$
$C_{H_2O_2,t}$	Concentración de H_2O_2 a tiempo t
C_i	Molar concentration of each compound detected in liquid phase
C_M	Monomer concentration detected in liquid phase (g/L)
C_P	Sum of hemicellulose and cellulose in the sawdust (g/L)
d	Tamaño de cristalita (visto en quimisorción)
d	Distancia entre planos de átomos del cristal (visto en DRX)
D_p	Diámetro de poro (m)
E_a	Energía de activación
E_K	Energía cinética

EL	Energía de enlace de electrones del electrón expulsado
F_s	Factor estequiométrico en quimisorción
k_i	Constante cinética
K	Constante de Scherrer
K_i	Constante de adsorción del compuesto i
L	Tamaño medio de los cristales
M	Porcentaje de metal activo expresado en gramos de metal activo por cada gramo de muestra
m/z	Relación masa/carga
m_{cellulose}	Mass of cellulose introduced in the reactor
M_{cellulose}	Molar mass of cellulose (162 g/mol)
m_{sawdust}	Mass of delignified sawdust introduced in the reactor at the initial point
MW_C	Molar mass of carbon
n	Número entero
n_i	Number of carbons in the molecule of compound <i>i</i>
P	Presión real de N ₂ en los ensayos de fisisorción (Pa)
P_o	Presión de saturación de N ₂ en los ensayos de fisisorción (Pa)
S_i	Selectivity of compound i in liquid phase
t	Reaction time of hydrolysis in minutes
T	Reaction temperature
V	Total reaction volume
V_m	Volumen de gas quimisorbido (cm ₃ /g)
V_{mol}	Volumen molar de gas quimisorbido (cm ₃ /g)
V_{meso}	Volumen de mesoporos
V_{micro}	Volumen de microporos
W_a	Peso atómico del metal activo
X	Conversion
X_c	Liquid-phase carbon conversion



ARTÍCULOS CIENTÍFICOS

Scientific articles



Zeolite-assisted acid hydrolysis of cellulose: Optimization of reaction conditions and chemical pretreatments for enhancing HMF yields

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ABSTRACT

This study explores the hydrolysis of microcrystalline cellulose under soft conditions using a combination of both homogeneous (HCl) and heterogeneous catalysts (β -zeolite). The impact of temperature and HCl concentration is studied, revealing that the most favorable results (highest HMF yield) are achieved at 140°C with 0.02 %w/w of HCl (19% of selectivity, 23.5% of conversion). Nevertheless, the inherent recalcitrance of cellulose limits the conversion and the HMF concentration. Three chemical pretreatments (HCl, H_2O_2 , HNO_3) are considered, assessing the effect of concentration. Except when using 69% of HNO_3 , the bulk structure of cellulose remains largely unaffected (low effect on conversions). However, the surface of cellulose undergoes chemical alteration due to the acidic and predominantly oxidizing pretreatment, leading to the detection of C5 compounds. These modifications have a positive influence on the reaction, significantly enhancing the selectivity towards HMF up to 50% (34% of conversion).

1. Introduction

Recently, the production of renewable fuels and chemicals from biomass has focused the attention of the scientific community. There is total agreement on the essential role of lignocellulosic biomass (industrial crops or wastes) in boosting this industrial transition based on biorefineries and the circular economy as fundamental pillars (Velvizhi et al., 2022; Rathour et al., 2023).

In all the possible biorefinery schemes, the breakdown of biomass into sugars and other platform molecules for subsequent conversion into bioproducts is always the first step. However, one of the main challenges in using this biorefinery is its complex structure and recalcitrant nature, mainly due to the hydrophobicity of lignin that forms a physical barrier around cellulose and hemicellulose (Zoghalmi and Paës, 2019; Takkelapati et al., 2018; Gong et al., 2023) and the high crystallinity of cellulose (Schwarz, 2001). Hence, the depolymerization of cellulose, hemicellulose, or lignin fractions typically requires the application of cost-effective chemical or thermochemical methodologies, such as pyrolysis, gasification, or liquefaction. It is noteworthy that, in certain instances, the long-term sustainability of these processes may become questionable (Wang et al., 2014; Mika et al., 2018; Wu et al., 2023).

Hydrolysis is a liquid-phase alternative that requires softer conditions (100–250°C), allowing tighter control of the final products (Zhou

et al., 2023). This option is more recommended when the scope is obtaining chemical platform molecules for their subsequent valorization to chemicals. There are two types of hydrolysis: a) enzymatic and b) acid hydrolysis. Notwithstanding the merits inherent in the enzymatic approach, characterized by its high product yield, cost-effectiveness, and reduced toxicity (Vaidya et al., 2022), the remarkable specificity of enzymes hinders its universal applicability. Factors such as reaction duration, enzyme loading, and substrate concentration, alongside other pertinent parameters, require complex optimization steps (Bhatia et al., 2020). The studies on acid hydrolysis have emerged as a focal point, mainly to produce 5-hydroxymethylfurfural (HMF) and levulinic acid (Wang et al., 2014; Pileidis and Titirici, 2016). Both compounds are considered in the top ten of biomass-derived platform molecules, being interesting intermediates for liquid fuel production, and precursors of resins, solvents, polymers, and other fine chemicals (Bohre et al., 2015; Yan et al., 2015; Rout et al., 2016).

The reaction pathways for HMF and levulinic acid production are fairly similar, HMF is a key intermediate for levulinic acid formation, see Scheme 1. This reaction involves four consecutive steps: (1) hydrolysis of cellulose into glucose, (2) isomerization of glucose to fructose, (3) dehydration of glucose and, mainly, fructose into HMF, and (4) rehydration of HMF to levulinic acid (Mukherjee et al., 2015; Faba et al., 2019). Different catalysts have been proposed for this reaction,

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including organic and inorganic acids, salts, Lewis acids, and ion-exchange resins (Kang et al., 2018), concluding that the glucose to fructose isomerization (catalyzed by Lewis acids) is the rate-limiting step. Besides metal chlorides (homogeneous catalysis), zeolites such as metal-modified ZSM-5, zeolite Y, or mordenite have been tested to obtain a good isomerization activity (Moreau et al., 2000; Choudhary et al., 2013; Galadima et al., 2022). At this point, the combined use of zeolites and mineral acids has shown very good results for transforming glucose into HMF (Garcés et al., 2019), but its effect on those reactions combining hydrolysis and dehydration (as obtaining the HMF from the polymer) has not been studied yet, being one of the main novelties of this work.

However, the selective conversion of cellulose into HMF in aqueous medium is still not optimized, and very low yields are reported because of the low stability of this compound in aqueous medium. Different techniques are suggested to increase the HMF yield, including adjusting the process parameters (pH, temperature, pressure, reaction time, cellulose dosage), and conducting *in situ* extraction (Zhang et al., 2022; Shi et al., 2022). To sum up, temperatures in the range of 180–240°C, short reaction times, low acidity or acid concentration are preferred for HMF production (no HMF detected when pH > 4), whereas opposite conditions promote the levulinic acid one, being favored by pH < 3 (Kuster and Temmink, 1977; Takeuchi et al., 2008; Weingarten et al., 2012).

Regarding the kinetic, the high crystallinity of cellulose restricts the accessibility of the β -1,4-glycosidic bonds, which results in a slow hydrolysis rate (Meng et al., 2017; Liao et al., 2020). Biomass pretreatments reduce the polymerization degree of the cellulose. Several physical and chemical alternatives are proposed in the literature, highlighting milling, microwaves, ultrasounds, and acidic and alkali pretreatments, among others (Ni et al., 2015; Shimizu et al., 2018; Li et al., 2020; Tsalagkas et al., 2020; Lan et al., 2022). Most of these methods are designed to maximize the yields of sugars or acids, rather than aldehydes (i.e., HMF), due to their intermediate character and low stability. Thus, despite the existence of some studies (Steinbach et al., 2017; Rezayan et al., 2023), no conclusive results regarding the optimum pretreatment conditions are presented. In general, physical methods usually require long processing times (from 12 to 16 h) to obtain good results, whereas chemical ones use high concentrations of alkalis/acids, casting doubt on their sustainability. Thus, most of the

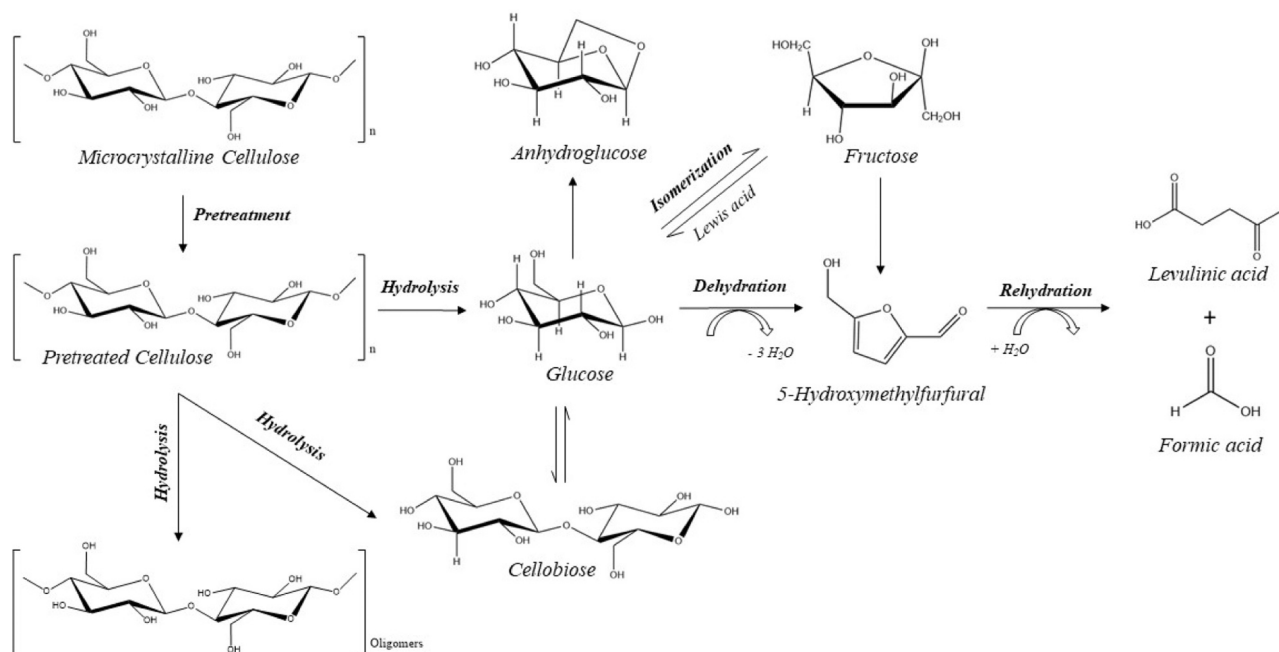
references in the literature consider the pretreatment conditions optimized for the first step of sugar production and the use of organic solvents (against the principles of Green Chemistry) to maximize the HMF yield in the second step (Widsten et al., 2018).

Based on the conclusions of the previous literature, this work evaluates the cellulose hydrolysis using a bi-catalytic system, HCl and β -zeolite, to guarantee the Lewis and Bronsted acidity required to maximize the HMF productivity reducing the severity of the process. This zeolite has been chosen based on a previous work where the activity of different zeolites for glucose dehydration has been studied (Garcés et al., 2019). Three chemical pretreatments are considered: HCl, which introduces acidity; H_2O_2 , with oxidizing activity; and HNO_3 , which combines both effects. The influence on conversion and product distribution was studied as a function of the chemical dosage.

2. Materials and methods

2.1. Chemicals

Microcrystalline cellulose (CAS: 9004–34–6, Sigma Aldrich) is used as a reactant in this work. According to the supplier's specifications, this reagent is a cotton cellulose with high crystallinity (>80%) and a polymerization degree lower than 400. 5-Hydroxymethylfurfural ($\geq 99\%$), furfural ($\geq 99\%$), levulinic acid (98%), and hydrogen peroxide (30%) were also supplied by Sigma-Aldrich. D-glucose ($\geq 99.5\%$) and cellobiose (98%) for HPLC calibration were purchased from Panreac Applichem. Nitric acid (69%) was acquired from Van Waters and Rogers (VWR) and hydrochloric acid (37%) was purchased from Fisher Chemical. β -Zeolite CP814E ($SiO_2/Al_2O_3=25$) was acquired from Zeolyst International. Commercial β -Zeolite was activated to remove NH_4^+ functional groups by a heat treatment at 550°C according to methods applied by Patet et al. (2017). A deep characterization of this catalysts is provided in (Gancedo et al., 2022), highlighting its high acidity ($10.1 \text{ mmol } NH_3 \cdot g^{-1}$) and its $6.1 \text{ \AA}$ of crystallographic pore diameter. The reactants were used without any further purification. Solutions were prepared using distilled water.



Scheme 1. Reaction pathway for cellulose conversion into HMF and levulinic acid by hydrolysis (Faba et al., 2019).

2.2. Pretreatments

Pretreatments were carried out at room temperature. 10 g of cellulose was added in solutions of 250 mL of HCl, HNO₃, and H₂O₂ at different concentrations (1%, 5%, 10% and, in case of HNO₃, also 69%). After 6 h under stirring, the pretreated cellulose samples were filtered and washed with distilled water until neutral pH. Finally, the samples were dried in an oven at 105°C for 24 h.

2.3. Characterization of cellulose samples

The morphology of the different celluloses (fresh and pretreated ones) was investigated by using a scanning electron microscope (SEM, JEOL-6610LV). The change of crystalline structure was evaluated by X-ray diffraction on a Philips X'Pert Pro diffractometer, using Cu-K α radiation. The scanning degree ranged from 5 to 50°, with a rate of 2°/s at 45 kV and 40 mA. The crystalline index (CrI) was calculated by the Segal equation that evaluates the crystalline portion ($I_{200}-I_{AM}$) over the total intensity of the crystalline peak portion (I_{200}). The Segal equation applied to cellulose type I is evaluated at 22–23° and 18–19° for the crystalline peak and the amorphous area, respectively.

The amount of amorphous cellulose was determined by gravimetry. The sample of cellulose was suspended in a NaOH solution (20 g/L) and brought to a boil for 3.5 h, using a cooling coil to ensure a constant volume. After cooling, the sample was filtered using a Büchner funnel and a nitrocellulose filter (0.45 μ m), washed and dried. The content of amorphous cellulose is evaluated as the difference in weight between the initial mass and the treated one. This procedure has been originally developed for determining the hemicellulosic fraction of biomass-derived materials, characterized by lower crystallinity and higher reactivity.

2.4. Reactions

The hydrolysis was performed in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) with a back pressure regulator and a PID temperature controller. In each experiment, 0.175 L of an aqueous suspension of 5.83 g of cellulose (untreated or pretreated cellulose as a function of the experiments, as detailed in each section) was loaded in the reactor. Air was purged with N₂ and hydrolysis was carried out with 10 bar of N₂. Once the mixture reaches the desired temperature, 50 mL of a hydrochloric acid solution and β -zeolite (0.467 g) is added. The acid concentration as well as the temperature depends on the experiment, and it is specified in the results and discussion section.

The reaction is carried out for 8 h under continuous stirring (700 rpm). Samples were taken from the sampling port, filtered by using 0.22 μ m nylon syringe filters and diluted in water to a final 1:20 ratio, and analyzed by HPLC (1200 Series, Agilent) using a refraction index detector and 0.5 mL/min of a 5 mM H₂SO₄ solution as the mobile phase. The column (Hi-Plex H, 300 $\times$ 7.7 mm, Agilent) and detector operate at 50°C. Cellobiose is identified as the majority dimer (>95%), but the presence of other isomers, such as maltose, cannot be discarded. However, the low resolution of the analytic method to isolate both compounds (differences in the retention times lower than 0.2 min) discourage the distinction. Thus, the term “dimer” is used in all the manuscript for the simultaneous consideration of both compounds.

Results were described in terms of conversion, carbon balance closure and selectivity. The cellulose conversion is calculated in terms of liquid-phase carbon yield, i.e., the theoretical cellulose required to obtain all compounds detected in the liquid phase (cellobiose and maltose, glucose, HMF, formic and levulinic acid), according to Eq. (1):

$$x_C = \frac{[V \cdot \sum (n_i \cdot C_i)]_{aq}}{0.4421 \cdot \frac{m_{cellulose}}{M_{cellulose}}} \quad (1)$$

where x_C is the liquid-phase carbon conversion, V is the total reaction

volume, C_i the molar concentration of each compound detected in liquid phase, n_i the number of carbons in the molecule of compound i , $m_{cellulose}$ the mass of cellulose introduced in the reactor (5.83 g), $M_{cellulose}$ the molar mass of cellulose (162 g/mol), and 0.4421 corresponds to the atomic percentage of carbon in this cellulose, according to results obtained by ICP analysis of the raw material (44.21% C, 6.2% H, 49.59% O).

Carbon balance closure (C.B.) and selectivity were calculated as follows:

$$C.B. (\%) = \frac{\sum_{i=1}^n m_{C_i} + m_{C_i}}{m_{C_{i=0}}} \cdot 100 \quad (2)$$

where $\sum_{i=1}^n m_{C_i}$ is the sum of the carbon mass present in all the reaction products; $m_{C_{i=0}}$ is the mass of carbon present in the cellulose initially introduced into the reactor; and m_{C_i} is the carbon mass of the cellulose collected by filtering and drying after the reaction.

$$S_i (\%) = \frac{n_i}{\sum_{j=1 \dots i}^n n_j} \cdot 100 \quad (3)$$

where n_i is the moles of carbon that contains the reaction product i and $\sum_{j=1 \dots i}^n n_j$ is the sum of the moles of carbon corresponding to reaction products.

3. Results and discussion

3.1. Hydrolysis of the non-pretreated cellulose

The initial experiments evaluate the influence of HCl on cellulose hydrolysis in the presence of β -zeolite to identify the optimum concentration of this homogeneous catalyst considering the equilibrium between activity, selectivity, and process sustainability. By sustainability criteria, a maximum value of 0.4% w/w (400 mg/L) was established to prevent corrosive effects in the equipment and to guarantee that the wastewater produced could be assimilated to a municipal wastewater stream, being far from the maximum allowed by the normative (2000 mg/L in the Spanish laws). It is expected that these low concentrations also minimize levulinic acid production (promoted by strong acidity). All reactions were performed in the presence of β -zeolite to promote the HMF formation by the glucose isomerization route, this study is the first one reporting the co-utilization of homogeneous and heterogeneous acids for treating polymeric biomaterials. Results are analyzed in Fig. 1.

Results shown in Fig. 1 are in good agreement with the general hydrolytic mechanism. Thus, dimers (mainly cellobiose but traces of maltose are also detected) are the first products obtained in the reaction, with very high selectivities at low cellulose conversion. The presence of heavier oligomers cannot be discarded but they cannot be analyzed because of their insoluble character (only the liquid phase is analyzed). For those reactions with low acidity, the initial selectivity of dimers is not 100% (close to 80%) because of the presence of glucose, even at very low conversions. This fact suggests the existence of terminal anhydroglucose units weakly linked to the general polymeric structure. These terminal units are easily hydrolyzed, resulting in an initial mixture containing oligomers but also glucose, as previously reported in the literature (Faba et al., 2019). When using 0.02 and, mainly, 0.04%w/w, the high acidity increases the hydrolytic rate, and the relative weight of this glucose decreases because of the higher concentration of cellobiose.

As the reaction progresses, the decreasing selectivity of these dimers observed (more pronounced at higher acidity) is compatible with their hydrolysis into monomeric units. This behavior suggests that the hydrolysis at these diluted acidic conditions is limited, making total conversion not possible to reach. In fact, cellulose conversion never exceeds 50%, although results with 0.04% demonstrate the advance of the

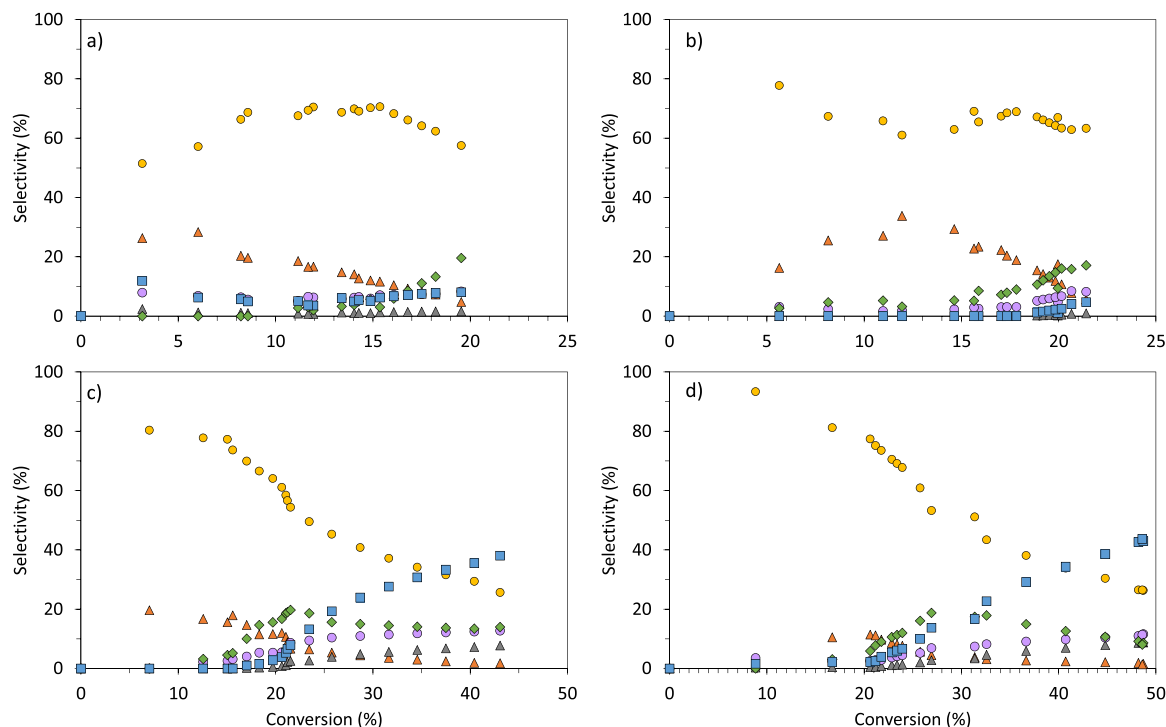


Fig. 1. Selectivity vs. conversion plots obtained for the cellulose hydrolysis at 140°C using 8% β -zeolite as a function of the HCl concentration: (a) absence of HCl; (b) 0.005%; (c) 0.02%; (d) 0.04%. Symbols: (●) dimers; (▲) glucose; (◆) HMF; (●) AHG; (■) levulinic acid.

reaction to subsequent steps once reached this threshold. According to the literature, glucose suffers dimerization in an acidic medium, establishing an equilibrium with cellobiose (Pedersen et al., 2015; Garcés et al., 2017). Analyzing the results in concentration units (see Fig. S1), this contribution cannot be discarded.

Glucose selectivity decreases with the advance of the reaction because of the simultaneous appearance of two different compounds: HMF and anhydroglucose (AHG). Both compounds are obtained by glucose dehydration, being catalyzed by the same acidic sites. In the presence of β -zeolite, HMF prevails over AHG because the Lewis acidity of the zeolite promotes the previous glucose isomerization into fructose, a requirement to promote the pathway to HMF, according to the literature (Ohara et al., 2010; Choudhary et al., 2012). However, fructose is not included in Fig. 1 since its selectivity is always lower than 1% (it dehydrates rapidly).

AHG is a final product, with a soft but continuous increasing trend. On the other hand, HMF can suffer rehydration, mainly under strong acidity, obtaining levulinic and formic acids. Both compounds are equimolar produced, their differences in selectivity being explained by the equation used (in carbon basis). These compounds are very relevant when cellulose conversion exceeds 30%.

This analysis was done considering the theoretical cellulose conversion since its solid character makes impossible its sampling with the actual reaction system. To evaluate the carbon balance and determine the representativeness of these results, the reactions were repeated, reducing the time to 8 h (time that is expected to be the optimum one to maximize the HMF selectivity). The temporal profiles of all the products are included in the Supplementary Information (Fig. S1), observing a discrepancy lower than 5% between both repetitions. Fig. 2 compares the results obtained after 8 h, in this case considering the conversion as the difference in weight between the solid initially introduced and the one recovered after the reaction. The recovered solids maintain their white color, discarding the presence of adsorbed humins, polymers

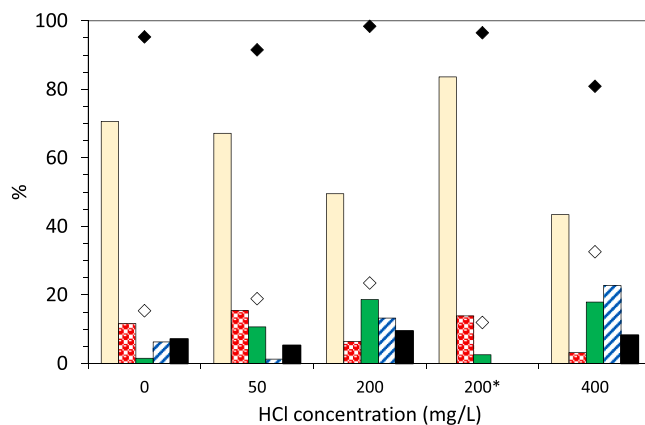


Fig. 2. Cellulose conversion (◇), carbon balance (◆) and products selectivity obtained in the cellulose hydrolysis at 140°C using 8% of zeolite as a function of the amount of HCl. Bars corresponding to dimer (yellow), glucose (red bubbles), HMF (green), levulinic acid (blue lines) and anhydroglucose (black). (*) Experiment in the absence of zeolite.

obtained from glucose derivatives under high temperature and/or acidity (Girisuta et al., 2007; Fan et al., 2013).

The reaction performed in the absence of HCl mainly produces the dimer (9 mM), the compound that represents 70.6% of the products detected. Glucose is also obtained, being an 11.7% selectivity. In the absence of any catalyst, the dehydration is almost negligible, HMF being less than 3% of the total products. The high carbon balance (95.3%) indicates the representativeness of these data, suggesting that the production of soluble humins or other undetected liquid compounds is not very relevant.

The positive action of HCl is observed, leading to a linear dependence

of cellulose conversion on acid concentration, from 15.4% in the absence of HCl to 32.6% when working with 0.04% of this acid (results after 8 h). The concentration of glucose dimer (cellobiose) remains almost constant despite the amount of HCl present, reaching final values (9–10 mM). These values are far from the maximum solubility of this compound (1 g/8 mL) discarding the saturation of the sample. Acidity also promotes the HMF formation and the selectivity toward this compound rises to 10.7, 16.4, and 17.9%, with 0.005, 0.02, and 0.04% of HCl, respectively. At 0.02, and 0.04% of HCl, the rehydration of this compound is significantly promoted, levulinic and formic acid being the majority compounds detected (31.3 and 40.6 mM, selectivities of 13.6 and 22.7%, respectively). The good carbon balances obtained when working at 0.005 and 0.02% of HCl (91.5 and 98.4%) demonstrate a high control of the reaction. On the contrary, the significant depletion observed at 0.04% (80.9%) suggests that a relevant amount of cellulose is transformed into soluble humins. In global terms, 0.02% of HCl (pH 2.03) is suggested as the optimum acidity to enhance the HMF production.

As introduced before, fructose is only detected in traces. To identify if this fact is due to a null activity of the zeolite (i.e., all the HMF is produced directly by glucose dehydration) or if the fructose dehydration is so fast that fructose instantaneously disappears, a particular experiment with 0.02% of HCl but in the absence of zeolite is performed (see Fig. 2). Results after 8 h demonstrate the relevance of these Lewis sites. When no zeolite is included, the HMF selectivity decreases by more than 84% (from 16.4% to 2.5%). Moreover, conversion is reduced by half in absence of zeolite, and the final mixture is enriched in dimers (83.6%), indicating the greater difficulty of breaking these structures and allowing the reaction to progress toward the final products. These effects are assumed to be due to the presence of Bronsted sites in the zeolite (proton form). Thus, solid cellulose particles migrate to the surface of the zeolite, which donates protons. The solid protonated cellulose on the surface of cellulose particles can degrade since part of it can dissolve and react with water. The corresponding chemisorption of oligomers justifies the improvement in glucose production, whereas the increase in 5-HMF is justified by the previously mentioned role of Lewis sites. This experiment also corroborates the dimerization equilibrium between glucose and cellobiose since comparing the results at the same cellulose conversion, the total yield to products obtained without the zeolite is significantly lower than with it. As dehydration steps consume glucose, this equilibrium is shifted.

To sum up, both catalysts (HCl and zeolite) contribute to all the steps of the hydrolysis of cellulose. Increasing the acidity is discarded as a valid option to promote HMF production since the impact on the levulinic acid formation is more relevant, with the subsequent decrease in the HMF selectivity. Thus, increasing the HMF concentration and selectivity requires evaluating other options, such as modifying the temperature, considering cellulose pretreatments to increase the hydrolysis capacity, or working with biphasic systems that could selectively extract the HMF to prevent its decomposition into levulinic and formic acid.

3.2. Influence of the severity of the reaction conditions

According to the literature, temperatures lower than 200–220°C limit the depolymerization of cellulose only to its amorphous content (Chen et al., 2017). However, the presence of levulinic acid is relevant at 140°C and higher temperatures are assumed to increase its production. Thus, higher temperatures are not contemplated in this work, trying to balance the thermal activation by the co-presence of two catalysts (HCl and β -zeolite). Two lower temperatures were studied (120 and 130°C) considering that these conditions could minimize the HMF rehydration (Pedersen et al., 2015), increasing the selectivity by reducing its degradation into levulinic and formic acid. The main results after 8 h are summarized in Fig. 3.

As expected, cellulose conversion decreases when reducing the

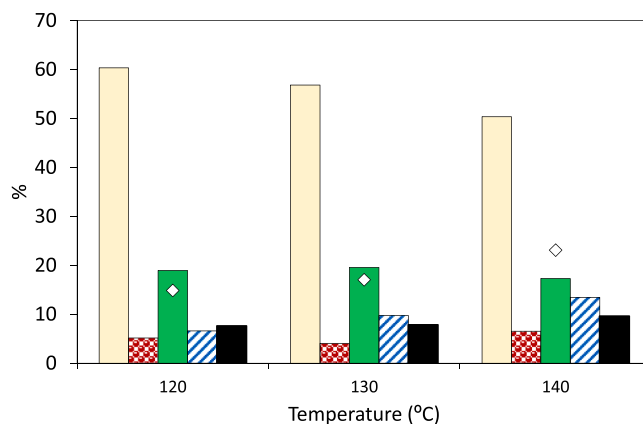


Fig. 3. Cellulose conversion (◊) and products selectivity obtained in the cellulose hydrolysis using 8% of β -zeolite and 0.02% of HCl as a function of the temperature. Bars corresponding to dimer (yellow), glucose (red bubbles), HMF (green), levulinic acid (blue lines) and anhydroglucose (black).

temperature (from 23.1% to 14.9%, from 140 to 120°C). Higher temperatures promote all the steps, decreasing the dimer selectivity (from 60.4 to 50.9) and increasing the final products, levulinic and formic acids (from 6.6% to 13.6%). As to HMF, its selectivity is maximum at 130°C (19.6%) but differences are not relevant enough to balance the differences in conversion. Thus, the maximum amount of HMF (18.6% of selectivity) is obtained at 140°C.

The temporal evolution of all the compounds (see Fig. S2) is congruent with the intermediate character of the target compound (HMF). Thus, larger reaction times increase the cellulose conversion (20.5, 28.3 and 43.1% of cellulose conversion after 24 h with 200 mg/L of HCl at 120, 130 and 140°C, respectively) but the HMF concentration slightly increases (from 4.5 to 5.0 mM, from 5.3 to 6.8 mM, and from 6 mM to 9.6 mM, after 8 and 24 h at the temperatures considered in this study) because of the promotion of further steps.

Consequently, maximizing the HMF selectivity requires an equilibrium between temperature, acidity, and time. The combined severity factor (CSF) concept was used to integrate the effects of these three conditions (Fockink et al., 2018):

$$CSF = \log \left(t \cdot \exp \left(\frac{T}{14.75} \right) \right) - pH$$

where t is the reaction time of hydrolysis in minutes, T is the reaction temperature in Celsius, and pH is the acidity of the aqueous solution measures before the reaction (4.92, 2.76, 2.03 and 1.76, for 0, 0.005, 0.02, and 0.04% of HCl, respectively).

Fig. 4 displays the effect of variations in conditions (CSF) on the HMF and levulinic acid concentration. In the case of HMF, the results show a cloud of data points where the results with 0.005 and 0.02% of HCl overlap. In other words, the concentration of HMF increases as the severity of the process increases, regardless of whether this increase was achieved by increasing reaction time, temperature, or HCl concentration.

The results obtained with the highest HCl concentration (0.04%) show a different profile, characterized by lower concentrations at low CSF values and a very narrow area of higher concentrations (never exceeding those obtained with 0.02%). This instability rules out the use of these conditions.

The evolution of levulinic acid demonstrates increasing trends with CSF, requiring a minimum CSF of 4 to start observing it, and an exponential increase for values greater than this value. However, unlike what was observed with HMF, the results are scattered depending on the acid concentration. Thus, when working with 0.04%, higher levulinic acid values are obtained at lower CSF values.

In conclusion, the maximum HMF selectivity (18.6%) obtained in

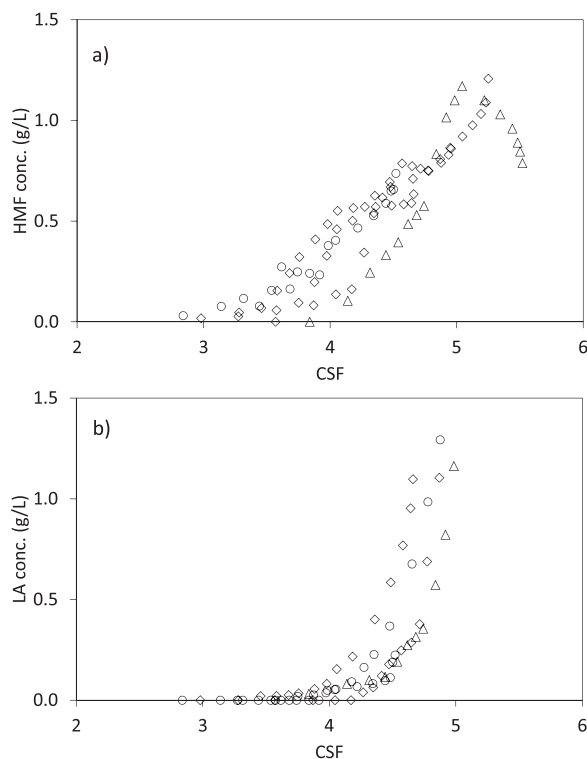


Fig. 4. Effects of CSF on concentration of (a) HMF, and (b) levulinic acid. Data obtained with 0.005% of HCl (○); 0.02% of HCl (◇); 0.04% of HCl (Δ).

this parametric study is higher than most of the typical values proposed in the literature for similar systems (10% at 150°C (Gliozzi et al., 2014), 15.5% at 220°C (Wen et al., 2019)), suggesting a good activity of the catalytic system considered. Higher selectivities (up to 33%) have recently been proposed for a similar aqueous-phase system, using modified zeolites as heterogeneous catalysts (Gromov et al., 2023). Although this result is very relevant, a direct comparison with this work is not possible because of the different crystallinity degree of the raw material used, from 33% to 55% in the case of the bibliography, >82% in this case.

On the other hand, this study also demonstrates an HMF final yield (4.3%) conditioned by the low cellulose reactivity (23% conversion). This yield is congruent with previous literature, with values in the range of 2–7% (Gliozzi et al., 2014; Wen et al., 2019), suggesting the need for other strategies to increase the reactivity of cellulose.

3.3. Improving hydrolysis behavior by chemical liquid-phase pretreatments

The production of HMF by cellulose hydrolysis under dilute acid conditions is limited by the refractory character of the cellulose. Its almost complete crystallinity restricts the access of the catalyst to surface irregularities. A previous pretreatment of this cellulose could reduce the crystallinity of the raw material, increasing the number of potential active sites in the cellulose fiber for starting hydrolysis reactions and, subsequently, increasing the HMF production.

Three different chemical pretreatments were considered in this work, using a mineral acid (HCl), an oxidant (H₂O₂), and a chemical with both properties (HNO₃). In the three cases, the influence of the dosage in the pretreatment was studied. All the pretreatments were carried out at room temperature (20–25°C) to limit the activity of these acids to reduce the crystallinity of the cellulose, making its surface more accessible during the reaction but without promoting its hydrolysis or any degradation of the bulk structure that could produce liquid compounds during the pretreatment. Thus, pretreated cellulose could be

recovered by filtration and the acid solution could be reused, minimizing the environmental and economic impact of using these chemicals.

Fig. 5 shows the results obtained after 24 h of hydrolysis. Despite the intermediate character of HMF, this reaction time corresponds to the maximum selectivity towards this compound of all the pretreated samples (the complete temporal profiles are included in the Supplementary Information, Fig. S3-S5).

In terms of conversion, pretreatments with HCl do not offer any improvement, obtaining very similar values in the three case studies (36–37.5%). These conversions are lower than the one obtained with the fresh cellulose (43%). This fact suggests that the potential surface degradation produced by this pretreatment does not lead to more accessible terminal glucose, but rather, a portion of the original terminal glucose (amorphous region) is dissolved during the pretreatment, removing the active sites of the fiber for starting hydrolysis reaction.

To support this hypothesis, fresh and pretreated celluloses were characterized by different techniques, trying to identify the main effect of each pretreatment on the cellulose structure. Figure S6 shows the diffractograms of all the samples, including the theoretical main diffraction peaks of the three polymorphs of cellulose, according to the molecular orientation and hydrogen-bonding network: cellulose I, cellulose II, and cellulose III. The analysis of these XRD results is shown in Table 1.

Native cellulose shows the typical XRD patterns of cellulose I (the expected polymorph of cotton cellulose), with diffraction peaks at $2\theta = 14.5^\circ$, 16.5° , and 22.5° attributed to the planes of (1 $\bar{1}$ 0), (110) y (200), respectively (French, 2014). This cellulose has a crystallinity index of 82.5% and, according to Scherrer's equation, a crystallite size of 7.3 nm. The region around $2\theta=21^\circ$ could be initially attributed to the plane (200) of cellulose type III. However, the lack of signals at 11.7° and 17° (planes (1 $\bar{1}$ 0) and (110) of this polymorph) discards this hypothesis suggesting a contribution of a no well-ordered polymeric region. The typical rod-like structure of crystalline cellulose is observed by SEM (Fig. S7). The purity of this material is corroborated by the results after treating this sample with NaOH; the sample has a non-cellulosic material percentage of less than 2%.

Cellulose type I remains the predominant polymorph in samples pretreated with HCl, with no significant differences observed in comparison to the untreated cellulose. In fact, SEM micrographs do not reveal any significant difference (see Fig. S7). The effects of the pretreatments become evident through an increase in the crystallite size (from 7 to 9–10 nm) with a minimal rise in the crystallinity index. Both effects are congruent with the solubilization of the weakest parts of the

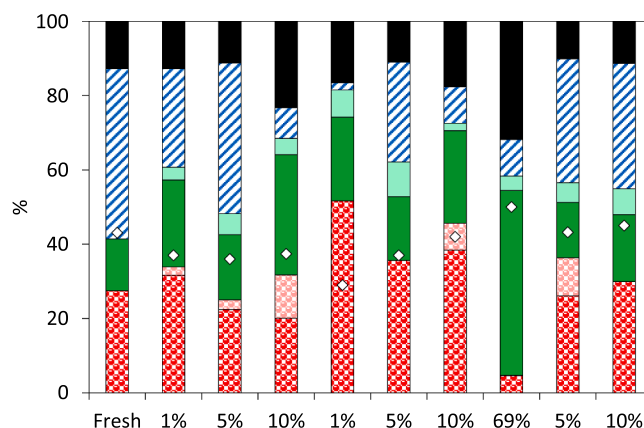


Fig. 5. Results after 24 h of cellulose hydrolysis at 140°C using 8% of β -zeolite and 0.02% of HCl as a function of the cellulose pretreatment used. Diamonds correspond to cellulose conversion, selectivities are shown in bars: C6 sugars (red bubbles), C5 sugar (pink bubbles), HMF (green), furfural (light green), acids (blue bars), AHG (black).

Table 1

Crystallinity index (CrI), average crystallite size and non-cellulosic phase concentration of fresh and pretreated celluloses.

Sample	CrI	Crystallite size (nm)	Non-cellulosic phase (%)
Fresh cellulose	82.1	7.3	1.8
1% HCl	82.4	9.2	3.6
5% HCl	82.4	9.5	13.4
10% HCl	82.5	9.9	24.2
5% H ₂ O ₂	82.9	7.9	48.6
10% H ₂ O ₂	83.2	9.2	49.1
1% HNO ₃	82.8	9.3	38.3
5% HNO ₃	83.1	9.5	38.8
10% HNO ₃	83.2	10.0	39.9
69% HNO ₃	37.8	7.8	41.9

surface (amorphous regions). The limited amount of weak β -glucosidic bonds on the parent surface (those susceptible to attack at these soft conditions) explains the low sensitivity of these results to the amount of HCl used.

The progressive increase in the percentage of non-cellulosic material, from 1.8% to 24.2%, explains the product distribution obtained, with an increasing selectivity in C5 derivatives, both sugars (arabinose) and aldehyde (furfural), as the HCl concentration increases. It is suggested that the acidic pretreatment interacts with the terminal glucose of cellulose, altering their structure in such a way that, under reaction conditions (140°C, copresence of a heterogeneous catalyst), these terminal units suffer not only hydrolysis but also decarbonylation, leading to arabinose and its aldehyde (total selectivity of 16% with 10% HCl). The presence of these molecules, although not the most common situation, has already been referenced in the literature under oxidative conditions (Zhang et al., 2017). The hydrolysis and dehydration rates of C5 sugars are slower than the corresponding ones of glucose (Istasse and Richel, 2020), justifying the lower conversions obtained. Moreover, furfural is significantly more stable than HMF, also explaining the lower relevance of acids in the reaction mixture. As to the target compound, the selectivity to HMF increases as the HCl concentration does, reaching a maximum of 32.3%, a value almost three times higher than the one obtained in the absence of any pretreatment.

Regarding the oxidizing pretreatment (H₂O₂), the conversion obtained with 5% of H₂O₂ is the same as with the fresh sample (43%). A slight increase is obtained when using 10% of H₂O₂, reaching a final conversion of 45%. Analyzing the products, the presence of C5 sugars and aldehydes is also relevant (similar selectivities than when using HCl), but the percentage of HMF only increases from 14% to 18%.

XRD diffractograms of these samples discard a deep change in the surface crystallography, cellulose type I being the main polymorph observed. With this chemical, the effects on the crystallinity index and the crystallite size are more evident than with HCl. The high percentage of “amorphous phase” (>45% in both cases) is not congruent with the conversion reached or the product distribution, suggesting that this pretreatment partially damages the cellulose surface, obtaining a solid that cannot lead sugars by acidic hydrolysis. Based on this fact, higher H₂O₂ concentrations were not tested.

Results with HNO₃ (acidic and oxidizing activity) demonstrate a high influence of the concentration, obtaining lower conversions when using 1% (29%) and higher conversions (50%) when using a high-concentrated acid. This evolution is the result of two opposite effects: the acidic behavior of HNO₃ promotes the hydrolysis and solubilization of terminal oligomers during the pretreatment, limiting the potential conversion, whereas its oxidation activity (stronger than in the case of H₂O₂) partially degrades the cellulose surface increasing the terminal units available for the reaction. Increasing the concentration remarks this positive effect because the number of sugars available for solubilization during pretreatment is limited, while the capacity to degrade the surface through the oxidative action increases. Based on this analysis, oxidative pretreatment is more effective than the acidic one.

The morphology and crystalline structure of samples treated with 1, 5, and 10% of HNO₃ are very similar and the cellulose I polymorph is the predominant one in the three cases. 1% of nitric acid is enough to produce the main differences, both in the crystallinity index and the crystalline size, whereas almost null differences were observed when increasing the nitric acid concentration. In agreement with XRD results, a continuous but soft increase in the amount of non-cellulosic percentage is observed, highlighting that more than 95% is obtained with only 1% of HNO₃. This analysis does not allow us to determine the specific amorphous character of this fraction. Conversion results suggest that this fraction is easier to hydrolyze after being treated with high HNO₃ concentration.

The pretreatment with 69% of HNO₃ demonstrates to be significantly more effective in deeply modifying the cellulose surface. Diffraction peaks of cellulose type I and type II (20=12°, 20°, and 22° (French, 2014)) coexist in this sample. The probable explanation for this result is that the crystalline regions swelled during the attack with HNO₃, leading to a rearrangement of the cellulose crystalline structure. This effect has been previously observed when cellulose is treated with strong mineral acids (Gong et al., 2017). Cellulose type II is more stable than cellulose type I, justifying the low effect on conversion of this relevant change.

The degradation produced by this pretreatment is very effective in terms of selectivity, reaching 50% of HMF. Furfural is also obtained, reaching a final selectivity of 4%. The low sugar selectivity (<5%) demonstrates that, despite this pretreatment having limited effectiveness in increasing the availability of hydrolysable sugars, it does reduce the stability of glucosidic bonds, favoring the progression of the reaction toward the dehydration stage.

Selectivity results are comparable to those proposed in the literature, even when using more severe pretreatment conditions (Yao et al., 2022). The selective extraction of HMF in an organic solvent could be an interesting option for increasing its selectivity. The purification of the stream is out of the scope of this work, but we have deeply studied this approach in a previous study using glucose as a reactant and the main conclusions could be extrapolated to this system (Faba et al., 2019). On the contrary, the maximum yield obtained in this study (18%) is slightly lower than the optimum values reported in the literature (up to 60% for aqueous reactions), as discussed in the review previously indicated. However, the direct comparison is unrealistic due to the different conditions under which they are conducted. Those employed in this study, both for pretreatment and reaction, including temperatures, acid concentrations, and catalyst amounts, are significantly milder than those suggested in previous studies, resulting in a more sustainable process.

3.4. Reusability tests

The solid after 24 h of reaction time (using cellulose pretreated with 69% of HNO₃) was recovered by filtration and resuspended in a fresh HCl solution for a new hydrolytic batch. This solid includes the zeolite as well as the non-reacted cellulose, and the lack of any reaction (conversion lower than 1%) and, more relevant, the absence of glucose is congruent with the recalcitrant character of cellulose since the first step of the hydrolysis does not need the catalytic activity of the zeolite. Thus, extending the reaction over 24 h is not a good approach to increase the HMF productivity.

This result does not give clear information about the possible zeolite deactivation since the role of this catalyst is mainly relevant for the glucose isomerization. To study the zeolite stability, a new cycle feeding the recovered solid (mixture of used zeolite and recalcitrant cellulose) into a new cellulose suspension (using pretreated cellulose as fresh reactant) was performed. In this batch, the recalcitrant cellulose is considered as an inert solid and new pretreated-cellulose (69% HNO₃) and HCl is introduced to guarantee the initial conditions. Results after 24 h are plotted in Fig. 6. As observed, the final mixture is enriched in reductive sugars, with a total selectivity of 76.3% (28.6% of arabinose, 23.6% of fructose and 24.1% glucose). A quite relevant HMF selectivity

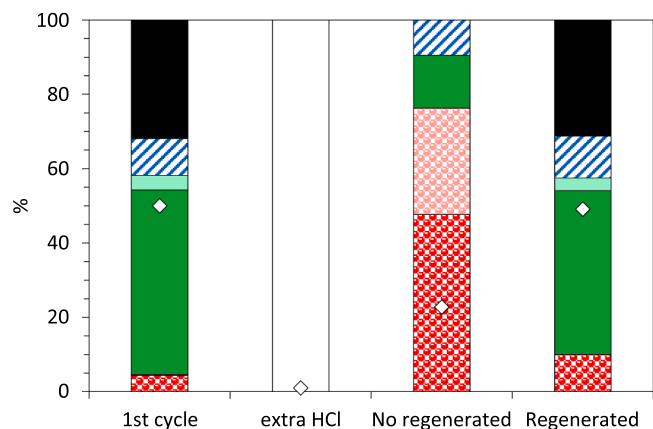


Fig. 6. Stability tests of pretreated cellulose (69% HNO_3) hydrolysis at 140°C using 8% of β -zeolite and 0.02% of HCl . Results obtained after 24 h. Diamonds correspond to cellulose conversion, selectivities are shown in bars: C6 sugars (red bubbles), C5 sugar (pink bubbles), HMF (green), furfural (light green), acids (blue bars), AHG (black).

is also observed (14.2%). The presence of fructose indicates that the zeolite is still partially active (glucose isomerization is catalyzed by Lewis acidity). The lower conversion reached in this second cycle (22.8 % vs. 50%) as well as the lack of total fructose dehydration corroborates the initial hypothesis that Bronsted acid sites of the zeolite collaborate with HCl catalyzing the cellulose hydrolysis and the dehydration steps (see Section 3.1) and these sites are at least partially deactivated after the first cycle. A possible reason for this deactivation could be the adsorption of cellulose oligomers or humins precursors, both aspects being discarded according to the good carbon balance obtained at these mild conditions (98.4%, see Fig. 2).

An alternative explanation of these results is related to the method used to get the catalyst after the first reaction, suggesting that the remaining cellulose could be stuck on the zeolite surface, blocking the access to the active sites. To check this hypothesis, the solid recovered after the first cycle was calcined in furnace (550°C , 8 h) to remove the cellulose. The zeolite after the thermal treatment was introduced in a new cycle with pretreated cellulose, the results after 24 h being summarized in Fig. 6. As observed, the zeolite recovers its initial activity, obtaining very similar conversion (49.1%) and a product distribution enriched in HMF (44.1%) and AHG (32.2%). These results reinforce the interesting results obtained in the cellulose hydrolysis at soft conditions using a pretreatment based on HNO_3 .

4. Conclusions

The effectiveness of the bicatalytic system (HCl and beta zeolite) in the hydrolysis of microcrystalline cotton cellulose has been verified. As a result, HMF is produced due to the synergy between Bronsted centers (favoring hydrolysis) and Lewis centers (facilitating sugar dehydration through prior isomerization of glucose into fructose).

Analysis in terms of severity (CSF) rules out a preferential effect of temperature, reaction time, or acid concentration, yielding similar selectivities for equal combined severity factors. Based on this analysis, 140°C and 0.02% of HCl are defined as the optimal parameters to maximize HMF production (19% of selectivity). However, these results are limited by the low reactivity of the cellulose (recalcitrant character). Due to this, obtaining HMF requires high temperatures and reaction times so long that the control of the reaction is poor and a relevant concentration of acids is obtained (HMF degradation).

Three chemical pretreatments (HCl , H_2O_2 , and HNO_3) were proposed to solve this drawback. The mildness of these pretreatments (room temperature) does not allow for complete alteration of the crystalline structure but generates a more reactive surface (mainly after treatment

with HNO_3) that produces a significant increase in HMF production, achieving HMF selectivities higher than 50%. Reusability tests indicate that the zeolite remains active once the unreacted cellulose is removed by calcination, obtaining a perfect correspondence in conversion and product distribution (49% of cellulose conversion, >44% of HMF selectivity).

Future work in this field must integrate this reaction system that produces the HMF with high selectivity at soft conditions and using dilute acid systems, with the use of green organic solvents for the HMF selective extraction, expecting to obtain a suitable process to produce this relevant platform molecule.

CRediT authorship contribution statement

Paula Rapado: Methodology, Investigation, Data curation. **Diego Garcés:** Methodology, Investigation. **Salvador Ordóñez:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Laura Faba:** Writing – original draft, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.118309.

References

- Bhatia, S.K., Jagtap, S.S., Bedekar, A.A., Bhatia, R.K., Patel, A.K., Pant, D., Banu, J.R., Rao, C.V., Kim, Y.G., Yang, Y.H., 2020. Recent developments in pretreatment technologies on lignocellulosic biomass: effect of key parameters, technological improvements, and challenges. *Bioresour. Technol.* 300, 122724 <https://doi.org/10.1016/j.biortech.2019.122724>.
- Bohre, A., Saha, B., Abuomar, M.M., 2015. Catalytic upgrading of 5-hydroxymethylfurfural to drop-in biofuels by solid base and bifunctional metal-acid catalysts. *ChemSusChem* 8, 4022–4029. <https://doi.org/10.1002/cssc.201501136>.
- Chen, S.S., Yun, I.K.M., Tsang, D.C.W., Yip, A.C.K., Khan, E., Wang, L., Ok, Y.S., Poon, C.S., 2017. Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous Bronsted acids: temperature and solvent effects. *Chem. Eng. J.* 327, 328–335. <https://doi.org/10.1016/j.cej.2017.06.108>.
- Choudhary, V., Burnett, R.L., Vlachos, D.G., Sandler, S.I., 2012. Dehydration of glucose to 5-(hydroxymethyl) furfural and anhydroglucose: thermodynamic insights. *J. Phys. Chem. C* 116, 5116–5120. <https://doi.org/10.1021/jp2113895>.
- Choudhary, V., Mushrif, S.H., Ho, C., Anderko, A., Nikolakis, V., Marinkovic, N.S., Frenkel, A.I., Sandler, S.I., Vlachos, D.G., 2013. Insights into the interplay of Lewis and Bronsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media. *J. Am. Chem. Soc.* 135, 3997–4006. <https://doi.org/10.1021/ja3122763>.
- Faba, L., Garcés, D., Díaz, E., Ordóñez, S., 2019. Carbon materials as phase-transfer promoters for obtaining 5-hydroxymethylfurfural from cellulose in a biphasic system. *ChemSusChem* 12, 3769–3777. <https://doi.org/10.1002/cssc.201901264>.
- Fan, J., De Bruyn, M., Budarin, V.L., Gronnow, M.J., Shuttlesworth, P.S., Breiden, S., Macquarrie, D.J., Clark, J.H., 2013. Direct microwave-assisted hydrothermal depolymerisation of cellulose. *J. Am. Chem. Soc.* 135, 11728–11731. <https://doi.org/10.1021/ja4056273>.
- Fockink, D.H., Sánchez, J.H., J. H. Ramos, L.P., 2018. Comprehensive analysis of sugarcane bagasse steam explosion using autocatalysis and dilute acid hydrolysis (H_3PO_4 and H_2SO_4) at equivalent combined severity factors. *Ind. Crop. Prod.* 123, 563–572. <https://doi.org/10.1016/j.indcrop.2018.07.017>.

- French, A.D., 2014. Idealized powder diffraction patterns for cellulose polymorphs. *Cellulose* 21, 885–896. <https://doi.org/10.1007/s10570-013-0030-4>.
- Galadima, A., Masudi, A., Muraza, O., 2022. Conversion of cellulose to glucose and further transformation into fuels over solid acid catalyst: a mini review. *Microporous Mesoporous Mater.* 336, 111846 <https://doi.org/10.1016/j.micromeso.2022.111846>.
- Gancedo, J., Faba, L., Ordóñez, S., 2022. Tuning the selectivity on the furan-propylene Diels-Alder condensation over acid catalysts: role of pore topology and surface acidity. *Appl. Catal. A* 641, 118683. <https://doi.org/10.1016/j.apcata.2022.118683>.
- Garcés, D., Díaz, E., Ordóñez, S., 2017. Aqueous phase conversion of hexoses into 5-hydroxymethylfurfural and levulinic acid in the presence of hydrochloric acid: mechanism and kinetics. *Ind. Eng. Chem. Res.* 56, 5221–5230. <https://doi.org/10.1021/acs.iecr.7b00952>.
- Garcés, D., Faba, L., Díaz, E., Ordóñez, S., 2019. Aqueous-phase transformation of glucose into hydroxymethylfurfural and levulinic acid by combining homogeneous and heterogeneous catalysis. *ChemSusChem* 12, 924–934. <https://doi.org/10.1002/cssc.201802315>.
- Girisuta, B., Janssen, L.P.B.M., Heeres, H.J., 2007. Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid. *Ind. Eng. Chem. Res.* 46, 1696–1708. <https://doi.org/10.1021/ie061186z>.
- Gliozzi, G., Innorta, A., Mancini, A., Bortolo, R., Perego, C., Ricci, M., Cavani, F., 2014. Zr/P/O catalyst for the direct acid chemo-hydrolysis of non-pretreated microcrystalline cellulose and softwood sawdust. *Appl. Catal. B* 145, 24–33. <https://doi.org/10.1016/j.apcatb.2012.12.035>.
- Gong, C., Meng, X., Jin, C., Yang, M., Liu, J., Sheng, K., Zhang, X., 2023. Green synthesis of cellulose formate and its efficient conversion into 5-hydroxymethylfurfural. *Ind. Crop. Prod.* 192, 115985 <https://doi.org/10.1016/j.indcrop.2022.115985>.
- Gong, J., Li, J., Xu, J., Xiang, Z., Mo, L., 2017. Research on cellulose nanocrystals produced from cellulose sources with various polymorphs. *RSC Adv.* 7, 33486. <https://doi.org/10.1039/c7ra0622b>.
- Gromov, N.V., Ogorodnikova, O.L., Medvedeva, T.B., Panchenko, V.N., Yakovleva, I.S., Isupova, L.A., Timofeeva, M.N., Taran, O.P., Aymonier, C., Parmon, V.N., 2023. Hydrolysis-dehydration of cellulose: efficiency of NbZr catalysts under batch and flow conditions. *Catalysts* 13, 1298. <https://doi.org/10.3390/catal13091298>.
- Istasse, T., Richel, A., 2020. Mechanistic aspects of saccharide dehydration to furan derivatives for reaction media design. *RSC Adv.* 10, 23720–23742. <https://doi.org/10.1039/d0ra03892j>.
- Kang, S., Fu, J., Zhang, G., 2018. From lignocellulosic biomass to levulinic acid: a review on acid-catalyzed hydrolysis. *Renew. Sust. Energy Rev.* 94, 340–362. <https://doi.org/10.1016/j.rser.2018.06.016>.
- Kuster, B.F.M., Temmink, H.M.G., 1977. The influence of pH and weak-acid anions on the dehydration of D-fructose. *Carbohydr. Res.* 54, 185–191. [https://doi.org/10.1016/s0008-621\(00\)84808-9](https://doi.org/10.1016/s0008-621(00)84808-9).
- Lan, L., Chen, H.H., Lee, D., Xu, S.J., Skillen, N., Tedstone, A., Robertson, P., Garforth, A., Daly, H., Hardcre, C., 2022. Effect of ball-milling pretreatment of cellulose on its photoreforming for H₂ production. *ACS Sust. Chem. Eng.* 10, 4862–4871. <https://doi.org/10.1021/acscuschemeng.1c07301>.
- Li, G.H., Zhang, Y., Zhao, C., Xue, H.T., Yuan, L., 2020. Chemical variation in cell wall of sugar beet pulp caused by aqueous ammonia pretreatment influence enzymatic digestibility of cellulose. *Ind. Crop. Prod.* 155, 112786 <https://doi.org/10.1016/j.indcrop.2020.112786>.
- Liao, Y., Beeck, B.O., Thielemans, K., Ennaert, T., Snelders, J., Dusselier, M., Courtin, C. M., Sels, B.F., 2020. The role of pretreatment in the catalytic valorization of cellulose. *Mol. Catal.* 487, 110883 <https://doi.org/10.1016/j.mcat.2020.110883>.
- Meng, X., Pu, Y., Yoo, C.G., Li, M., Balli, G., Park, D.Y., Gjersing, E., Davis, M.F., Muchero, W., Tuskan, G.A., Tschaplinski, T.J., Ragauskas, A.J., 2017. An in-depth understanding of biomass recalcitrance using poplar variants as the feedstock. *ChemSusChem* 10, 139–150. <https://doi.org/10.1002/cssc.201601303>.
- Mika, L.T., Cséfalvay, E., Németh, A., 2018. Catalytic conversion of carbohydrates to initial platform chemicals: chemistry and sustainability. *Chem. Rev.* 118, 505–613. <https://doi.org/10.1021/acs.chemrev.7b00395>.
- Moreau, C., Durand, R., Roux, A., Tichit, D., 2000. Isomerization of glucose into fructose in the presence of cation-exchanged zeolites and hydrotalcites. *Appl. Catal. A* 193, 257–264. [https://doi.org/10.1016/S0926-860X\(99\)00435-4](https://doi.org/10.1016/S0926-860X(99)00435-4).
- Mukherjee, A., Dumont, M.J., Rahavan, V., 2015. Review: sustainable production of hydroxymethylfurfural and levulinic acid: challenges and opportunities. *Biomass Bioenerg.* 72, 143–183. <https://doi.org/10.1016/j.biombioe.2014.11.007>.
- Ni, J., Teng, N., Chen, H., Wang, J., Zhu, J., Na, H., 2015. Hydrolysis behavior of regenerated celluloses with different degree of polymerization under microwave radiation. *Bioresour. Technol.* 191, 229–233. <https://doi.org/10.1016/j.biotech.2015.05.036>.
- Ohara, M., Takagaki, A., Nishimura, S., Ebitani, K., 2010. Syntheses of 5-hydroxymethylfurfural and levoglucosan by selective dehydration of glucose using solid acid and base catalysts. *Appl. Catal. A* 383, 149–155. <https://doi.org/10.1016/j.apcata.2010.05.040>.
- Patet, R.E., Koehle, M., Lobo, R.F., Caratzoulas, S., Vlachos, D.G., 2017. General acid-catalysis in the dehydrative aromatization of furans to aromatics in H-[Al]-BEA, H-[Fe]-BEA, H-[Ga]-BEA, and H-[B]-BEA zeolites. *J. Phys. Chem. C* 121, 1366–13679. <https://doi.org/10.1021/acs.jpcc.7b02344>.
- Pedersen, A.T., Ringborg, R., Grotkjær, T., Pedersen, S., Woodley, J.M., 2015. Syntheses of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose-fructose mixtures. *Chem. Eng. J.* 273, 455–464. <https://doi.org/10.1016/j.cej.2015.03.094>.
- Pileidis, F.D., Titirici, M.M., 2016. Levulinic acid biorefineries: new challenges for efficiently utilization of biomass. *ChemSusChem* 9, 562–582. <https://doi.org/10.1002/cssc.201501405>.
- Rathour, R.K., Behl, M., Dhashmana, K., Sakhuja, D., Ghai, H., Sharma, N., Meena, K.R., Bhatt, A.K., Bhatia, R.K., 2023. Non-food crops derived lignocellulose biorefinery for sustainable production of biomaterials, biochemicals and bioenergy: a review on trends and techniques. *Ind. Crop. Prod.* 204, 117220 <https://doi.org/10.1016/j.indcrop.2023.117220>.
- Rezayan, A., Zhang, Y.S., Li, B.J., Xu, C.C., 2023. Catalytic conversion of cellulose to 5-hydroxymethylfurfural: advancements in heterogeneous catalysts and cutting-edge hydrolysis strategies (early access) *ChemCatChem*. <https://doi.org/10.1002/cctc.202300973>.
- Rout, P.K., Nannaware, A.D., Prakash, O., Kalra, A., Rajasekharan, R., 2016. Synthesis of hydroxymethylfurfural from cellulose using green processes: a promising biochemical and biofuel feedstock. *Chem. Eng. Sci.* 142, 318–346. <https://doi.org/10.1016/j.ces.2015.12.002>.
- Schwarz, W.H., 2001. The cellulosome and cellulose degradation by anaerobic bacteria. *Appl. Microbiol. Biotechnol.* 56, 634–649. <https://doi.org/10.1007/s002530100710>.
- Shi, N., Zhu, Y., Qin, B., Zhu, T., Huang, H., Liu, Y., 2022. Conversion of cellulose into 5-hydroxymethylfurfural in a biphasic system catalyzed by aluminum sulfate and byproduct characterization. *ACS Sust. Chem. Eng.* 10, 10444–10456. <https://doi.org/10.1021/acssuschemeng.1c08239>.
- Shimizu, F.L., Monteiro, P.Q., Ghiraldi, P.H.C., Melati, R.B., Pagnocca, F.C., de Souza, W., Sant'Anna, C., Brienza, M., 2018. Acid, alkali and peroxide pretreatments increase the cellulose accessibility and glucose yield of banana pseudostem. *Ind. Crop. Prod.* 115, 62–68. <https://doi.org/10.1016/j.indcrop.2018.02.024>.
- Steinbach, D., Kruse, A., Sauer, J., 2017. Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production – a review. *Biomass Conv. Bioref.* 7, 247–274. <https://doi.org/10.1007/s13399-017-0243-0>.
- Takeuchi, Y., Jin, F., Tohji, K., 2008. Acid catalytic hydrothermal conversion of carbohydrate biomass into useful substances. *J. Mater. Sci.* 43, 2472–2475. <https://doi.org/10.1007/s10853-007-2121-z>.
- Takkellapati, S., Li, T., Gonzalez, M.A., 2018. An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery. *Clean. Technol. Environ. Policy* 20, 1615–1630. <https://doi.org/10.1007/s10098-018-1568-5>.
- Tsalagkas, D., Zhai, L.D., Kafy, A., Kim, J.W., Kim, H.C., Kim, J., 2020. Production of micro- and nanofibrillated cellulose through an aqueous counter collision system followed by ultrasound: effect of mechanical pretreatments. *J. Nat. Fibers* 17, 1099–1110. <https://doi.org/10.1080/15440478.2018.1558144>.
- Vaidya, A.A., Murton, K.D., Smith, D.A., Dedual, G., 2022. A review on organosolv pretreatment of softwood with a focus on enzymatic hydrolysis of cellulose. *Biomass Conv. Bioref.* 12, 5427–5442. <https://doi.org/10.1007/s13399-022-02373-9>.
- Velvizhi, G., Balakumar, K., Shetti, N.P., Ahmad, E., Pant, K.K., Aminabhavi, T.M., 2022. Integrated biorefinery processes for conversion of lignocellulosic biomass to value added materials: paving a path towards circular economy. *Bioresour. Technol.* 343, 126151 <https://doi.org/10.1016/j.biortech.2021.126151>.
- Wang, T.F., Nolte, M.W., Shanks, B.H., 2014a. Catalytic dehydration of C6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. *Green. Chem.* 45, 548–572. <https://doi.org/10.1039/c3gc41365a>.
- Wang, Y., Song, H., Peng, L., Zhang, Q., Yao, S., 2014b. Recent developments in the catalytic conversion of cellulose. *Biotechnol. Equip.* 28, 981–988. <https://doi.org/10.1080/13102818.2014.980049>.
- Weingarten, R., Cho, J., Xing, R., Conner, W.C., Huber, G.W., 2012. Kinetics and reaction engineering of levulinic acid production from aqueous glucose solutions. *ChemSusChem* 5, 1280–1290. <https://doi.org/10.1002/cssc.201100717>.
- Wen, Z., Yu, L., Mai, F., Ma, Z., Chen, H., Li, Y., 2019. Catalytic conversion of microcrystalline cellulose to glucose and 5-hydroxymethylfurfural over a niobic acid catalyst. *Ind. Eng. Chem. Res.* 58, 17675–17681. <https://doi.org/10.1021/acs.iecr.9b03824>.
- Widsten, P., Murton, K., West, M., 2018. Production of 5-hydroxymethylfurfural and furfural from a mixed saccharide feedstock in biphasic solvent systems. *Ind. Crop. Prod.* 119, 237–242. <https://doi.org/10.1016/j.indcrop.2018.04.032>.
- Wu, Y., Wang, H., Peng, J., Ding, M., 2023. Advances in catalytic valorization of cellulose into value-added chemicals and fuels over heterogeneous catalysts. *Catal. Today* 408, 92–110. <https://doi.org/10.1016/j.cattod.2022.08.012>.
- Yan, K., Jarvis, C., Gu, J., Yan, Y., 2015. Production and catalytic transformation of levulinic acid: a platform for specialty chemicals and fuels. *Renew. Sustain. Energy Rev.* 51, 986–997. <https://doi.org/10.1016/j.rser.2015.07.021>.
- Yao, Y., Chen, S., Zhang, M., 2022. Sustainable approaches to selective conversion of cellulose into 5-hydroxymethylfurfural promoted by heterogeneous acid catalysts: a review. *Front. Chem.* 10, 880603 <https://doi.org/10.3389/fchem.2022.880603>.
- Zhang, L., Xi, G., Chen, Z., Jiang, D., Yu, H., Wang, X., 2017. Highly selective conversion of glucose into furfural over modified zeolites. *Chem. Eng. J.* 307, 868–876. <https://doi.org/10.1016/j.cej.2016.09.001>.
- Zhang, S., Jin, C., Sheng, K., Zhang, X., X., 2022. Mechanistic investigation of cellulose formate to 5-hydroxymethylfurfural conversion in DMSO-H₂O. *J. Mol. Liq.* 348, 118471 <https://doi.org/10.1016/j.molliq.2022.118471>.
- Zhou, S., Zhang, M., Zhu, L., Zhao, X., Chen, J., Chen, W., Chang, C., 2023. Hydrolysis of lignocellulose to succinic acid: a review of treatment methods and succinic acid applications. *Biotechnol. Biofuels Bioprod.* 16, 1–17. <https://doi.org/10.1186/s13068-022-02244-5>.
- Zoghalmi, A., Paës, G., 2019. Lignocellulosic biomass: understanding recalcitrance and predicting hydrolysis. *Front. Chem.* 7, 874. <https://doi.org/10.3389/fchem.2019.00874>.



Influence of delignification and reaction conditions in the aqueous phase transformation of lignocellulosic biomass to platform molecules

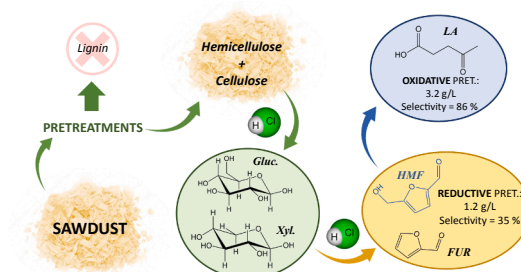
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HIGHLIGHTS

- Acid hydrolysis of pine sawdust was studied in a batch reactor at mild conditions.
- The effect of two delignification procedures (oxidative and reductive) was studied.
- Both procedures improve the yield to soluble products, specially the oxidative one.
- A kinetic model has been developed for understanding the hydrolysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

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ABSTRACT

The effect of oxidative and reductive delignification processes on the hydrolysis of pine sawdust at mild conditions (200–1000 ppm of HCl and 140–220 °C) is studied in this work. Dimers and reduced sugars are the main products obtained with the fresh sawdust (>82%), reaching a maximum liquid phase yield of 17% after 8 h, at the strongest conditions. This conversion increases up to almost 40% with the pretreated sawdust, obtaining selectivities higher than 87% of levulinic acid and a well-defined distribution of the relevant platform molecules (sugars, HMF, furfural, levulinic acid) as function of the severity of the reaction, decreasing the humins formation and being possible to define different conditions to maximize each yield. These conclusions were corroborated by the kinetic analysis, obtaining a clear decrease in the energy activation for all the individual steps involved in this process.

1. Introduction

Biomass is, after atmospheric CO₂, the most abundant carbon source. Considering its renewable character and its well-dispersed distribution around the planet, biomass is the most promising alternative to replace the mineral sources, mainly to obtain chemical compounds at large scale, in a biorefinery concept (Gallo and Trapp, 2017; McKendry, 2002;

Peters et al., 2011; Pileidis and Titirici, 2016). Thermochemical processes, such as pyrolysis, gasification or liquefaction, have been proposed for its global valorization obtaining favorable results (Dhyani and Bhaskar, 2018; Faba et al., 2015; Luque and Speight, 2015; Zhou et al., 2011). In the last years, catalytic routes have also focused the attention of many researchers (Gómez Millán et al., 2019; Mukherjee et al., 2015), considering different processes to specifically valorize one of the main

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fractions of the biomass: cellulose (38–50%), hemicellulose (23–32%) or lignin (15–30%) (Alonso et al., 2010; Gómez Millán et al., 2019). These processes are more sustainable than thermochemical routes (mild temperatures and low pressures) and produce the intermediates of a huge variety of commodities, as well as biofuel precursors (Gómez Millán et al., 2019). The hydrolysis is one of the main alternatives proposed in this field, allowing obtaining sugar monomers and derived aldehydes and acids from hemicellulose and cellulose fractions, interesting platform molecules as intermediates of high-value chemical products.

The presence of lignin fraction affects the efficiency and product distribution obtained with this process. Working at soft conditions, lignin decreases the hydrolysis rate, since it reduces the contact between the catalyst and the (hemi)cellulose polymers. On the other hand, if reaction conditions are strong enough to alter the lignin structure, its decomposition could produce different undesired products or enhance oligomerization and humins productions, reducing the selectivity to the desired fractions (Zhou et al., 2017). In addition, a great effort has been recently paid in the lignin upgrading, especially to obtain oxygenated aromatic compounds (Van den Bosch et al., 2015). Thus, from both points of view, understanding the effect of the lignin on the hydrolysis mechanism, as well as determining the effect of the different delignification procedures on the reactivity of the resulting (hemi)cellulosic fraction is of key interest in the integral upgrading of lignocellulosic biomass and wastes.

Different procedures have been suggested to remove the lignin from lignocellulosic biomass (delignification). Some of them are already implemented in paper-mill industries. Thus, lignin can be removed using basic catalysis, such as KOH, NaOH and Na₂S (Kraft process), at moderate pressures and a temperature range of 140–170 °C (Schutyser et al., 2018; Vu et al., 2004). Strong acids, H₂SO₄ or HCl at mild conditions (120–210 °C) are also proposed, being not so often used because of the corrosion problems (Schutyser et al., 2018; Sturgeon et al., 2014). The extraction by the selective extraction in organic solvents (Organosolv process) is also proposed at industrial scale (Baig et al., 2019; Romání et al., 2011). All these pretreatments are focused on the valorisation of cellulosic fraction, producing irreversible damage in the hemicellulosic one.

Trying to prevent the damage to the hemicellulose, two softer alternatives were considered: oxidative and reductive methods. The oxidative method usually uses sodium chlorite, which is *in situ* transformed into chlorine dioxide. This compound breaks the lignin structure by a complex and non-well defined mechanism, without altering the cellulose and hemicellulose until removing around 60% of the lignin (Siqueira et al., 2013). On the contrary, reductive delignification is carried out with Ru/C catalyst under H₂ atmosphere, obtaining a “lignin oil” composed by monomers and short oligomers of aromatic compounds that are isolated from the sugar matrix with quality enough to be valorised in subsequent steps (Van den Bosch et al., 2015).

As to the hydrolysis, it could take place catalyzed by organic acids (oxalic acid), inorganic acids (H₂SO₄, HCl), salts ((NH₄)₂SO₄/SO₃), Lewis acids (AlCl₃, ZnCl₂) and ion exchange resins (Garcés et al., 2019; Kang et al., 2018). Mechanistic studies considering unaltered biomass or commercial polymers conclude that there is a sequential depolymerization, firstly in short oligomers (polysaccharides), being totally hydrolyzed in monosaccharides (mainly glucose, xylose and arabinose). Reaction conditions promote the dehydration of these sugars into the corresponding cyclic aldehydes (HMF, furfural) mainly when using Lewis acids (Marianou et al., 2018). These acids catalyze the isomerization of glucose into fructose, sugar that yields the highest HMF yields (Thapa et al., 2017). On the other hand, when using Brønsted acids, this isomerization does not take place and the cyclic dehydration is thermodynamically less favorable. In addition, Brønsted acidity promotes the degradation of HMF (cyclic break-up and rehydration), obtaining formic and levulinic acid (Garcés et al., 2017; Mukherjee et al., 2015; Van den Bosch et al., 2015). Thus, reaction conditions must be balanced to optimize the production of HMF or levulinic acid, the most relevant

platform molecules (Garcés et al., 2017; Gómez Millán et al., 2019). Despite the huge number of studies in this field, there is a relevant gap related to the effect of a previous biomass delignification on the final hydrolysis results.

This work analyses the effects of the oxidative and reductive delignification pretreatments in the subsequent hydrolysis of pine sawdust. The hydrolysis is studied using HCl as catalyst, considering the influence of temperature and acid concentration. The aim of this work is to identify the optimum conditions to enhance the production of different platform molecules, levulinic acid and HMF being the most relevant ones. Despite the HMF is faster produced after the isomerization of glucose into fructose by the presence of a Lewis acid (Rosatella et al., 2011; Toftgaard Pedersen et al., 2015), a mineral acid is proposed as catalyst considering that temperature and time could balance the kinetic without introducing a solid catalyst that could significantly reduce the kinetic of the first step of the reaction, due to the low efficiency of the solid-solid interactions (Chen et al., 2018).

2. Materials and methods

2.1. Materials

Pine sawdust was collected from a furniture factory located in Asturias, Spain. D-glucose (≥99.5%), xylose (≥99%), arabinose (≥99%), cellobiose (98%), maltotriose (98%) were purchased from Panreac Applichem. HMF (≥99%), furfural (≥99%), levulinic acid (98%) for HPLC calibration and acetic acid (98%) sodium chlorite (98%) and 5% Ru/C catalyst were purchased from Sigma-Aldrich. Methanol (98%) was purchased from VWR and hydrochloric acid (37%) was provided by Fisher Chemical. The reactants were used without any further purification. Solutions were prepared using distilled water.

2.2. Sawdust characterization

The determination of the content of carbon, hydrogen, nitrogen and sulfur of sawdust (raw and delignified ones) has been carried out using an elemental analyzer C, H, N, S Elemental Vario EL available at the Scientific-Technical Services of the University of Oviedo. Chemical component analysis including cellulose, hemicellulose, lignin, and extractives of sawdust (raw and delignified ones) was carried out following standard procedures (Li et al., 2004; Selvaraju and Bakar, 2017).

2.3. Delignification procedures

The oxidative delignification was carried out according to the procedure proposed in the literature (Yu et al., 2011), using sodium chlorite and acetic acid (w/v = 3:1) as reactants. 15 g of natural sawdust was mixed to 600 mL distilled water in a ball flask with a reflux. When the temperature reaches 80 °C, 7.5 g of acetic acid were added, and 22.5 g sodium chlorite were dosed in four times (every 30 min). After this time, the delignified sawdust was washed with distilled water until washings were colorless, then rinsed again with distilled water for 3 times. Finally, the sample was dried in an oven at 110 °C and milled to a particle size of 200 µm.

The reductive delignification was performed according to Van den Bosch proposal (Van den Bosch et al., 2015). 10 g of raw sawdust, 1.5 g of 5% Ru/C and 200 mL of methanol were loaded into a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal). The reactor was purged with N₂ and pressurized with 25 bar H₂ at room temperature. The mixture was stirred at 700 rpm and the temperature was increased to 150 °C for 6 h.

2.4. Sawdust hydrolysis

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) with a back-pressure regulator and a PID

temperature controller. 3 g of pine sawdust were suspended in 0.2 L of reaction volume. Once the desired temperature was reached (140–220 °C as function of the experiment), 12 mL of an HCl solution were added to achieve the desired concentration in each experiment (from 200 to 1000 ppm). Air was purged with N₂, and the hydrolysis was carried out with 10 bar of N₂ with a stirring of 700 rpm for 8 h. Samples were taken from the sampling port, filtered using 0.22 µm Nylon syringe filters and diluted in a 1:2 ratio. Reactants and products of hydrolysis were quantified by HPLC (1200 Series, Agilent) equipped with a RI detector and a Hi-Plex H column, using 0.5 mL/min of 5 mM H₂SO₄ as a mobile phase.

The sawdust conversion is calculated in terms of liquid-phase carbon yield, a concept involving the theoretical sawdust required to obtain all compounds detected in the liquid phase, extensively used in biomass conversion (Garcés et al., 2019; Giannakopoulou et al., 2010; Kluska et al., 2019). The direct use of the conversion calculated from solid weight measurement before and after the reaction is discarded since the temporal evolution cannot be analyzed based on this parameter, and the accurateness is limited by the presence of humins or other insoluble products (mainly the trimers). The liquid-phase carbon yield is calculated according to Eq. (1):

$$\varphi_s = \frac{V \cdot \sum (n_i \cdot C_i) \cdot MW_C}{\%C \cdot m_{\text{sawdust}}} \cdot 100 \quad (1)$$

where “V” is the volume of the solution; “C_i”, the molar concentration of each compound detected in each liquid phase; “n_i”, the number of carbons in the molecule of “i” compound; “m_{sawdust}” is the mass of cellulose introduced in the reactor at the initial point; “MW_C” is the molar mass of carbon; and “%C” corresponds to the mass percentage of carbon in this sawdust, according to the elemental analysis.

The selectivity to any individual product quantified in the liquid phase is indicated in carbon basis, according to Eq. (2):

$$S_i(\%) = \frac{n_i \cdot C_i}{\sum_{j=1}^n n_j \cdot C_j} \cdot 100 \quad (2)$$

being n_i·C_i the moles of carbon that contains the reaction product *i* and $\sum_{j=1}^n n_j \cdot C_j$ the sum of the moles of carbon corresponding to reaction products.

With the aim to guarantee the reproducibility of these analyses, each reaction was carried out at least twice. Considering the heterogeneity and complexity of this raw material, results were validated if the standard deviation between two experiments is lower than 7%. In case of a higher discrepancy, a third experiment allowed defining the good results. As consequence, all the values shown in this work correspond to the average of two experiments.

3. Results and discussion

3.1. Sawdust characterization before and after delignification

The amount of cellulose, hemicellulose and lignin was determined before and after the delignification pretreatments, the results being summarized in Table 1. Each analysis was carried out twice obtaining deviations lower than 3%. Results shown in Table 1 are the average values obtained with both analyses.

Data obtained for natural sawdust are in good agreement with typical composition of softwood, with percentages from 25 to 35% of the three main polymers and less cellulose than hardwood (Cotana et al., 2014). From a macroscopic point of view, the oxidative pretreatment seems to be quite efficient, since the original brown color of the pine sawdust disappears, obtaining a white material. This evolution is a clear consequence of the lignin removal (Trisant and Gunardi, 2020), and it is not totally observed in the case of the reductive pretreatment. However, the use of a carbonaceous support could alter this appreciation.

Considering the quantitative analysis, the lignin content decreases

Table 1

Sawdust characterization, in terms of fractionation and elemental analysis, before and after delignification pretreatment. Result expressed in dry basis.

	Natural Sawdust	Oxidative delignification	Reductive delignification
Extractives (%)	6.9	–	–
Cellulose (%)	24.9	58.1	38.5
Hemicellulose (%)	31.5	35.2	57.1
Lignin (%)	36.6	6.7	4.4
C (%)	46.9	40.7	42.6
O (%)	43.6	52.0	49.1
H (%)	6.2	6.3	5.5
N (%)	2.2	0.4	0.7
S (%)	1.1	0.6	2.1

considerably after both pretreatments, with the subsequent increase in the relative percentage of cellulose or hemicellulose. Thus, 81.5% of lignin is removed in case of the oxidative delignification, whereas this value increases up to more than 88% with the reductive method. These values are in good agreement with previous literature applied to other raw materials, suggesting that the reductive pretreatment is more effective than the oxidative one (Hubbell and Ragauskas, 2010; Van den Bosch et al., 2015). Despite the similar delignification efficiency, significant differences between both methods related to the effects on the hydrocarbon structure are observed. It can be concluded that the reductive method mainly affects the lignin fraction, since the decrease in the proportion of this fraction directly correlates with the increase in the cellulose and hemicellulose ones (theoretical values corresponding to this delignification ratio: 42.2% of cellulose and 53.4% of hemicellulose), with slight differences (less than 4%) in favor of hemicellulose. This fact indicates that only a small fraction of cellulose is partially degraded, obtaining a less crystalline structure with similar behavior as the hemicellulose. On the other hand, when the oxidative method is used, the expected percentages of cellulose and hemicellulose if only lignin was removed would be 41 and 52%, respectively. Considering the high discrepancy with respect to the values obtained, a partial degradation of hemicellulose is produced. It removes a relevant fraction of external functional groups, obtaining a high ordered polymer, with a structure closer to cellulose than to the initial hemicellulose one. This conformation evolution could affect the sawdust behavior in hydrolysis conditions, being not possible to determine if this is a positive or a negative effect before being tested in the reaction. According to these results, the reductive pretreatment is less aggressive with the hemicellulosic structure of the sawdust, obtaining a more selective delignification than with the oxidative one.

This hypothesis is corroborated by the elemental analysis, whose results are also summarized in Table 1. Regarding to the fresh material, values are similar to those proposed in the literature for other softwoods (Shen et al., 2010). Results related to delignified samples are congruent with the removal of lignin, with a decrease in N and C, and a slight increase in the oxygen percentage (present in high amount in sugar structures). The decrease in the C/H ratio is also congruent with the removal of aromatic rings, typical structures of lignin fractions, and the prevalence of saturated compounds. The more marked changes observed with the oxidative method are in good agreement with its more aggressive character. This fact suggests that samples after reductive pretreatment have lost the lignin fixed structure, but the total decomposition is not achieved, with some S and N still remaining in the solid sample.

3.2. Hydrolysis of fresh sawdust

The acidic hydrolysis of fresh sawdust (without any pretreatment) was carried out using HCl as catalyst, in the range 200–1000 ppm, in order to identify the optimum conditions, and to determine the effect the

pH in these reactions. The mineral acid has been reported as an active catalyst for the hydrolysis of biomass polymers (Marianou et al., 2018; Sarno et al., 2020; Yang et al., 2012), but it could also enhance the subsequent steps of sugar dehydrations and degradations, obtaining acids and humins (Clauser et al., 2020; Garcés et al., 2017, 2019). Thus, a balance between positive and negative effects requires a well-defined concentration, different for each type of wood, trying to enhance the production of desired platform molecules. A blank experiment was done to discard the hydrothermal hydrolysis, despite being not expected considering the temperatures of the non-catalytic hydrolysis reported in the literature (Kruse and Gawlik, 2003; Toor et al., 2011). The evolution of the liquid-phase carbon yield with the time is analyzed in Fig. 1a. Values plotted in this figure correspond to the average ones after two repetitions, obtaining standard deviations lower than 7% in all the cases, as observed by the small error bars than, in some cases, cannot be appreciated.

Results obtained with 200 ppm indicate an almost negligible degradation activity at these conditions, reaching constant yield in less than two hours (0.9%). Considering the total amount of carbohydrates present in the sawdust (cellulose and hemicellulose), this liquid-phase carbon yield represents 1.8% of the maximum theoretical grade of hydrolysis. A clear evolution is observed when increasing the acidity up to 600 ppm, with a maximum carbon yield obtained after 4 h of reaction (12.5%). This value corresponds to the hydrolysis of 24.6% of the total sugar fractions in this sawdust. Once the maximum is reached, it keeps constant with the time, without observing any evolution when the reaction is extended up to 24 h. This result suggests that conditions are not

severe enough to degrade the recalcitrant structure of biomass polymers. This hypothesis is congruent with results obtained with 1000 ppm of HCl, observing a faster hydrolysis that only reaches a maximum of 15.6% (equivalent to 31.4% of the sugar polymers). This value, obtained after 5 h, is not stable, followed by a continuous decrease for products detected, up to 9.8% after 24 h. Considering the irreversible character of this reaction, the decreasing trend suggests that, at these conditions, different side reactions involving solid products (humins production) take place. According to the literature, humins are formed by cross-polymerization reactions between HMF, furfural and sugars during the acid catalyzed hydrothermal hydrolysis (Patil et al., 2012; van Zandvoort et al., 2013). The fact that this is only observed at the most severe conditions suggests a different product distribution, which is analyzed in Fig. 2.

This figure analyses the results in terms of carbon selectivities. The compounds considered for this analysis represent a carbon balance closure higher than 60% in all the cases, the value being higher as the acidity decreases (70.4, 75.4 and 60.5%, for 200, 600 and 1000 ppm of HCl, respectively). Seven compounds derived from the typical route of acid-catalyzed biomass hydrolysis are detected: dimers (corresponding mainly, but not only, to cellobiose), three reduced sugars (glucose, arabinose and xylose), HMF (cyclic aldehyde derived from hexose), furfural (cyclic aldehyde derived from pentoses), levulinic and formic acids. These last two products are obtained by the rehydration of HMF in equimolar amounts. Considering that there is not any other reaction that consumes any of these acids, same concentrations of both acids are obtained, so only levulinic acid is shown in the graphs (to prevent repeated information). An almost perfect carbon balance closure is obtained (higher than 90% in all the cases) if this analysis is completed with light alcohols detected at significant extent. These alcohols are identified as terminal units of sugar polymers, this location justifying the high amount obtained. However, as these compounds do not interfere in the main reaction scheme, they are not included in the following analyses.

As anticipated by the soft conditions (low temperature and low acidity), dimers are the main product obtained during the first 7 h, despite the HCl concentration used. The absence of glucose and the detection of arabinose and xylose during the first 2 h is congruent with the recalcitrant structure of cellulose and the presence of pentoses in the external structure of hemicellulose (weakest bonds, the most easily hydrolyzed ones). With 200 and 600 ppm of HCl, the relative relevance of these pentoses decreases as the incomplete hydrolysis of cellulose increases, observing low amount of glucose and suggesting that most of the dimers correspond to cellobiose (experimentally tested). Thus, stable selectivities around 7% of total reduced sugars (TRS) are obtained during the first 7 h. A slight improvement with the time is observed, with an increase up to 17 and 13.7% of TRS, with 200 and 600 ppm. However, considering the low hydrolysis degree, these values only correspond to 68 and 277 ppm of TRS, respectively. As anticipated, no aldehydes or acids are observed at these conditions. The evolution with 1000 ppm is considerably different, with a relevant formation of TRS (24% after 7 h, 52.8% after 24 h, corresponding with 686 and 1020 ppm, respectively). Aldehydes formation is clearly observed after 24 h, with 8% of HMF and 10.2% of furfural, whereas levulinic acid is not detected in these experiments. The presence of aldehydes in the liquid phase is congruent with the promotion of humins and the decrease in the carbon balance.

According to these results, increasing the reaction temperature working with 1000 ppm of HCl is suggested as the following approach, trying to balance the promotion of the desired steps with the avoidance of side reactions. The influence of temperature was studied in the range 140–220 °C, obtaining the evolution of the liquid-phase carbon yield observed in Fig. 1b.

Experimental results follow the anticipated trend considering the positive effect of temperature in the kinetics and the relevance of side reactions obtained when working at 140 °C. Thus, there is a first increase

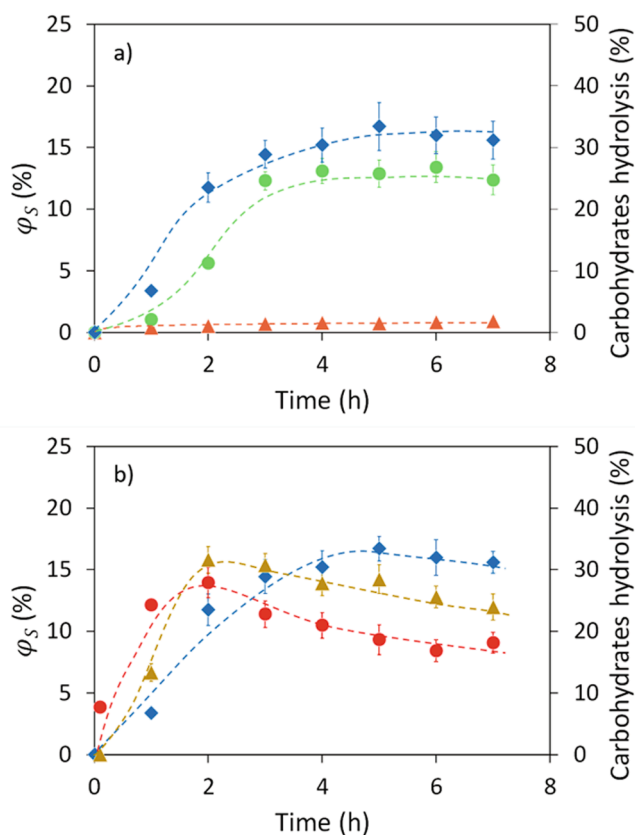


Fig. 1. Temporal evolution of the liquid-phase carbon yield obtained in the hydrolysis of fresh sawdust as function of: (a) the acid concentration and (b) the reaction temperature. Data analyzed considering the total amount of sawdust (left axes) and only the potential sugars, cellulose, and hemicellulose (right axes). Results corresponding to (▲) 200 ppm of HCl, 140 °C; (●) 600 ppm of HCl, 140 °C; (◆) 1000 ppm of HCl, 140 °C; (▲) 1000 ppm of HCl, 180 °C; (●) 1000 ppm of HCl, 220 °C.

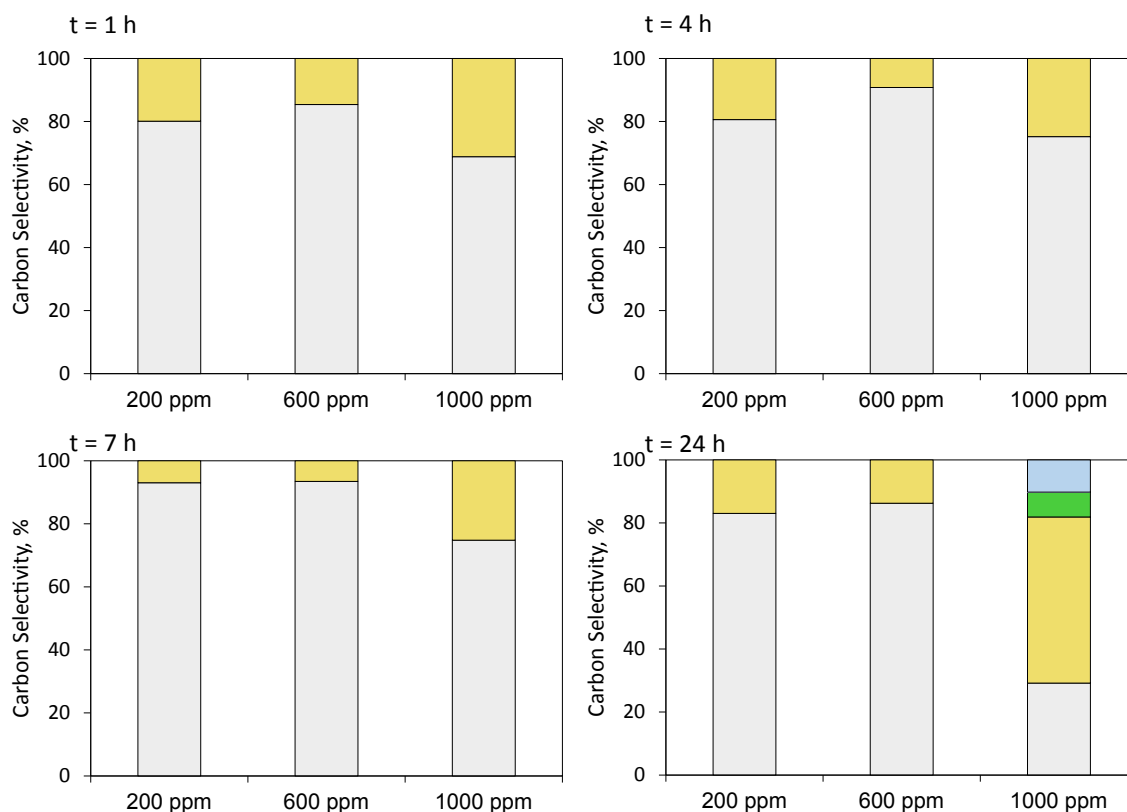


Fig. 2. Comparative distribution of products selectivities obtained with fresh sawdust as function of the acidity. Data corresponding to dimers (grey); TRS (yellow); HMF (green); furfural (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the liquid-phase carbon yield, reaching a maximum value of around 16%, despite the temperature. This result indicates the maximum hydrolysis efficiency at these conditions, corresponding with 34% of the potential amount of sugars. This result suggests that temperature is not the key parameter for this variable. However, it is worth noticing that this first step requires less time as the temperature increases, i.e., 4–5 h, 2 h and around 1.5–2 h at 140, 180 and 220 °C, respectively. After these maximums, the relevance of side reactions is clearly observed, being promoted by the temperature. In good agreement, final carbon balance closures after 24 h decrease from 59% to 54 and 33%, as the temperature increases.

These results only consider the solubilization of sugar fractions, the analysis of selectivities being required to determine the optimum conditions for recovering each platform molecule. The simultaneous comparison after different reaction times is plotted in Fig. 3.

A clear influence of reaction temperature is observed, being all the products observed from the first hour when temperature is higher than 140 °C. Xylose is the main product detected at intermediate temperatures and short times, whereas a fast dehydration is observed at 220 °C, aldehydes and acids prevailing over the TRS. The similar amount of arabinose obtained at 180 and 220 °C, not only in selectivity but also in concentration. This result suggests that furfural is mainly produced by the dehydration of xylose, pentose for which the differences are more marked. The glucose dehydration to produce HMF is observed at 180 and 220 °C, with selectivities of 5.6 and 14.5%, respectively, in less than 1 h. According to the previous literature, Lewis acidity is defined as a key factor to promote the HMF via glucose isomerization, since the fructose dehydration is thermodynamically favored (Marianou et al., 2018). The role of temperature in this step is more relevant when the catalyst is a Brønsted acid (such as the HCl), because of the higher activation energy of the direct glucose dehydration (Yang et al., 2012).

At larger reaction times, side reactions determine the observed product distribution. On the one hand, the almost total rehydration of

HMF into levulinic and formic acid is clearly observed at 220 °C, with the disappearance of this aldehyde and a relevant increase of levulinic acid selectivity (60, 66 and 68% after 4, 7 and 24 h). This effect is less marked at 180 °C. On the other hand, the furfural total amount reaches a maximum of 330 ppm at 180 °C after 4 h (selectivity of 21%), with a soft decrease to 250 ppm after 24 h (equivalent to 18% of selectivity). However, this effect is much more relevant at 220 °C, reaching the maximum furfural concentration (270 ppm) after only 2 h, with a total disappearance of this compound in less than 5 h, due to the promotion of humins.

According to these results, there is not a clear range of conditions to maximize the productivity and selectivity of almost any compound. This fact seems to be determined by the low rate of the first step of the process: the sugar solubilization to produce TRS. Thus, all the concentrations are quite low, and the reaction conditions required to promote this step are so strong that the subsequent steps occur too fast. In this context, the lignin pretreatment could play a relevant role since a feasible degradation of the recalcitrant structure of sugar polymers could reduce the severity requirements to enhance the hydrolysis. Then, the temperature and reaction time would have a key role in maximizing the productivity and selectivity of the platform molecules.

3.3. Influence of the oxidative and reductive pretreatments

To identify the effect of both pretreatments, the comparative analysis of liquid-phase carbon yield obtained is shown in Fig. 4 (Fig. 4a and b). In these plots, values over and below the diagonal line indicate higher or lower values once the pretreatments are applied with respect to the reaction with fresh sawdust, always comparing data at same conditions (temperature and acidity) and time on reaction. The discrepancies between results of each pair of experiments were lower than 8% in all the cases, 2–3% being the typical errors obtained. The error bars are included in the temporal profiles of concentration evolutions.

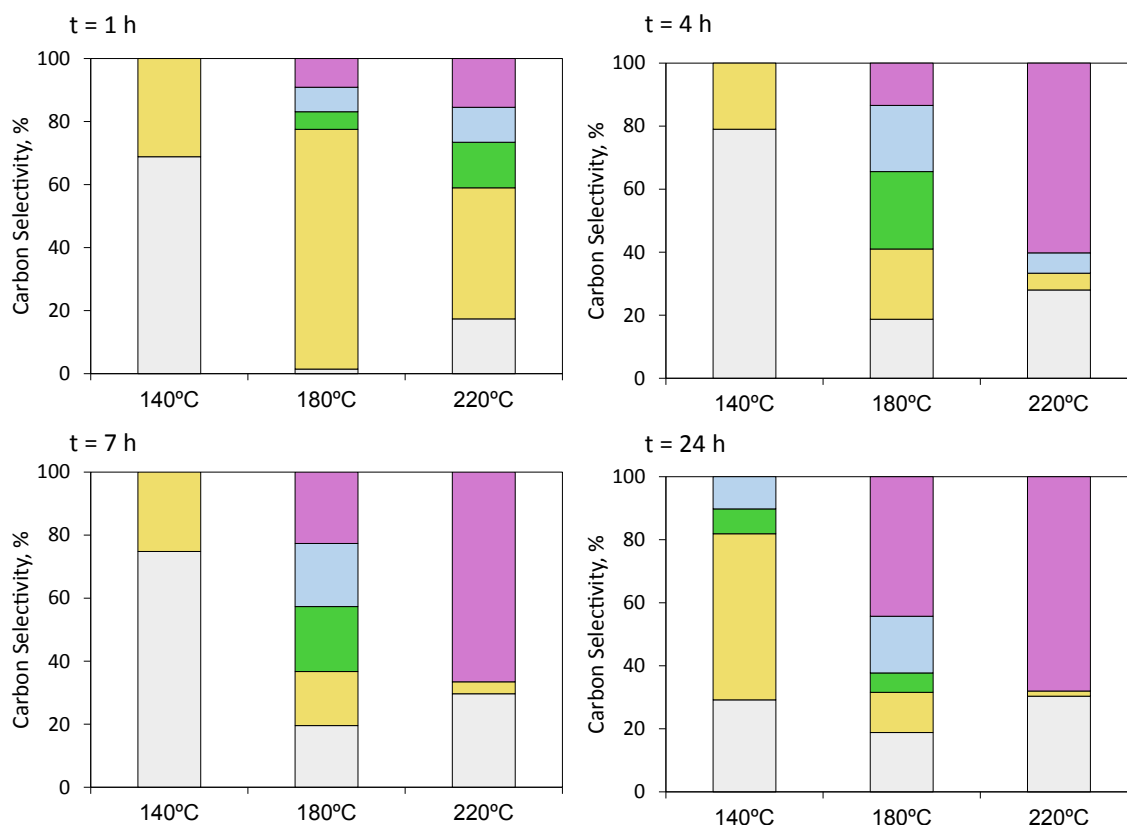


Fig. 3. Comparative distribution of products selectivities obtained with the fresh sawdust as function of the reaction temperature. Data corresponding to dimers (grey); TRS (yellow); HMF (green); furfural (blue); and levulinic acid (purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The comparison considering the total amount of sawdust treated (Fig. 4a) indicates that both pretreatments have a positive effect in the liquid-phase carbon yield, duplicating the values at almost all the conditions, reaching maxima close to 40% when the oxidative pretreatment is applied, at 180 and 220 °C. In addition, the humins production slows down, in good agreement with the increase of the carbon yield increases observed for the pretreated samples. For example, at 220 °C, a decreasing trend is observed after 2 h of reaction, this time being increased up to 5 and 7 h, after the reductive and oxidative pretreatment, respectively. However, if same values are analyzed considering only the potential maximum amount of sugars (Fig. 4b), these values are quite different, since they are strongly affected by the almost total absence of lignin in the pretreated samples. In this case, the differences between reductive and oxidative pretreatments are more evident, with a clear prevalence of the oxidative one, when working at with 1000 ppm of HCl and 180 or 220 °C. Softer conditions (600 ppm and 140 °C) do not imply any improvement with respect to the hydrolysis of fresh sawdust. Despite the low values obtained when working with 200 ppm of HCl, around 10% of liquid-phase carbon yields is reached with both pretreatments whereas no reaction is observed with the fresh material. Two main conclusions of these results can be drawn: i) pretreatments do not modify the potential amount of sugar polymers (increase or reduction) that can be hydrolyzed at these conditions; ii) these pretreatments seem to debilitate the glycosidic bonds, reducing the severity to obtain a similar hydrolytic efficiency. A deeper study of these pretreatments requires the analysis of the products distribution, these data being shown in Fig. 5.

Reactions carried out with 200 ppm of HCl mainly produce dimers and TRS, the dimer concentration being always higher with the oxidative pretreatment than with the reductive one. Thus, in the case of the oxidative pretreatment, dimers correspond to 90% of the total liquid

products during the first 4 h of reaction, decreasing only to 75% after 7 h. On the contrary, an initial 41% of dimer is obtained with the reductive pretreatment, with less than 6% observed after 7 h, when more than 89% of the total selectivity corresponds to TRS and small traces of aldehydes can be observed (1.5% of HMF and 3.7% of furfural). Thus, these conditions are identified as the optimum ones to selectively obtain these sugar monomers, the mixture being always enriched in xylose (75 and 80% when working with the oxidative and reductive treated sawdust). In concentration values, working with 200 ppm, 1.55 g/L of TRS is obtained when working with the treated sample (reductive pretreatment), this value being more than 3 times higher than the value obtained with the oxidative pretreated sample, and 140 times higher than the corresponding one obtained with the fresh sample.

A logical evolution with the acidity, temperature and reaction time is obtained, despite the samples analyzed, with an increase in the degradation process as all these parameters increase. In general, reactions with the oxidized samples suggest a more sensitivity to the reaction parameters, being difficult to control the reaction in the intermediate steps. Thus, levulinic and formic acid are the main compounds identified in the samples at 220 °C after only 1 h of reaction, 79% of selectivity, whereas the corresponding value obtained with the samples pretreated with Ru/C is lower than 10%. These results conclude that the oxidative pretreatment is the optimum one to maximize the production of these platform molecules, obtaining almost a total degradation of all the sugars in less than 7 h (selectivity to levulinic acid higher than 86%). This selectivity cannot be reached without a previous pretreatment, even increasing the reaction time up to 24 h. In concentration terms, this selectivity corresponds to 3.2 g/L of levulinic acid produced with the oxidative pretreatment. With the reductive pretreatment, this amount is limited to 2.4 g/L, these two values being significantly higher than the one obtained during the hydrolysis of the fresh sample (0.8 g/L). An

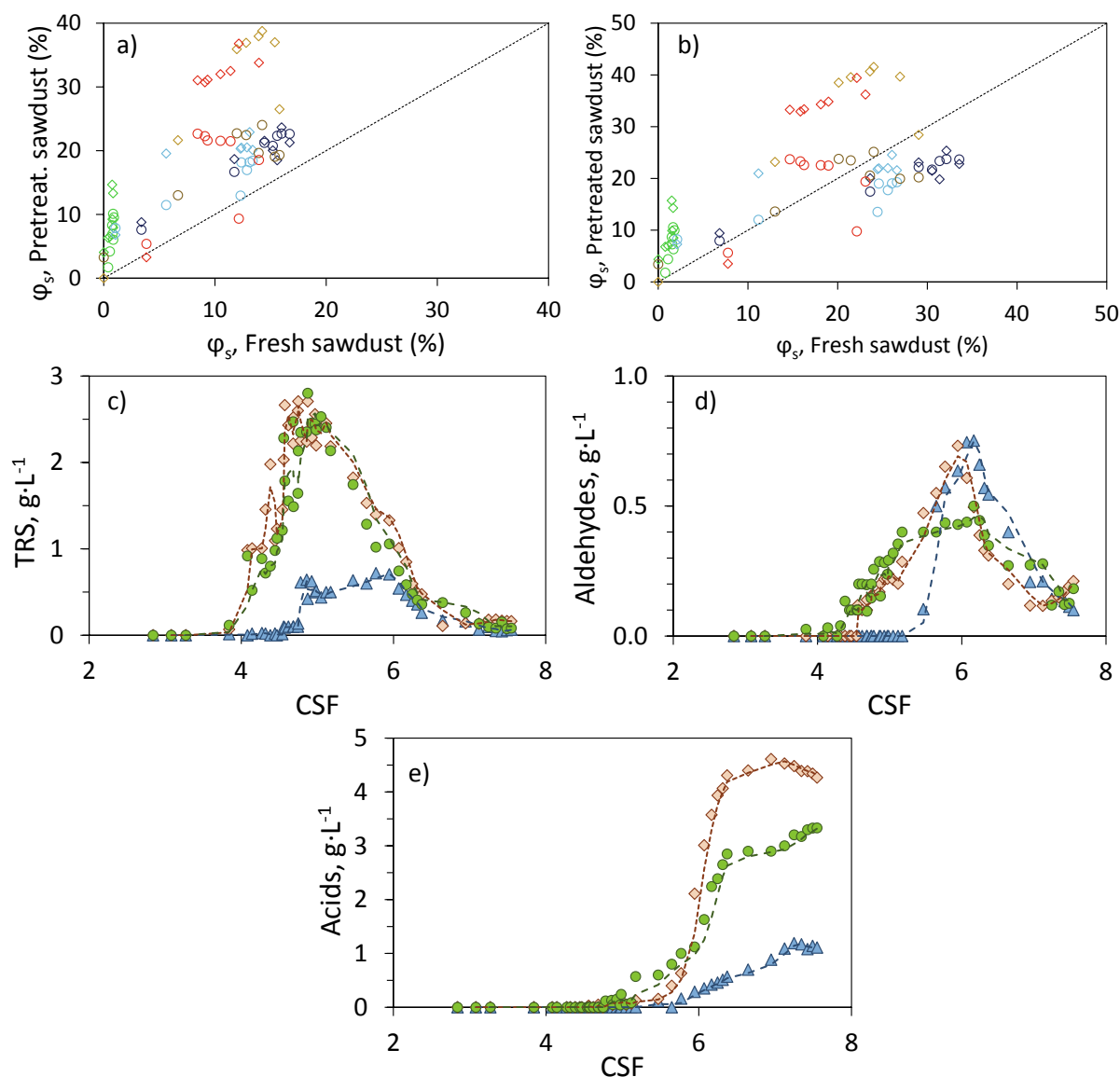


Fig. 4. Comparative analysis of liquid-phase carbon yields obtained with the pretreated (circles for the reductive delignification, diamonds for the oxidative one) and fresh sawdust considering (a) the total amount of sawdust; and (b) cellulose and hemicellulose. Results corresponding to: 200 ppm of HCl and 140 °C (green), 600 ppm of HCl and 140 °C (light blue), 1000 ppm of HCl and 140 °C (dark blue), 1000 ppm of HCl and 180 °C (gold), 1000 ppm of HCl and 220 °C (red). Evolution of (c) TRS, (d) aldehydes, and (e) acids as function of the CSF factor. Data correspond to (▲) fresh sawdust; delignified sawdust using (◆) oxidative and (●) reductive pretreatments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

analysis of variance (ANOVA) comparing values obtained with fresh and pretreated samples corroborates the statistical significance of these differences, obtaining F-values more than one order of magnitude higher than the maximum ones that could be accepted to consider the results as equal, with a level of confidence of 95%.

Concerning the aldehydes (HMF and furfural), a selective production of these intermediates is not possible, since HMF is faster degraded to levulinic acid and a high selectivity of furfural is limited by the undesired oligomerization. In any case, the pretreatments also imply an improvement at this point, the reductive process being the optimum to enhance the particular selectivity of furfural (19% after 3 h of reaction at 180 °C with 1000 ppm of HCl, this selectivity being reduced to 16% at 4 h). The maximum value obtained with the sawdust after the oxidative process is limited to 11%. Seeing both aldehydes together, 35.4% of both compounds are obtained in less than 1 h of reaction at 220 °C with the reductive pretreatment. This selectivity corresponds with the maximum concentration observed for these compounds (1.2 g/L). This

concentration is 1.8 times higher than the maximum one obtained with the fresh sawdust, 0.68 g/L after 4 h at 180 °C with 1000 ppm of HCl. A similar selectivity than with the reductive process (34%) is obtained with the oxidative pretreatment, even at softer conditions (180 °C, 4 h). However, considering the total conversion, this selectivity only corresponds with 0.75 g/L, this value being only half of the concentration reached after the oxidative pretreatment. As explained before, the ANOVA analysis of these results corroborates the significance of these results.

To globally identify the impacts of delignification processes in the sawdust hydrolysis, and considering the simultaneous effect of acidity, temperature and reaction time, the evolutions of different intermediates and final products are compared considering the combined severity factor (CSF). This parameter has been previously proposed in the literature to unify the role of all the variables involved in one coefficient, according to the following expression (Lee and Jeffries, 2011; Rogalinski et al., 2008):

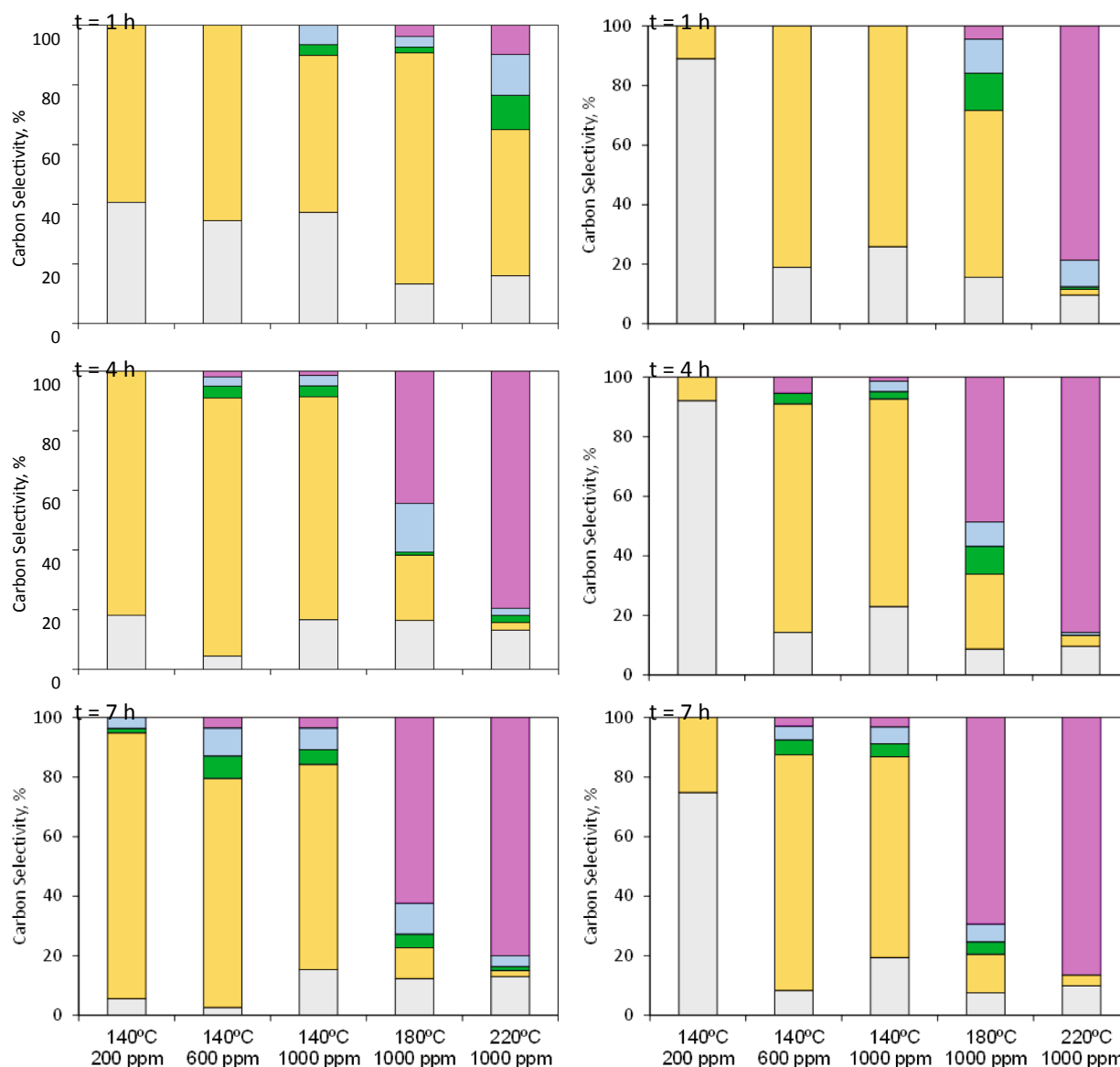


Fig. 5. Comparative distribution of products selectivities obtained with the hydrolysis of pretreated sawdust as function of the reaction time. Left graphs related to reductive pretreatment; right graphs related to the oxidative one. Data corresponding to dimers (grey); TRS (yellow); HMF (green); furfural (blue); and levulinic acid (purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$CSF = \log \left(t \cdot \exp \left(\frac{T - T_{ref}}{14.75} \right) \right) - pH$$

where “ t ” is the reaction time of hydrolysis in minutes, “ T ” is the reaction temperature in Celsius, “ T_{ref} ” is the reference temperature, most often 0 °C, and pH is the acidity of the aqueous solution measured before reaction. In this case, these values correspond to 2.1, 1.8 and 1.6, for reactions with 200, 600 and 1000 ppm of HCl, respectively. The concentrations of total reduced sugars (TRS), aldehydes and acids as function of the CSF values are plotted in Fig. 4 (parts c to e).

The soft trends obtained for all the compounds studied corroborate the utility of this parameter, showing distributions with clear maxima, which indicates a common evolution as function of the acidity, temperature, and reaction time for all the platform molecules. A similar effect of both pretreatments in the TRS productivity is observed (Fig. 4c), with a maximum clearly concentrated in CSF values 4.5–5 and a fast decrease in the concentration at both, lower and higher CSF values. In these two cases, the maximum concentration is close to 3 g·L⁻¹. More severe conditions are required in the hydrolysis of the fresh

sawdust, with and more extensive optimum CSF range from 5 to 6. Even at the optimum conditions, the total amount of sugars obtained is significantly lower than with the pretreated sawdust (maximum 0.75 g·L⁻¹).

As to the aldehydes (HMF and furfural), the maximum obtained with the fresh sawdust is concentrated in a very narrow range (5.8–6.4), without observing HMF nor FFL with CSF values under 5. The concentration at these optimum conditions, 0.8 g·L⁻¹, is also the optimum obtained with the oxidative pretreatment, the most relevant difference being the presence of aldehydes even at CSF values lower than 5. The most extended range is observed for the sawdust after the reductive pretreatment, obtaining aldehydes almost at all the conditions tested. However, this sawdust follows a flat evolution in the range 5–6.5, being not possible to identify clear optimum conditions, and with a maximum concentration lower than 0.5 g·L⁻¹.

In concentration terms, acids (levulinic and formic acid considered together) are the compounds more affected by the pretreatment used. However, the general trends are the same, and CSF values higher than 6.5 are required in all the cases to obtain these compounds in significant

amounts. The clearest difference is then the slope of this increasing trend, the oxidative pretreatment being the most efficient one to increase acid yields.

According to this analysis, the oxidative delignification method is considered as the best one to clearly identify different optimum conditions, in terms of productivity and selectivity, for each platform molecule. On the contrary, these optimum values are partially overlapped with the reductive pretreated and fresh sawdust.

3.4. Kinetic study

To sum up, relevant influences are observed as function of the pretreatment carried out. These higher reaction progresses can be analyzed in kinetic terms, proposing a kinetic model to describe the solubilization of hexoses and pentoses present in sawdust as well as their degradation to HMF, furfural and levulinic and formic acids. For this model, the quantity of sugar polymers is obtained as the difference between the initial amount (experimentally determined) and the sum of all compounds detected in liquid phase. The evolution of all the compounds (grouped by families) with the time could be assimilate to a sequence of irreversible first-order steps in series configuration, see Eq. (3):



where:

C_P is the sum of hemicellulose and cellulose in the sawdust; C_D and C_M are the dimer and monomer (hexoses and pentoses) concentrations detected in the liquid phase, respectively; $C_{ald.}$ the sum of HMF and furfural; and $C_{ac.}$ the amount of formic and levulinic acid. All concentrations are expressed in g/L.

To guarantee the absence of any limitation because of the amount of HCl, only the set of reactions obtained with 1000 ppm of this catalyst were considered for the adjustment. This decision is justified by the negligible pH evolution observed in these experiments during the 8 h analyzed. Considering the possible humins formation, as well as the subsequent alteration in the theoretical amount of polymers, a fifth rate was evaluated, being the responsible of aldehyde oligomerization to obtain these solid deposits. Experimental data were fitted to this kinetic model using MATLAB code ("ode45"). The fitting of the unknown parameters was accomplished by the least-square method using the "lsqcurvefit" function and the Levenberg-Marquardt algorithm, obtaining the kinetic rates summarized in Table 2. The comparison of these data requires corroborating the reliability of these values. An ANOVA analysis confirms that temperature is a significant model terms that influences the kinetic of the hydrolysis, for fresh and pretreated samples, with p-values lower than 0.5 in all the cases (0.028, 0.022 and 0.016 for fresh samples and sawdust after oxidative and reductive pretreatments,

respectively). The sawdust pretreatments also produce a relevant influence in the kinetic, mainly at 220 °C, when the p value is 0.036. This influence is not so significant at lower temperatures, with p-values a bit higher: 0.17 and 0.11, for 140 and 180 °C, respectively. These values are too high to conclude a clear influence of these pretreatments at low temperatures at this level of confidence (95%). The p-values decrease up to less than 0.07 if only the first steps of the reaction are considered (sugar solubilization), in good agreement with the suggested hypothesis of a main effect of these pretreatments making easier the cellulose and hemicellulose hydrolysis, whereas the subsequent steps of the process are mainly conditioned by the acidity of the medium.

The good fit of this model with experimental values is shown in Fig. 6, including the reactions at 220 °C as examples. The good regression coefficients of kinetic rates as function of the temperature indicates an optimum adjustment of experimental data according to Arrhenius model. This model, previously proposed in the literature (Clauser et al., 2020; Rodríguez-Chong et al., 2004; Tsoutsos and Bethanis, 2011) represents a first approach to the kinetic since a deeper analysis would require individual steps for the hydrolysis of each sugar polymer, as well as particular steps of degradation of each monomer. However, the common existence of glucose in both polymers, cellulose and hemicellulose, prevents this possibility. Despite this general character, the influence of delignification pretreatments is clearly observed, with significant decreases in the activation energy of all the kinetic rates of the hydrolysis pathway. On the contrary, significant increases in the activation energy of undesired reaction is observed after both pretreatments, being more evident in the case of the oxidation one. All these results are congruent with the initial assumption, considering that removing lignin has a positive effect increasing the accessibility to the sugar polymers, promoting their solubility and the subsequent steps. In addition, removing lignin as well as the external functional groups of hemicellulose (more evident in the case of oxidative pretreatment) significantly decreases the humins formation, preventing the oligomerization of aldehydes involved in the reaction.

4. Conclusions

Lignin strongly limits the hydrolysis of pine sawdust requiring so strong conditions that humins production restricts the process. Reductive and oxidative delignifications produce a positive effect, marked by a productivity of TRS 140 times higher than with the fresh sawdust and a relevant decrease in humins production. The best results obtained are 3.2 g/L of levulinic acid with a selectivity of 86% after 7 h of reaction at 220 °C and 1000 ppm of HCl applying the oxidative pretreatment, and 1.2 g/L of aldehydes (selectivity of 35.4%) in less than 1 h, with the reductive pretreatment.

Table 2

Kinetic model parameters for the hydrolysis of sawdust catalysed by 1000 ppm of HCl.

Raw Material	Temp. (°C)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	k_3 (s ⁻¹)	k_4 (s ⁻¹)	k_5 (s ⁻¹)
Fresh sawdust	140	$4.0 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$	$2.5 \cdot 10^{-7}$	$7.0 \cdot 10^{-5}$
	180	$7.7 \cdot 10^{-5}$	$8.5 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
	220	$2.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$
	Ea (kJ·mol ⁻¹)	33.7	54.1	120.0	193.3	31.9
	r ²	0.93	0.95	0.99	0.96	0.93
Delignified by oxidative method	140	$4.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$3.5 \cdot 10^{-5}$	0
	180	$8.6 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$	$6.4 \cdot 10^{-4}$	$3.7 \cdot 10^{-6}$
	220	$1.6 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$	$9.1 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$
	Ea (kJ·mol ⁻¹)	27.8	49.1	78.9	113.9	205.1
	r ²	0.999	0.95	0.83	0.999	0.999
Delignified by reductive method	140	1.1310^{-5}	$5.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$3.4 \cdot 10^{-5}$	$4.7 \cdot 10^{-8}$
	180	$2.9 \cdot 10^{-5}$	$7.6 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	$5.3 \cdot 10^{-4}$	$7.0 \cdot 10^{-5}$
	220	$3.9 \cdot 10^{-5}$	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$5.8 \cdot 10^{-4}$
	Ea (kJ·mol ⁻¹)	29.0	14.0	45.9	84.1	202.0
	r ²	0.93	0.997	0.95	0.97	0.94

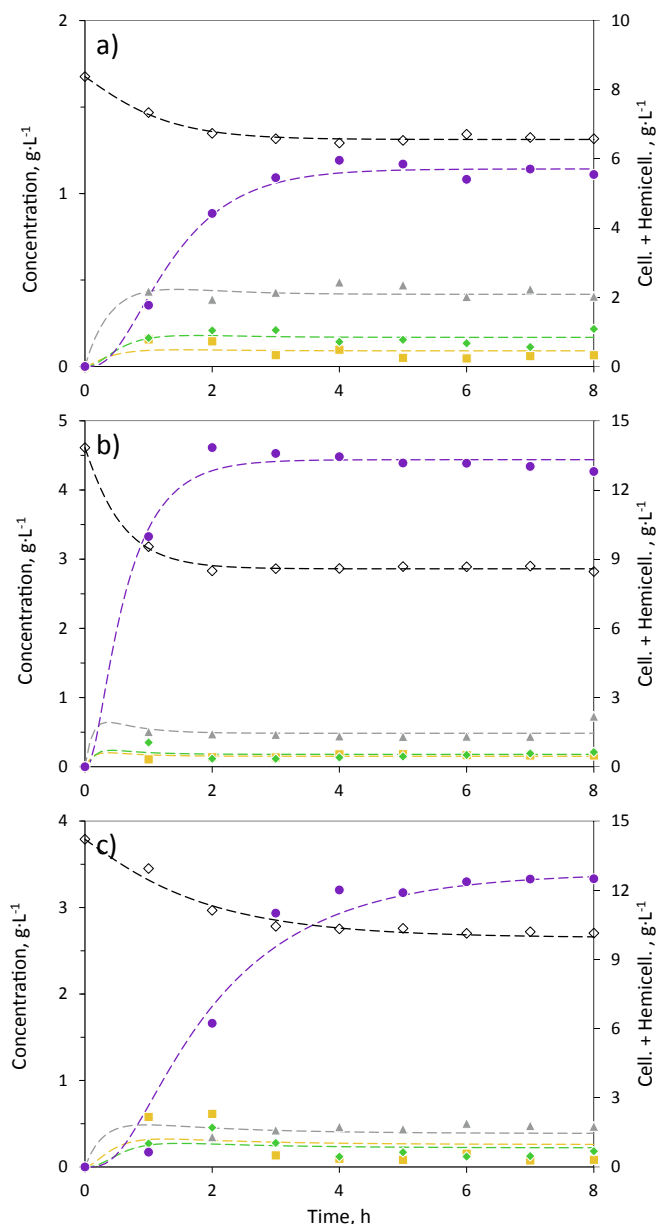


Fig. 6. Kinetic adjustment of experimental data according to the kinetic model proposed. Results corresponding to hydrolysis at 220 °C with 1000 ppm of HCl of the (a) fresh sawdust; (b) pretreated sawdust by oxidative method; and (c) pretreated sawdust by reductive method. Symbols: (◇) sugar polymer; (■) dimers; (▲) TRS; (◆) aldehydes; (●) acids.

CRediT authorship contribution statement

Paula Rapado: Investigation, Data curation, Writing - original draft.
Laura Faba: Methodology, Supervision, Validation, Writing - review & editing.
Salvador Ordóñez: Conceptualization, Supervision, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2020.124500>.

References

- Alonso, D.M., Bond, J.Q., Dumesic, J.A., 2010. Catalytic conversion of biomass to biofuels. *Green Chem.* 12, 1493–1513.
- Baig, K.S., Wu, J., Turcotte, G., 2019. Future prospects of delignification pretreatments for the lignocellulosic materials to produce second generation bioethanol. *Int. J. Energy Res.* 43, 1411–1427.
- Clauser, N.M., Felissia, F.E., Area, M.C., Vallejos, M.E., Gutiérrez, S., 2020. An energy-saving re-use strategy for the treatment of lignocellulosic biomass applied to the production of levulinic acid. *J. Clean. Prod.* 257, 120549.
- Cotana, F., Cavallaglio, G., Gelosia, M., Nicolini, A., Coccia, V., Petrozzi, A., 2014. Production of bioethanol in a second generation prototype from pine wood chips. *Energy Proc.* 45, 42–51.
- Chen, S.S., Wang, L., Iris, K., Tsang, D.C., Hunt, A.J., Jérôme, F., Zhang, S., Ok, Y.S., Poon, C.S., 2018. Valorization of lignocellulosic fibres of paper waste into levulinic acid using solid and aqueous Brønsted acid. *Bioresour. Technol.* 247, 387–394.
- Dhyani, V., Bhaskar, T., 2018. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew. Energy* 129, 695–716.
- Faba, L., Díaz, E., Ordóñez, S., 2015. Recent developments on the catalytic technologies for the transformation of biomass into biofuels: a patent survey. *Renew. Sustain. Energy Rev.* 51, 273–287.
- Gallo, J.M.R., Trapp, M.A., 2017. The chemical conversion of biomass-derived saccharides: an overview. *J. Brazil Chem. Soc.* 28, 1586–1607.
- Garcés, D., Díaz, E., Ordóñez, S., 2017. Aqueous phase conversion of hexoses into 5-hydroxymethylfurfural and levulinic acid in the presence of hydrochloric acid: mechanism and kinetics. *Ind. Eng. Chem. Res.* 56, 5221–5230.
- Garcés, D., Faba, L., Díaz, E., Ordóñez, S., 2019. Aqueous-phase transformation of glucose into hydroxymethylfurfural and levulinic acid by combining homogeneous and heterogeneous catalysis. *ChemSusChem* 12, 924–934.
- Giannakopoulou, K., Lukas, M., Vasiliev, A., Brunner, C., Schnitzer, H., 2010. Conversion of rapeseed cake into bio-fuel in a batch reactor: effect of catalytic vapor upgrading. *Micropor. Mesopor. Mater.* 128, 126–135.
- Gómez Millán, G., Hellsten, S., Llorca, J., Luque, R., Sixta, H., Balu, A.M., 2019. Recent advances in the catalytic production of platform chemicals from holocellulosic biomass. *ChemCatChem* 11, 2022–2042.
- Hubbell, C.A., Ragauskas, A.J., 2010. Effect of acid-chlorite delignification on cellulose degree of polymerization. *Bioresour. Technol.* 101, 7410–7415.
- Kang, S., Fu, J., Zhang, G., 2018. From lignocellulosic biomass to levulinic acid: a review on acid-catalyzed hydrolysis. *Renew. Sustain. Energy Rev.* 94, 340–362.
- Kluska, J., Ochnio, M., Kardaś, D., Heda, Ł., 2019. The influence of temperature on the physicochemical properties of products of pyrolysis of leather-tannery waste. *Waste Manage.* 88, 248–256.
- Kruse, A., Gawlik, A., 2003. Biomass conversion in water at 330–410 °C and 30–50 MPa. Identification of key compounds for indicating different chemical reaction pathways. *Ind. Eng. Chem. Res.* 42, 267–279.
- Lee, J.-W., Jeffries, T.W., 2011. Efficiencies of acid catalysts in the hydrolysis of lignocellulosic biomass over a range of combined severity factors. *Bioresour. Technol.* 102, 5884–5890.
- Li, S., Xu, S., Liu, S., Yang, C., Lu, Q., 2004. Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Process. Technol.* 85, 1201–1211.
- Luque, R., Speight, J.G., 2015. 1 – Gasification and synthetic liquid fuel production: an overview. In: Luque, R., Speight, J.G. (Eds.), *Gasification for Synthetic Fuel Production*. Woodhead Publishing, pp. 3–27.
- Marianou, A.A., Michailof, C.M., Pineda, A., Iliopoulou, E., Triantafyllidis, K., Lappas, A., 2018. Effect of Lewis and Brønsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media. *Appl. Catal. A* 555, 75–87.
- McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. *Bioresour. Technol.* 83, 37–46.
- Mukherjee, A., Dumont, M.-J., Raghavan, V., 2015. Sustainable production of hydroxymethylfurfural and levulinic acid: challenges and opportunities. *Biomass Bioenergy* 72, 143–183.
- Patil, S.K., Heltzel, J., Lund, C.R., 2012. Comparison of structural features of humins formed catalytically from glucose, fructose, and 5-hydroxymethylfurfuraldehyde. *Energy Fuel* 26, 5281–5293.
- Peters, M., Köhler, B., Kuckshinrichs, W., Leitner, W., Markewitz, P., Müller, T.E., 2011. Chemical technologies for exploiting and recycling carbon dioxide into the value chain. *ChemSusChem* 4, 1216–1240.
- Pileidis, F.D., Titirici, M.M., 2016. Levulinic acid biorefineries: new challenges for efficient utilization of biomass. *ChemSusChem* 9, 562–582.

- Rodriguez-Chong, A., Alberto Ramirez, J., Garrote, G., Vázquez, M., 2004. Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment. *J. Food Eng.* 61, 143–152.
- Rogalinski, T., Ingram, T., Brunner, G., 2008. Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. *J. Supercrit. Fluid* 47, 54–63.
- Romaní, A., Garrote, G., López, F., Parajó, J.C., 2011. Eucalyptus globulus wood fractionation by autohydrolysis and organosolv delignification. *Bioresour. Technol.* 102, 5896–5904.
- Rosatella, A.A., Simeonov, S.P., Frade, R.F.M., Afonso, C.A.M., 2011. 5-Hydroxymethylfurfural (HMF) as a building block platform: biological properties, synthesis and synthetic applications. *Green Chem.* 13, 754–793.
- Sarno, M., Iuliano, M., De Pasquale, S., Ponticorvo, E., 2020. A new nano-catalyst for sawdust hydrolysis. *Appl. Catal. A* 602, 117686.
- Schutyser, W., Renders, A.T., Van den Bosch, S., Koelewijn, S.-F., Beckham, G., Sels, B.F., 2018. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. *Chem. Soc. Rev.* 47, 852–908.
- Selvaraju, G., Bakar, N.K.A., 2017. Production of a new industrially viable green-activated carbon from Artocarpus integer fruit processing waste and evaluation of its chemical, morphological and adsorption properties. *J. Clean. Prod.* 141, 989–999.
- Shen, J., Zhu, S., Liu, X., Zhang, H., Tan, J., 2010. The prediction of elemental composition of biomass based on proximate analysis. *Energy Convers. Manage.* 51, 983–987.
- Siqueira, G., Várnai, A., Ferraz, A., Milagres, A.M., 2013. Enhancement of cellulose hydrolysis in sugarcane bagasse by the selective removal of lignin with sodium chlorite. *Appl. Energy* 102, 399–402.
- Sturgeon, M.R., Kim, S., Lawrence, K., Paton, R.S., Chmely, S.C., Nimlos, M., Foust, T.D., Beckham, G.T., 2014. A mechanistic investigation of acid-catalyzed cleavage of aryl-ether linkages: implications for lignin depolymerization in acidic environments. *ACS Sustain. Chem. Eng.* 2, 472–485.
- Thapa, I., Mullen, B., Saleem, A., Leibig, C., Baker, R.T., Giorgi, J.B., 2017. Efficient green catalysis for the conversion of fructose to levulinic acid. *Appl. Catal. A* 539, 70–79.
- Toftgaard Pedersen, A., Ringborg, R., Grotkjær, T., Pedersen, S., Woodley, J.M., 2015. Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose–fructose mixtures. *Chem. Eng. J.* 273, 455–464.
- Toor, S.S., Rosendahl, L., Rudolf, A., 2011. Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy* 36, 2328–2342.
- Trisant, P.N., Gunardi, I., 2020. The Influence of Hydrolysis Time in Hydrothermal Process of Cellulose from Sengon Wood Sawdust, *Macromolecular Symposia*. Wiley Online Library 2000016.
- Tsoutsos, T., Bethanis, D., 2011. Optimization of the dilute acid hydrolyzator for cellulose-to-bioethanol saccharification. *Energies* 4, 1601–1623.
- Van den Bosch, S., Schutyser, W., Vanholme, R., Driessen, T., Koelewijn, S.-F., Renders, T., De Meester, B., Huijgen, W., Dehaen, W., Courtin, C., 2015. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. *Energy Environ. Sci.* 8, 1748–1763.
- van Zandvoort, I., Wang, Y., Rasrendra, C.B., van Eck, E.R., Bruijninx, P.C., Heeres, H.J., Weckhuysen, B.M., 2013. Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions. *ChemSusChem* 6, 1745–1758.
- Vu, T.H.M., Pakkanen, H., Alén, R., 2004. Delignification of bamboo (*Bambusa procera* acher): Part 1. Kraft pulping and the subsequent oxygen delignification to pulp with a low kappa number. *Ind. Crop. Prod.* 19, 49–57.
- Yang, G., Pidko, E.A., Hensen, E.J.M., 2012. Mechanism of Brønsted acid-catalyzed conversion of carbohydrates. *J. Catal.* 295, 122–132.
- Yu, Z., Jameel, H., Chang, H.-M., Park, S., 2011. The effect of delignification of forest biomass on enzymatic hydrolysis. *Bioresour. Technol.* 102, 9083–9089.
- Zhou, C.-H., Xia, X., Lin, C.-X., Tong, D.-S., Beltrami, J., 2011. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem. Soc. Rev.* 40, 5588–5617.
- Zhou, C., Zhao, J., Yagoub, A.E.A., Ma, H., Yu, X., Hu, J., Bao, X., Liu, S., 2017. Conversion of glucose into 5-hydroxymethylfurfural in different solvents and catalysts: reaction kinetics and mechanism. *Egypt. J. Petrol.* 26, 477–487.



Role of the different catalytic sites in the H₂O₂-mediated aqueous-phase furfural partial oxidation

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ABSTRACT

The potential of hydrogen peroxide as oxidizing agent for furfural partial oxidation is studied in this work. Hydrogen peroxide is proposed as an alternative to air, the most typical oxidant, to reduce the severity and complexity of the process, as the reaction occurs in the liquid phase at ambient pressure. Comparing the activity of different catalysts and the selectivity for different oxidation products, including furoic acid, 2(5 H)furanone, and maleic and malic acids, a comprehensive mechanistic kinetic model is presented. This model identifies the critical catalytic properties ruling the selectivity of the process for each target compound. The results of this study emphasize the role of acidity in promoting the oxidations, the function of basicity for stabilizing the intermediate acids, and the impact of redox properties and metal particle size, which synergistically influence selectivity. This study concludes that Au/TiO₂ is the optimum catalyst to produce furoic acid (42% of selectivity). Additionally, Pt/MgZr selectively produces 2(5 H)furanone (100%), and Pd/TiO₂ and Pt/CeO₂ maximize the production of maleic acid (76.5%) and malic acid (78.5%), respectively.

1. Introduction

Lignocellulosic-based biorefineries represent the most promising and feasible alternatives to petroleum refineries to produce essential bulk chemicals needed in the current chemical processes. The extensive number of compounds required, involving polymers, liquid fuels, lubricants, agrochemicals, and pharmaceuticals, among others, can be obtained by specific chemical routes based on a limited number of key compounds, known as bioplateform molecules [1,2].

Furfural stands out as one of the most interesting bioplateform molecules. This five-carbon cyclic aldehyde is derived through the acid-catalyzed dehydration of pentoses obtained from the hemicellulose fraction of biomass [3–5]. Given the low value of this fraction, pathways centered around furfural offers an added advantage from both a circular economy and sustainability perspective. At this point, furfural catalytic oxidation is described as one of the interesting alternatives to produce various commodities, using air, molecular O₂, or hydrogen peroxide (H₂O₂) as oxidizing agents [6,7].

When using molecular oxygen for this oxidation, furoic acid (FCA) can be obtained with high selectivity [8]. FCA is the chemical precursor of 2,5-furandicarboxylic acid (FDCA), a crucial sustainable monomer

with promising applications in the synthesis of green polymers. FDCA has the potential to replace terephthalic acid, one of the most widely used petroleum-based monomers, in the manufacture of polyethylene terephthalate (PET) [9]. Previous studies demonstrate a high activity in an O₂-rich atmosphere with typical oxidizing metals [10], achieving FCA yields of 63% and 69% with Au/Mg(OH)₂ and Pd/Mg(OH)₂ [11]. These yields increase up to 92% when using Ag₂O/CuO [12] or MnO₂@CeO₂ [13].

However, this process requires temperatures above 120 °C and high pressures, increasing the operation costs and promoting furfural polymerization. Some of these studies work with very high catalytic loadings (up to 20%w/w), which limits the applicability in a future scale-up of this approach, and strong basic conditions (NaOH) are still needed to prevent catalytic deactivation due to leaching or the permanent adsorption of furoic acid on the metal nanoparticles [14,15].

Using H₂O₂ as an alternative oxidizing agent, which is considered a green oxidant that does not produce any waste, prevents these drawbacks since the reaction occurs at softer temperatures (both reactants are in the liquid phase). The natural H₂O₂ decomposition leads to an autocatalytic process, further enhanced by the acids produced in the reaction mixture (homogeneous catalysis) [16]. These advantages, as well as the

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significant growth in industrial H_2O_2 production in recent decades and the possibility of in situ generation via photocatalytic or electrocatalytic methods justify the increasing interest in researching new and greener production processes (including direct synthesis) and new applications of this green industrial oxidant [17].

The furfural oxidation using H_2O_2 has been studied in the literature describing an intricate mechanistic pathway marked by a combination of parallel and sequential reaction steps. Previous literature has primarily focused on the synthesis of diacids or acid anhydrides, particularly maleic [18–26] and succinic acid [27–29], and, at lower extent, 2-(5 H)furanone (FN) [30–32] and furoic acid [33]. In most cases, relatively low selectivities are reported, due to the high reactivity of H_2O_2 and the coexistence of different reaction pathways.

Despite these individual studies, there is gap in systematic research aimed at proposing a comprehensive mechanism and determining the catalytic properties that optimize the yields of each interesting compound: FCA, MA, MAL, and FN. To our knowledge, only a previous work proposed a simplified mechanism based on homogeneous catalysis [32], without considering the presence of solid catalysts. A more complete mechanistic analysis was done by Murzin and co-workers [6], at different temperatures, but without distinguishing between homogeneous and heterogeneous contributions, and not considering the impact on the H_2O_2 decomposition rate. Regarding the catalytic properties that influence selectivity, it is established that the introduction of acid/basic or redox activity can either inhibit or promote different steps [16,34]. Consequently, basic materials promote the production of FCA, whereas acidic materials enhance a parallel route, yielding 2-hydroxyfuran (HF) as the first intermediate [35].

In this study, we assess several materials as potential catalysts for the partial oxidation of furfural using H_2O_2 . Four bulk oxides with different catalytic properties were used in this work: TiO_2 and CeO_2 , representing redox materials, and MgAl and MgZr , as typical mixed oxides with basic-acid sites. To enhance the catalytic activity, bifunctional materials were prepared by incorporating Au, Pd, and Pt, three of the most active metals for oxidations [36,37]. These four chosen supports have been previously proposed in different studies using lignocellulosic platform molecules. Thus, CeO_2 has been successfully tested in the selective oxidation of HMF, highlighting the close contact between metal and support obtained, and the crucial role of ceria defects in the oxidation [38,39]. TiO_2 has been widely used as support for bifunctional catalysts used in HMF oxidations, revealing a strong interaction with metal nanoparticles that alters the parent properties, increasing the surface area and the concentration of active sites, which contributes to high activity, selectivity, and stability [40,41]. Hydrotalcite-derived mixed oxides (MgAl) and other oxides (including Mg and Zr) were also considered for the HMF oxidation [42,43], mainly using Rh as the metal active site. Despite the limited literature on these materials in oxidations, they are widely used in other reactions involving furfural, such as condensation [44] or hydrogenation [45]. Thus, a good activity in this reaction could expand their versatility, increasing the spectrum of reactions related to biomass-derived molecules that can catalyze.

The reactions have been studied in a stirred batch reactor, and the results were fitted to a kinetic model that accounts for both homogeneous and heterogeneous contributions. This modeling not only aids in understanding the reaction pathways and the role of the different catalyst sites but also facilitates the optimization of the reactor design for renewable production of different commodities.

2. Experimental section

2.1. Catalysts preparation

TiO_2 (P25, Sigma Aldrich) was calcined in air for 2 h ($5^\circ\text{C}\cdot\text{min}^{-1}$) at 500°C to activate it [46]. CeO_2 , MgAl and MgZr were synthesized in laboratory, as detailed in the Supplementary Information.

Metal modified catalysts: Pd and Pt, (1 wt% as theoretical metal

loading) were supported using the incipient wetness impregnation method and $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ as precursors (Sigma Aldrich, >99.99%). The Au was deposited at 1% wt. into the different supports by deposition-precipitation method [46] using $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ (Sigma Aldrich, 99%) as precursor. All the materials were calcined for 3 h at the same temperature as their bulk materials (i.e., 400°C , 500°C , 600°C , and 700°C for CeO_2 , TiO_2 , MgZr , and MgAl) [16,47]. The materials were reduced in H_2 (10 v/v% in Ar) for 4 h, at 300°C for those catalysts with Au, and 400°C for the rest of them (in all the cases, with a slope of $5^\circ\text{C}\cdot\text{min}^{-1}$) [48–50].

2.2. Catalysts characterization

Morphological properties (surface area, pore diameter and pore volume) were determined by N_2 physisorption at -196°C using an ASAP 2020 (Micromeritics), applying the BET and BJH approaches (desorption data used for the pore diameter and volume). The same instrument was used to determine the particle size and metal dispersion by carbon monoxide chemisorption at 35°C .

These data were corroborated by transmission electronic microscopy (TEM), using a JEOL JEL 2100 microscope. Histograms and average particle size were calculated by analyzing at least 100 particles in each sample, using the software Confocal ImageJ. The metal dispersion was calculated according to Eq. (1), where v_m , a_m , and $\langle d_p \rangle$ correspond to volume, surface, and average particle diameter, respectively:

$$D(\%) = \frac{6 \cdot \frac{v_m}{a_m}}{\langle d_p \rangle} \cdot 100 \quad \text{Eq. (1)}$$

The crystallographic structure of the mixed oxides was determined by X-ray diffraction (XRD) using a Philips PW 1710 diffractometer, working with a $\text{CuK}\alpha$ line ($1.54 \text{ \AA}$) in the 2θ range between 5° and 80° , at a scanning rate of $2^\circ \cdot \text{min}^{-1}$.

The metal loading of the bifunctional catalysts was determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) using a HP 7900 of Agilent. Approximately 50 mg of the sample were inserted into a microwave-assisted Teflon bomb; adding HCl (2.25 mL) and HNO_3 (0.75 mL) to dissolve the sample.

The surface chemistry was analysed by temperature programmed desorption (TPD) in a Micromeritics 2900 TPD/TPR. 50 mg of solid were pretreated in He flow and saturated with CO_2 or NH_3 to determine the basicity or acidity, respectively. The evolution of CO_2 and NH_3 signals were followed using a Pfeiffer Vacuum Omnistar Prisma mass spectrometer while the temperature increases at $2.5^\circ\text{C}\cdot\text{min}^{-1}$ from 25 to 550°C . Signals were quantitatively related to concentration values after the corresponding calibration.

2.3. Reaction studies

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) equipped with a backpressure regulator and a PID temperature controller. The system was loaded with the catalyst (0.5 g, $50\text{--}80 \mu\text{m}$) and 215 mL of an aqueous solution of furfural (0.6 M). Once the desired temperature was reached (50°C), 35 mL of a H_2O_2 (33%, Sigma Aldrich) solution were added to achieve 1.5 M of H_2O_2 and 0.5 M of FFL in a total volume of 250 mL. Air was purged with N_2 , and the oxidation was carried out with 10 bar of N_2 with a stirring of 700 rpm for 8 h. Samples were taken from the sampling port, filtered using a $0.22 \mu\text{m}$ nylon syringe filter, and diluted in a 1:2 ratio to avoid signal saturations during the analysis.

The evolution of the different involved compounds (organics and H_2O_2) was quantified by HPLC (1200 Series, Agilent) equipped with a RI detector and a Hi-Plex H column, using $0.5 \text{ mL}\cdot\text{min}^{-1}$ of 0.5 mM H_2SO_4 solution as mobile phase and commercial standards for the identification and calibration. Each sample was analysed at least twice, with an error margin of less than 5%. The analysis of the reaction is present in terms of

conversion, selectivity, yield, and carbon balance closure, according to the following expressions:

$$x_{FFL} (\%) = \frac{C_{FFL,0} - C_{FFL,t}}{C_{FFL,0}} \cdot 100 \quad (2)$$

$$x_{H_2O_2} (\%) = \frac{C_{H_2O_2,0} - C_{H_2O_2,t}}{C_{H_2O_2,0}} \cdot 100 \quad (3)$$

$$Selectivity (\%) = \frac{n_i \cdot C_i}{\sum (n_i \cdot C_i)} \cdot 100 \quad (4)$$

$$Yield (\%) = \frac{n_i \cdot C_i}{5 \cdot C_{FFL,0}} \cdot 100 \quad (5)$$

$$C.B. (\%) = \frac{\sum (n_i \cdot C_i)}{5 \cdot C_{FFL,0}} \cdot 100 \quad (6)$$

MATLAB code was used to perform the kinetic calculations and to solve the set of ordinary differential equations ("ode45") that mathematically explains the mechanism proposed. All the experimental data were considered for these calculations to ensure that data provided represent the behavior of all the catalysts tested. The fitting of the unknown parameters was accomplished by the least-square method using the "lsqcurvefit" function and the Levenberg-Marquardt algorithm.

3. Results and discussion

3.1. Reaction pathway in absence of heterogeneous catalysts

According to literature [32], compounds with five but also four carbon atoms are expected to be obtained during the furfural oxidation, releasing formic acid that acts as a homogeneous catalyst. Considering the high oxidation capacity of H_2O_2 , a contribution of the autocatalytic process is not discarded, with the subsequent formic acid production that triggers the homogeneous catalytic mechanism. Thus, a correct study of the heterogeneous catalytic mechanism requires a preliminary analysis of these concomitant effects.

An initial experiment in the absence of heterogeneous catalysts was carried out at 50 °C, with a 3/1 H_2O_2 /furfural molar ratio, to study the influence of autocatalytic and homogeneous catalytic mechanisms. The evolution of reactants and products concentration is plotted in Fig. 1. A continuous H_2O_2 conversion is observed, more markedly during the first 2 h, reaching 55% of conversion after 8 h. A similar furfural conversion

is observed (58%), but the temporal profile indicates a faster reaction rate after 2 h. This profile is congruent with the presence of catalytic steps activated by an intermediate.

The product distribution is congruent with previous literature, despite the diverging values because of the different temperatures used [51]. Formic acid (FA) is the main reaction product, with a clear increasing trend, yielding more than $0.2 \text{ mol}\cdot\text{L}^{-1}$ after 6 h. 2-Hydroxyfuran is also relevant (HF, $0.12 \text{ mol}\cdot\text{L}^{-1}$), showing a typical profile of a primary compound, with an almost flat concentration after 4 h justified by its decomposition. The same trend is detected for furoic acid (FCA), although FCA is obtained with significantly lower concentrations (max. value of $0.03 \text{ mol}\cdot\text{L}^{-1}$). The stable phase of HF and FCA corresponds with an increase in minority products, 2(5 H)-furanone (FN) and maleic acid (MA), suggesting that these compounds are obtained by the oxidation of one or both of these precursors (HF and FCA). Consequently, their formation is equilibrated with their decomposition. The final concentrations of FN and MA, 0.018 and $0.015 \text{ mol}\cdot\text{L}^{-1}$, are too low to support a strong discussion about the mechanistic route to their formation.

The final carbon balance in the liquid phase is 85.4%, suggesting a significant carbon loss in the gas phase. The presence of any other condensed product in the liquid phase or humins was discarded considering the lack of any unknown signal on the HPLC chromatograms. Moreover, solids were not recovered after the reaction. This loss is then compatible with CO_2 released because of the total oxidation of the different compounds. A separate analysis of the gas phase by a mass-spectrometer identifies CO_2 as the only carbon-containing molecule of the gas sample.

These results suggest that formic acid (FA) is a common product obtained by all the routes that produce C4 compounds from furfural (C5). In fact, there is a good correspondence between FA concentration and the difference between the furfural converted and the furoic acid obtained (once the carbon balance closure is considered). Based on this premise, FA is excluded from the selectivity analysis (see Fig. 2), only considering the C4-C5 compounds. Thus, in carbon basis (Eq. 4), the reaction in absence of catalyst produces 60% of HF and similar selectivity of FCA (20.5%) and the mixture of FN and MA (9% and 10.5%). In global terms, these results indicate that the 2-hydroxyfuran route (Baeyer-Villiger mechanism, henceforth, B-V) prevails, the compounds of this pathway being 80% of the total mixture. It is expected that introducing an heterogeneous catalysts could modify the ratio between the two main routes of furfural partial oxidation and, subsequently, the relative distribution of products.

3.2. Influence of the catalytic support

Once the relevance of the homogeneous reaction pathways was determined, the activity of the considered bulk supports was compared. The main characterization results in terms of morphology, acidity, and basicity of the considered supports are summarized in Table 1. Data shown in this table are obtained by the analysis of N_2 physisorption isotherms, NH_3 and CO_2 spectra included in the Supplementary Information (Fig. S1-S3).

All the catalysts are mesoporous materials with surface areas from 60 (TiO_2) to $180 \text{ m}^2\cdot\text{g}^{-1}$ (MgAl) and pore diameters significantly higher than the kinetic diameter of all the molecules involved in the process. The absence of diffusional limitations, that could be assumed based on these data, has been theoretically corroborated, considering the Carberry number (Ca) and the Wheeler-Weisz criteria. The complete discussion is included in the Supplementary Information (Table S1). To sum up, external and internal mass transfer limitations are discarded since all the Ca and the Thiele modulus values are lower than $7 \cdot 10^{-7}$ (the limit to consider it as relevant being in 0.05) and $2 \cdot 10^{-3}$ (0.1 is the limit to being relevant). Thus, the reaction is under kinetic control and the different activity is related to the chemical surface properties, in terms of acidity and basicity, or the redox capacity, in the case of TiO_2 and CeO_2 .

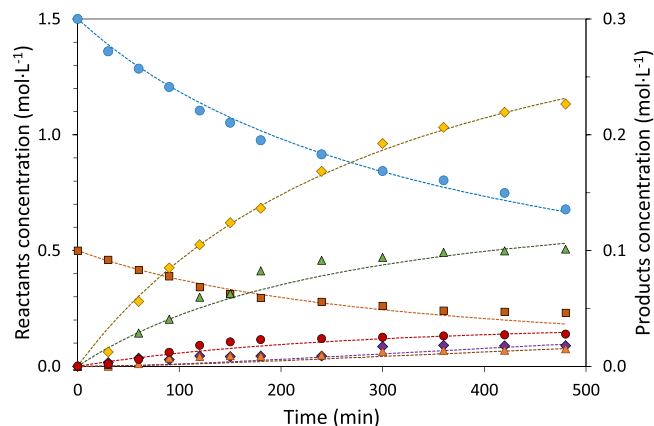


Fig. 1. Furfural oxidation with H_2O_2 at 50 °C in absence of a catalyst. Symbols: H_2O_2 (●); furfural (■); formic acid (◆); 2-hydroxyfuran (▲); furoic acid (●); maleic acid (◆); and 2(5 H) furanone (▲). Broken lines correspond to the kinetic model predictions.

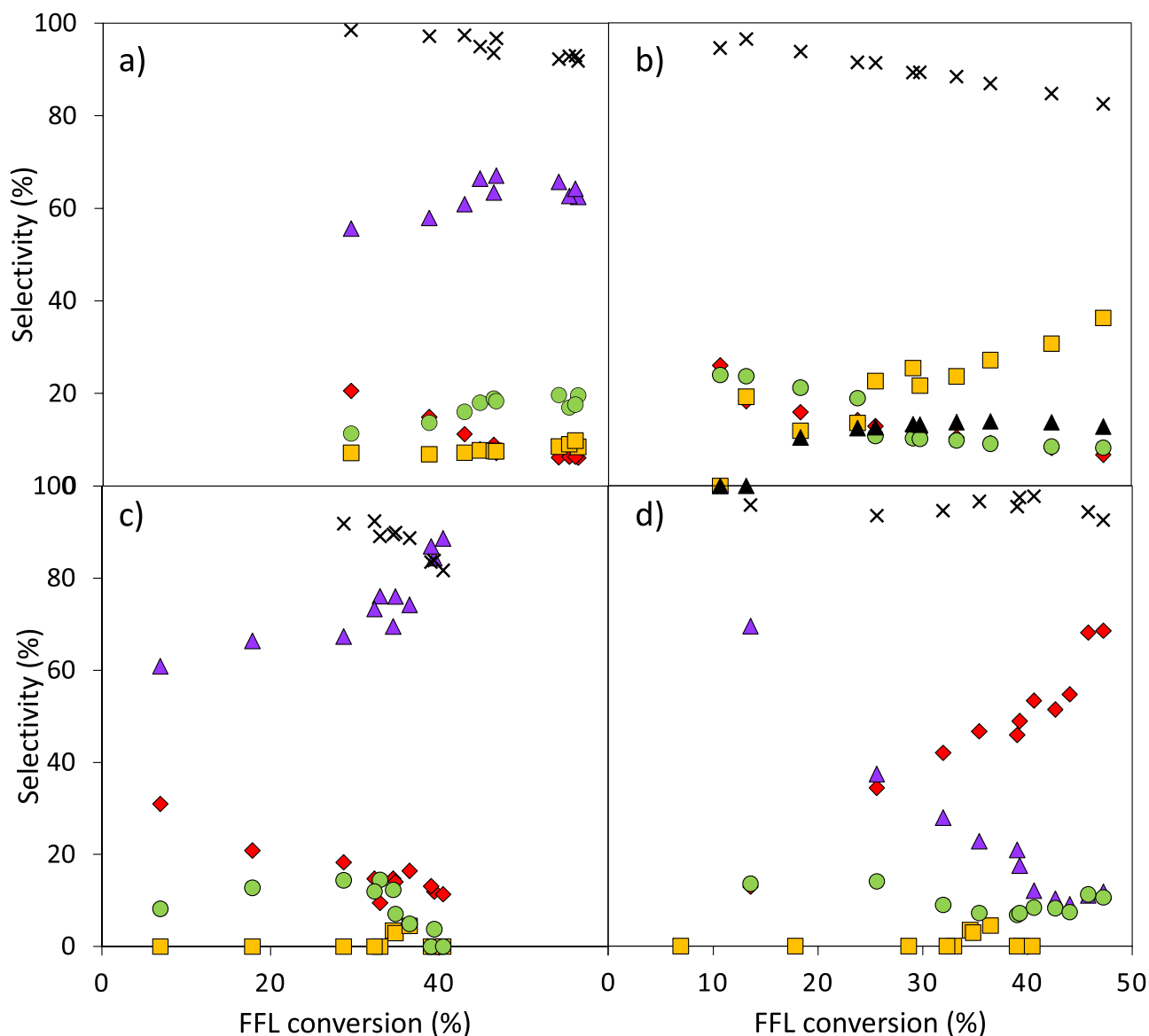


Fig. 2. Conversion - selectivity plots for furfural oxidation using H_2O_2 at 50 °C over (a) MgAl, (b) MgZr, (c) CeO_2 , and (d) TiO_2 . Data correspond to carbon balance (x), and selectivities to MA (◆), FN (■), HF (▲), FCA (●), and HFN (▲).

Fig. 2 illustrates, in terms of selectivity vs. conversion, the experimental data obtained with the four metal oxides tested, keeping the temperature (50 °C) and the initial H_2O_2 /furfural ratio (3) of the homogeneous experiments described in the previous section. Results obtained with MgAl match those obtained in the absence of a catalyst, whereas the other three supports present relevant differences, including the formation of other intermediates, such as 5-hydroxy-2(5 H)furanone (HFN), β -formylacrylic acid (BFA), and malic acid (MAL). The presence of these compounds suggests that some steps of the global mechanism require a heterogeneous catalysts to be feasible.

Obtained results can be turned by the reactivity of the hydrogen peroxide. Relevant differences between materials were found, from a slight increase with MgAl and MgZr (64% and 70% at the final reaction time) to an almost total decomposition in the case of CeO_2 (93.7%), with an intermediate behaviour for the TiO_2 .

Furfural conversions are lower than the one reached without a catalyst, detecting values from 33% (MgZr) to 46.7% (MgAl), with an opposite trend than the one observed for H_2O_2 conversion,. These results

indicate that H_2O_2 is involved in all the steps where furfural is. Thus, the fast decrease of H_2O_2 concentration leads to a reduction in the rates of these reactions, with the subsequent reduction in the furfural conversion. This conclusion is supported by the literature. López Granados and co-workers demonstrate that the larger the H_2O_2 concentration, the faster the furfural conversion rate [22], and several authors propose using different oxides as catalysts for hydrogen peroxide decomposition [52,53].

According to the previous discussion, the H_2O_2 conversion and, subsequently, the furfural one is improved by the redox properties of Ce [54], Ti [14], and Zr [55]. However, the comparison between the blank and experiments with MgZr suggests that the role of acidic/basic properties of the catalysts in the product distribution and the reaction control cannot be discarded.

With MgAl, the distribution of the main products is quite similar than in absence of any catalyst, obtaining a final sample enriched in HF (66.6%) with 18.3% of FCA and 17% of the sum of FN, MA and HFN (catalytic route not observed with the blank). The high carbon balance

Table 1

Main characterization properties of the different supports used in this work.

	MgAl	MgZr	TiO ₂	CeO ₂
N ₂ physisorption				
Surface area (m ² ·g ⁻¹)	179	111	59	123
Pore volume (cm ³ ·g ⁻¹)	0.4	0.7	0.3	0.3
Pore diameter (nm)	7	18	19	8
Acidity (μmol NH ₃ ·g ⁻¹)				
Physisorbed (<100 °C)	109.6	16.3	17.4	0
Weak (100 – 200 °C)	181.5	227.0	67.3	45.7
Medium (200–400 °C)	78.5	147.4	127.7	177.3
Strong (>400 °C)	161.2	183.7	18.6	9.2
Total	530.7	574.4	231.1	232.2
Basicity (μmol CO ₂ ·g ⁻¹)				
Physisorbed (<100 °C)	14.2	17.9	15.6	22.5
Weak (100 – 200 °C)	40.1	50.3	0	0
Medium (200–400 °C)	0	97.2	11.3	9.5
Strong (>400 °C)	268.5	0	11.0	6.1
Total	322.7	165.3	37.9	38.2

(93%) and the constant concentration of FCA suggests a positive role of strong basic sites preventing CO₂ formation and stabilizing the resulting organic acids.

In the case of MgZr, the higher strength of the acid sites promotes B-V oxidation pathways [56], observing a significant decrease in the furoic acid selectivity (10.1%), as well as an increase in the formation of acyclic compounds (selectivity of 33.7% of BFA), and their total decomposition to CO₂, fostered by the absence of strong basic sites that could stabilize the organic acids.

With CeO₂, furoic acid is only observed in traces at the beginning of the reaction and FN, HFN, BFA or MAL are not detected. This material presents the highest production of 2-hydroxyfuran (HF), with almost constant selectivity during all the reaction (~90%). In addition to the redox activity of this catalyst, its marked medium-strength acidity (see data in Table 1), with the subsequent total H₂O₂ decomposition (only observed with this material) explains the promotion of this route. The carbon balance (83.2%) suggests that the decomposition of organic compounds is relevant. The maleic acid selectivity is not negligible (11.3%). These results are explained by the easy Ce³⁺/Ce⁴⁺ redox transition, increasing the oxygen mobility and storage capacity, favoring total oxidations [57].

TiO₂ highlights by the fast decomposition of primary products, with maximum selectivities of 67.2% for HF (after 30 min), and 17.4% for FCA (after 1 h). Due to their decomposition, maleic acid represents more than 66% of the total selectivity after 8 h, result that corresponds to 20.7% of the product yield. This material presents the best carbon balance (94.8%), discarding relevant decomposition to CO₂. The acidity and basicity properties of this material cannot explain these results, its redox capacity being proposed as the main responsible of it. In the case of TiO₂, oxidations are enhanced but not the decompositions, suggesting a complex effect of support oxygen vacancies.

According to this support screening, the role of heterogeneous catalysts tuning the selectivity is very relevant, in such a way that CeO₂ is proposed for the selective production of hydroxyfuran (HF), whereas maleic acid (MA) formation is promoted with TiO₂. This analysis is not so conclusive concerning other reaction intermediates, such as furoic acid. For this compound, a maximum selectivity of 28% is obtained with MgZr, but this result corresponds to a low FFL conversion (9.2%, 1 h) and the FCA yield is then almost negligible (1.2%). On the contrary, results with MgAl present a better balance between conversion and selectivity, reaching a maximum yield of 6.7% after 6 h. To sum up, the analysis of relevant reaction intermediates requires a balance between the catalytic activity and the reaction time to prevent the advance of the reaction to more oxidized compounds.

3.3. Kinetic study

With the temporal evolution of reactants and products obtained with and without catalysts, and considering the literature [10,17,18], the mechanism shown in Scheme 1 is proposed.

According to this mechanism, furfural is oxidized by two parallel pathways, obtaining furoic acid and 2-hydroxyfuran, respectively, as primary compounds. Through the second pathway (B-V), oxidation implies a partial decomposition, releasing formic acid. 2-Hydroxyfuran is a reactive intermediate that undergoes dehydration, yielding 2(5 H) furanone. The co-presence of hydrogen peroxide and formic acid catalyzes the oxidation of furoic acid and 2(5 H)furanone into maleic and fumaric acid, two isomers in cis-trans rearrangement equilibrium. The low pH (2.8 after 8 h) and the oxidizing medium promotes the degradation of these compounds through consecutive oxidative decarboxylations, releasing CO₂ and water [6]. The absence of a direct correspondence between the products and the hydrogen peroxide conversion suggests an independent self-decomposition of this reactant.

Experimental results were fitted to the kinetic model obtained by applying the mass balances suggested by the reaction mechanism and considering the hypothesis of an ideal stirred batch reactor, according to Eq. (7) to (14). In these equations, fumaric and maleic acid are considered together. All the compounds are labeled as indicated in Scheme 1 to simplify the mathematical expressions.

$$\frac{dC_H}{dt} = -k_1 \cdot H - k_2 \cdot FFL \cdot H - k_3 \cdot FCA \cdot H - k_4 \cdot FFL \cdot H - k_6 \cdot FN \cdot H - k_7 \cdot HF \cdot H - k_8 \cdot HFN \cdot H - k_9 \cdot MA \cdot H - k_{10} \cdot MA \cdot H \quad (7)$$

$$\frac{dC_{FFL}}{dt} = -k_2 \cdot FFL \cdot H - k_4 \cdot FFL \cdot H \quad (8)$$

$$\frac{dC_{FCA}}{dt} = k_2 \cdot FFL \cdot H - k_3 \cdot FCA \cdot H \quad (9)$$

$$\frac{dC_{FA}}{dt} = k_3 \cdot FCA \cdot H + k_4 \cdot FFL \cdot H - k_9 \cdot MA \cdot H \quad (10)$$

$$\frac{dC_{MA}}{dt} = k_3 \cdot FCA \cdot H + k_6 \cdot FN \cdot H + k_8 \cdot HFN \cdot H - k_{10} \cdot MA \cdot H \quad (11)$$

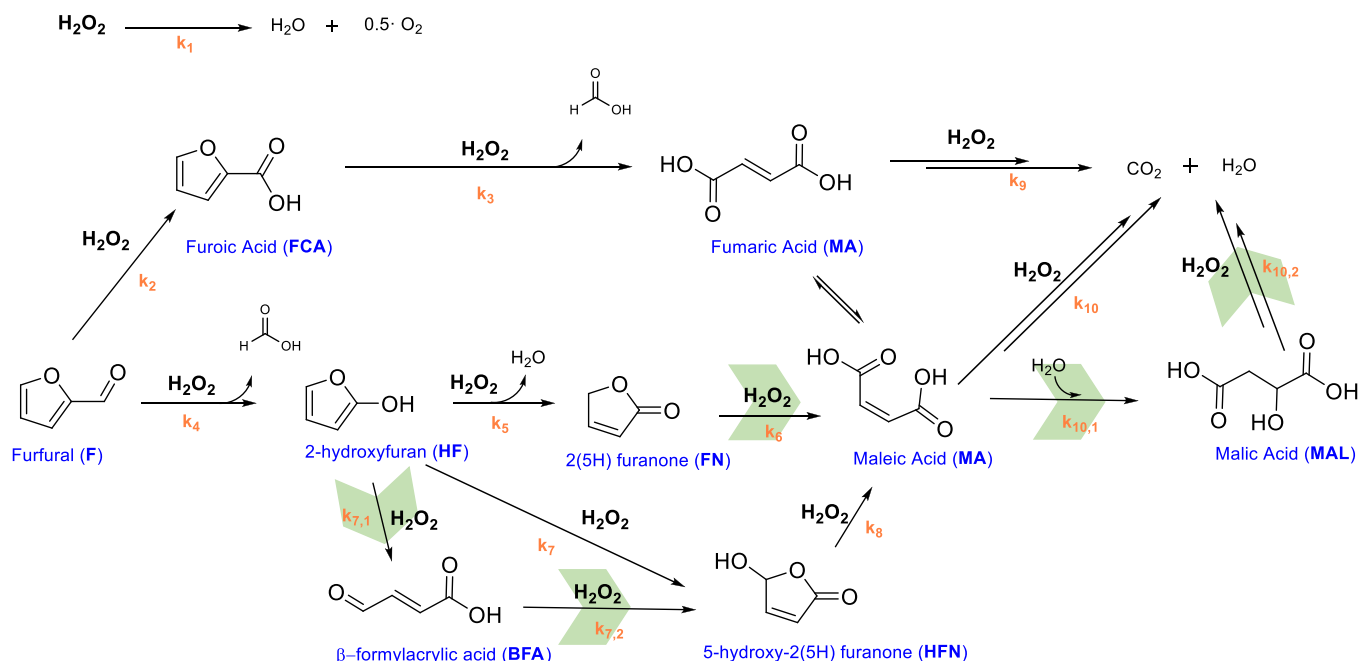
$$\frac{dC_{HF}}{dt} = k_4 \cdot FFL \cdot H - k_5 \cdot HF \cdot H - k_7 \cdot FN \cdot H \quad (12)$$

$$\frac{dC_{FN}}{dt} = k_5 \cdot HF \cdot H - k_6 \cdot FN \cdot H \quad (13)$$

$$\frac{dC_{HFN}}{dt} = k_7 \cdot FN \cdot H - k_8 \cdot HFN \cdot H \quad (14)$$

The coexistence of homogeneous and heterogeneous reaction pathways is modeled considering each kinetic rate constant as the sum of two values: a constant one due to the homogeneous contribution (related to the activity of hydrogen peroxide and protons), and a variable one related to the solid catalyst. Due to the extended number of terms, this disaggregation ($k_i = k_{i,hom} + k_{i,het}$) is not specified in the equations. This methodology requires a previous analysis of the blank experiment to isolate the contribution of the homogeneous rates in those steps identified without a solid catalyst. This analysis also allows identifying those steps that require a solid catalyst to be promoted (identified with green shadow in Scheme 1).

The low pH (<3) obtained in less than 2 h allows considering the homogeneous catalysis is due to the presence of protons as constant. Based on these appreciations, the effect of the acidity is embedded in the common contribution (homogeneous terms) without including any extra term in the mass balances. Since no relevant differences between the acids that could release these protons were observed, the main contribution is attributed to formic acid because of its significantly higher



Scheme 1. Reaction network of furfural oxidation using H_2O_2 as oxidizing agent. Steps highlighted in green require a heterogeneous catalyst.

concentration (more than 90% in some cases).

In contrast, experimental results demonstrate a marked influence of the hydrogen peroxide concentration on the different steps, as well as a different evolution of its concentration as a function of the catalyst used. Therefore, it is a relevant parameter in the mass balances for the heterogeneous catalysis, leading to an apparent second order kinetics for most of the steps, as well as a decomposition rate (k_1) with a homogeneous and a heterogeneous contribution, in the same way as for the organic compounds.

The kinetic rates of the main steps (k_1 – k_4) are summarized in Table 2, whereas the values for secondary steps that could be affected by a higher inaccuracy (due to the lower concentrations to be fit) are included in the Supplementary Information (Table S2). The kinetic rates reported for the different supports correspond only to the heterogeneous contribution. The real rates are obtained by the sum of both terms, but the discussion is more clearly based only on those terms affected by the solid catalysts.

The goodness of fit for the blank experiment is illustrated in Fig. 1, observing a great correspondence between experimental (dots) and fitted values (broken lines). These values represent a common homogeneous contribution for those experiments with a solid catalyst.

As illustrated in Scheme 1, when a solid catalyst is involved, the quantification of all the intermediates suggests that steps 7 and 10 of the original mechanism must be decomposed into two intermediate ones, justifying the detection of β -formylacrylic (BFA) and malic acid (MAL), compounds not detected without a catalyst. The detailed temporal

Table 2

Reaction rate constants based on the proposed reaction network. Units: k_1 (s^{-1}); $k_2 - k_4$ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$). Except in the case of the blank experiment, values shown correspond to the heterogeneous contribution to each step, the total rate being obtained as the sum of the homogeneous rate (blank experiment) and each value.

	Blank	MgAl	MgZr	CeO ₂	TiO ₂
k_1	$1.8\cdot 10^{-5}$	0	$3.2\cdot 10^{-5}$	$2.2\cdot 10^{-4}$	$9.3\cdot 10^{-6}$
k_2	$1.0\cdot 10^{-5}$	$2.1\cdot 10^{-5}$	$1.4\cdot 10^{-5}$	$1.1\cdot 10^{-5}$	$1.8\cdot 10^{-5}$
k_3	$5.2\cdot 10^{-5}$	$3.9\cdot 10^{-1}$	$3.9\cdot 10^{-1}$	$6.4\cdot 10^{-2}$	$1.1\cdot 10^{-1}$
k_4	$1.9\cdot 10^{-5}$	$3.4\cdot 10^{-6}$	$3.4\cdot 10^{-6}$	$2.8\cdot 10^{-5}$	$9.9\cdot 10^{-6}$
r^2	0.914	0.909	0.903	0.919	0.931

profiles comparing experimental and fitted data obtained with the most promising supports (TiO₂ and MgAl) are included in Fig. 3, whereas the corresponding ones with MgZr and CeO₂ are incorporated in the Supplementary Information (Fig. S4).

The complexity of the mechanism limits the analysis based on the characterization parameters. However, a clear correspondence between the main kinetic rates and the catalyst acidity is observed, as shown in Fig. 4.

As anticipated by the literature [58,59] and corroborated with our experimental results, the lateral route of 2-hydroxyfuran formation (B-V mechanism) is promoted by the acidity (k_4), the medium-strength sites being the most relevant ones for this step. An opposite influence is observed for the furoic acid production, supporting the negative role of acidity to maximize its yield. In the same way, a positive effect of acidity is observed also for the following oxidizing steps, with a higher relevance of the strong acidic sites for the total decomposition of the two main products of the reaction, the 2-hydroxyfuran, and furoic acid, producing CO₂ as the final compound.

The parallel analysis considering the basicity of these materials is not conclusive. The lack of a clear correlation between oxidizing steps and basicity discards the prevalence of the Cannizzaro disproportionation mechanism also proposed in the literature [11,60]. In good agreement, furfuryl alcohol is not observed. Although a positive role of basicity is suggested by the experimental results (increasing the acids stability and preventing their total decomposition into CO₂), the redox properties of some of these catalysts alter the H_2O_2 available to produce the furfural conversion, this fact prevailing over the basicity. These effects are more relevant for first intermediates, such as the furoic acid (FCA), compounds whose production is more sensitive to the weak equilibrium between activity, selectivity and stability.

3.4. Activity of bifunctional catalysts

Bifunctional catalysts were prepared with a theoretical 1% of Pt, Pd, or Au. These metals were chosen considering their high oxidation capacity demonstrated for similar systems [57], with the aim to analyze their influence tuning the selectivity of the reaction. The low metal loading leads to good metal dispersions, maximizing the activity of these metal particles and enabling a direct comparison with the bulk material.

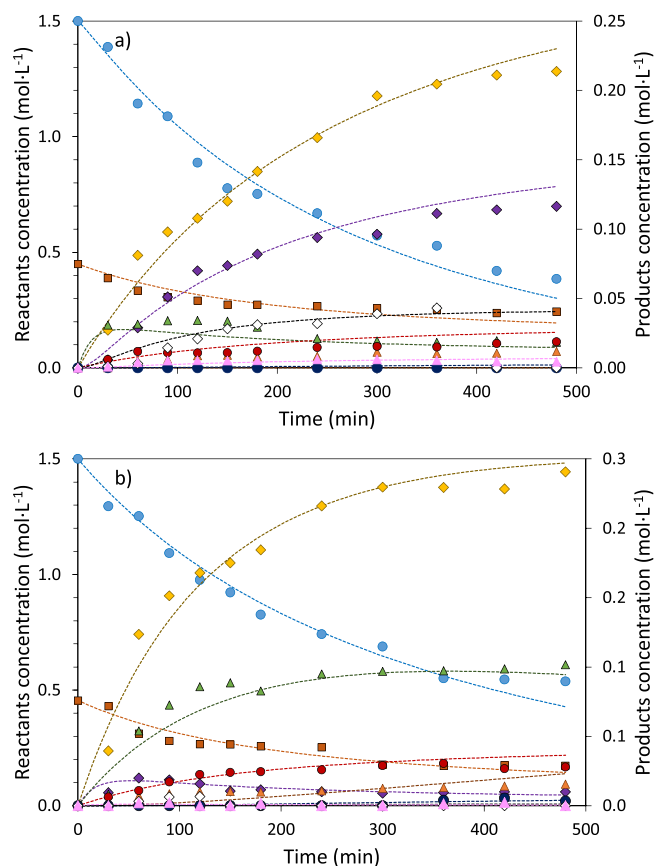


Fig. 3. Furfural oxidation with H_2O_2 at 50 °C in presence of (a) TiO_2 and (b) MgAl . Symbols: H_2O_2 (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (○); MAL (▲). Broken lines correspond to the kinetic model predictions.

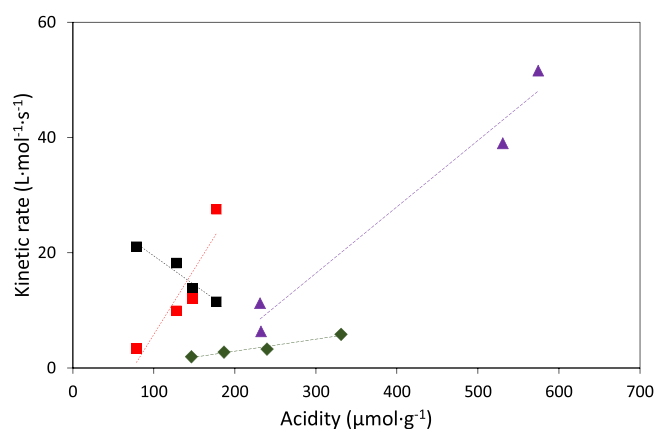


Fig. 4. Evolution of the kinetic constants for furfural conversion considering both pathways, k_2 (■, $\times 10^{-5}$) and k_4 (■, $\times 10^{-6}$), as a function of the medium-strength acidity; HF oxidation, $k_5 + k_7 + k_{11}$ (◆, $\times 10^{-4}$) as a function of the medium-strength and strong acid sites, and the furoic acid oxidation, k_3 (▲, $\times 10^{-2}$) as a function of the total acidity of the oxides used as catalysts.

In good agreement, there is a complete correspondence between the surface structure of the bulk and the metal-modified catalysts, as observed by XRD (Figure S5-S8). Table 3 shows the main

characterization results, in terms of morphology, metal loading and dispersion, and surface chemistry.

Bifunctional catalysts keep the surface properties of the bulk materials, observing slight decreases in the surface area due to the non-porous surface of metal nanoparticles. The N_2 isotherms are included in the Supplementary Information (Fig. S9). Considering the preparation methodology (dry impregnation except in the case of Au materials), these particles are located inside the pores. Consequently, there is a slight increase in the average size of the pores because the smallest ones can be completely blocked, increasing the relative weight of the biggest ones. This partial blockage is also congruent with the differences observed in the surface chemistry. In most cases, the total concentration of the acid sites is lower than the one of the bulk materials, keeping the same relative weight in strength terms. The highest decrease is observed with Pt/MgAl (70.1% with respect to the total concentration of the parent material), being also very significant with Pd/TiO_2 (33.4%), Pd/TiO_2 (54.9%) and Au/TiO_2 (43.7%). For the other materials, the decrease is less relevant, in general lower than 20%. The effect on the basicity is not so clear. There is a relevant decrease in basicity with Au/TiO_2 and Pt/MgAl (~33%), whereas the basicity of other materials, such as Pt/TiO_2 and Pd/TiO_2 significantly increases. The TPD data are included in the supplementary information (Fig. S10-S11).

The dispersion values indicated in these tables correspond to TEM results. The CO chemisorption analyses were also carried out, obtaining discrepancies lower than 5% in most cases (see Table S3). However, these results were not included in these tables since this technique could not be efficiently applied to Au-catalysts. TEM results demonstrate the presence of reduced metal particles in the range of 5.5–7.5 nm, with slightly lower values for Pt/CeO_2 and Pd/CeO_2 (4.6 and 1.5 nm). These values were obtained after measuring more than 100 particles from micrographs such as those shown in the supplementary information (Fig. S12-S15). In agreement with these similar particle sizes, most of these materials have a similar metal dispersion, from 18% to 30%, reaching values up to 45% for those catalysts with the smallest particle size.

These dispersion results, as well as the own nature of these metals and their synergetic effect with the surface chemistry of the catalytic support, are assumed to be the most relevant parameters to discuss the catalytic activity of these bifunctional catalysts. TPR analyses of the spent catalysts discard that experimental results are affected by a total or partial oxidation of metal particles. As indicated in the introduction section, furoic acid (FCA), 2(5 H) furanone (FN), maleic and malic acids (MA and MAL, respectively) are the most interesting compounds obtained by the furfural partial oxidation. 2(5 H) furanone (FN) is not significantly produced with almost none of the catalysts tested, with the exception of Pt/MgZr , a catalyst that selectively produces this compound (100%).

Fig. 5 shows the FCA selectivity-conversion plots for the different catalysts, whereas main results after 8 h reaction time are summarized in Table 4 (the detailed products distribution is included in the supplementary information (Table S4)). As observed in Fig. 5, the presence of noble metals increases the maximum selectivity of FCA obtained with each support. Platinum is the only exception, its behaviour strongly depending on the support. Thus, using MgZr and CeO_2 , FCA is not detected whereas, with the other two oxides (MgAl and TiO_2), the maximum selectivities (40.8% and 23.3%) are reached in less than 1 h. In the case of Pt/MgAl , the corresponding FFL conversion is almost negligible (1.5%), whereas Pt/TiO_2 is significantly more active, with 18.9% of FFL conversion after this 0.5 h.

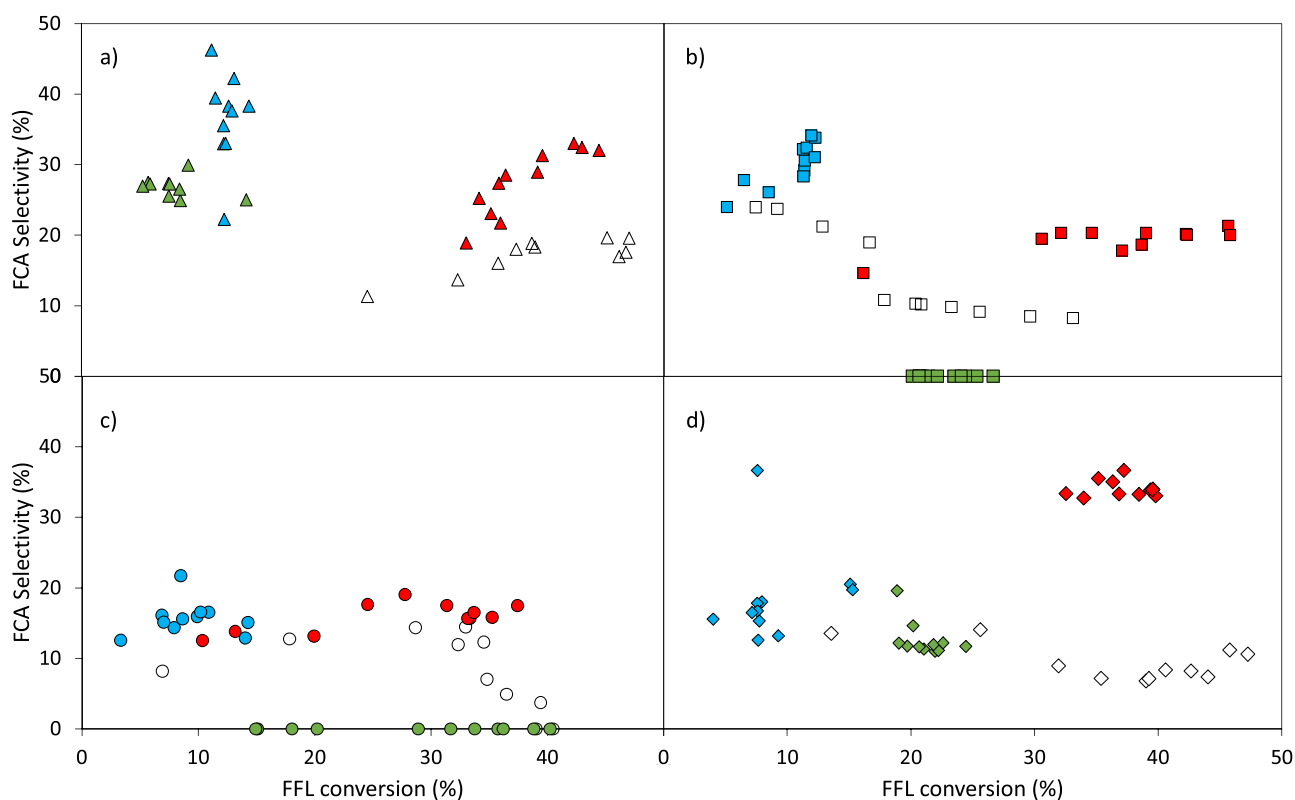
Pt/MgAl shows the slowest kinetic (9.2% of FFL conversion after 8 h), but its selectivity and stability to FCA is quite high, with a remaining selectivity of 34.8%. Both results are congruent with the significant blockage of acidic sites produced by Pt nanoparticles, slowing down all the oxidizing reactions. On the contrary, Pt/TiO_2 is discarded because of the poor FCA stability observed.

Pd/MgAl is the catalyst that produces the maximum FCA selectivity

Table 3

Main characterization properties of the different bifunctional oxides used in this work.

	Pd/ MgAl	Pt/ MgAl	Au/ MgAl	Pd/ MgZr	Pt/ MgZr	Au/ MgZr	Pd/ CeO ₂	Pt/ CeO ₂	Au/ CeO ₂	Pd/ TiO ₂	Pt/ TiO ₂	Au/ TiO ₂
N ₂ physisorption												
Surface area (m ² ·g ⁻¹)	151	165	196	82	128	78	118	114	115	66	54	63
Pore volume (cm ³ ·g ⁻¹)	0.4	0.3	0.4	0.7	0.6	0.3	0.2	0.2	0.2	0.4	0.4	0.7
Pore diameter (nm)	8.0	12.1	5.6	23.1	17.7	11.9	4.8	4.4	4.7	21.0	24.4	35.9
ICP, Metal loading (%)	0.87	0.87	1.05	0.97	0.88	0.89	0.80	0.79	1.06	0.85	0.82	1.01
TEM												
Particle size (nm)	8.3	7.7	9.9	7.8	11.9	8.6	1.5	4.6	9.3	8.5	10.8	6.5
Dispersion (%)	14.1	21.6	15.9	16.5	15.4	14.7	49.4	36.4	13.8	13.1	11.0	24.2
Acidity												
(μmol NH ₃ ·g ⁻¹)												
Physisorbed (<100 °C)	0	19.7	116.1	0	52.4	75.5	0	0	35.5	22.9	25.4	22.2
Weak	0	58.9	158.1	119.8	116.7	191.7	201.3	231.1	36.2	81.4	78.3	52.9
(100 – 200 °C)												
Medium	315.0	36.5	64.1	109.3	148.0	130.0	0	22.9	124.2	0	50.3	54.9
(200–400 °C)												
Strong (>400 °C)	50.7	43.5	0	192.3	86.3	0	0	0	0	0	0	0
Total	365.7	158.6	338.3	421.5	403.4	397.3	201.3	254.0	195.9	104.3	153.9	130.0
Basicity												
(μmol CO ₂ ·g ⁻¹)												
Physisorbed (<100 °C)	24.8	12.2	36.4	6.6	40.3	13.8	24.1	110.5	28.3	17.1	24.5	15.0
Weak	0	58.0	80.3	37.5	78.3	33.1	0	0	8.1	0	0	0
(100 – 200 °C)												
Medium	116.5	93.1	199.2	50.4	110.1	70.2	0.8	16.4	0	4.9	3.1	6.5
(200–400 °C)												
Strong (>400 °C)	156.7	56.5	0	25.9	20.9	0	4.5	37.8	14.1	46.7	38.8	3.8
Total	298.1	219.8	315.8	120.3	249.7	117.1	29.4	164.4	50.5	68.6	66.3	25.2

**Fig. 5.** Conversion vs. FCA selectivity plots for furfural oxidation using H₂O₂ at 50 °C over (a) MgAl-supported, (b) MgZr-supported, (c) CeO₂-supported, and (d) TiO₂-supported catalysts. Red dots correspond to Au-based catalysts, green dots to Pt-based catalysts, blue dots to Pd-based catalysts, and white dots to bulk supports.

(49.2% after 3 h of reaction, with a 11.2% of FFL conversion). The slow activity also observed with this material results in a quite stable FCA production (remaining selectivity after 8 h of 37.1%). Very similar results are reached with Pd/MgZr (37.1% of selectivity with 12% of FFL conversion). The FCA selectivities obtained when using supports with

redox activity are significantly lower, both comparing the maximum values (22.3% and 23.3% with Pd/CeO₂ and Pt/TiO₂, respectively), and final results after 8 h.

Both using Pt and Pd, almost total H₂O₂ conversion is reached in less than 3 h (>99%), this fact strongly affecting the distribution of the

Table 4

Furfural conversion and selectivity distribution after 8 h of reaction at 50 °C as a function of the catalyst used.

	FFL Conv. (%)	Selectivity (%)			
		FCA	FN	MA	MAL
MgAl	49.2	1.8	66.6	0	0
Pd/MgAl	14.4	37.4	0	5.9	18.8
Pt/MgAl	9.2	34.8	4	3.9	10.1
Au/MgAl	49.2	37.1	2.2	17.9	0.3
MgZr	33.1	10.1	35.6	6.6	1.4
Pd/MgZr	12	37.1	0	7.7	27.5
Pt/MgZr	21.4	0	100	0	0
Au/MgZr	45.8	23.8	4	18	1.9
CeO ₂	40.5	0	0	11.3	0
Pd/CeO ₂	14	13.8	0	7.1	21.4
Pt/CeO ₂	27.8	0	0	0	78.5
Au/CeO ₂	37.4	20.9	0	5.6	0
TiO ₂	45.8	13.6	6.9	66.2	2.6
Pd/TiO ₂	15.3	23.0	0	76.5	0
Pt/TiO ₂	22.6	14.8	6.8	9.8	7.7
Au/TiO ₂	39.5	39.1	0	0	38.1

products. These results could be different modifying the reactor configuration to allow a continuous addition of H₂O₂. Despite the high interest of this configuration (previously tested in the literature [32]), the continuous change in volume limits the use of temporal data to evaluate the kinetic of the systems as well as the influence of the catalyst in the H₂O₂ decomposition rate. These points will be deeply discussed below.

Concerning the Au-modified catalysts, the maximum FCA selectivities are quite high (38.1%, 24.2%, 22.7%, and 42%, with Au/MgAl, Au/MgZr, Au/CeO₂, and Au/TiO₂, respectively). This metal offers the maximum stability of this production, and their final FFL conversion are the highest ones (from 37 to almost 50%), resulting in the maximum

FCA yields obtained with all the screening of catalysts tested in this work (8.5%, 7.5% and 7.1% with Au/MgAl, Au/MgZr, and Au/TiO₂). These yields could be significantly increased by modifying the reaction configuration since FFL conversion increases by increasing the catalytic loading or recycling the unconverted reactant. Thus, the relevance of these results is directly related to the high selectivity obtained. Concerning to H₂O₂, although obtained conversions are very high (86.6%, 97.1%, 81.1%, and 97.3%, with Au/MgAl, Au/MgZr, Au/CeO₂, and Au/TiO₂ after 8 h), a remaining amount of oxidant is present in most of the experiments. In the same way, final carbon balances are always higher than 86% (see Table S4), the lack of information because of total FFL decomposition into CO₂ being not very relevant. The similar trends obtained with all the Au-modified catalysts suggests a positive role of this metal that can be discussed independently of the properties of the support (it will be analysed below). Based on these results, Au/TiO₂ is defined as the optimum catalyst to produce FCA.

The presence of noble metals also modifies the selectivity to lineal carboxylic acids, as β -formyl-acrylic (BFA), maleic (MA) and malic (MAL) acids productions. The maximum selectivities with the corresponding FFL conversions are compared in Fig. 6.

Maleic acid (MA) is produced with almost total selectivity using Pd/TiO₂ (84.8%), value reached after 5 h that corresponds to a very low FFL conversion (7.7%). The low basicity of this material suggests a low stabilization of previous intermediates, promoting their oxidation. In this case, the chemical properties seem to be more relevant than the own activity of the metal, observing the poor results obtained when using other supports.

The maximum selectivities obtained with Au/MgAl and Au/MgZr are also quite relevant (43.9% and 46.9%), but the stability of MA with these materials is very weak, suffering a fast disappearance, discarding the gold as a good metal to obtain this compound. Pt is also discarded, observing that this metal hinders the MA route.

Maleic acid (MAL) is a very unstable product that suffers fast oxidation with almost all the catalyst. Pt/CeO₂ is the only exception,

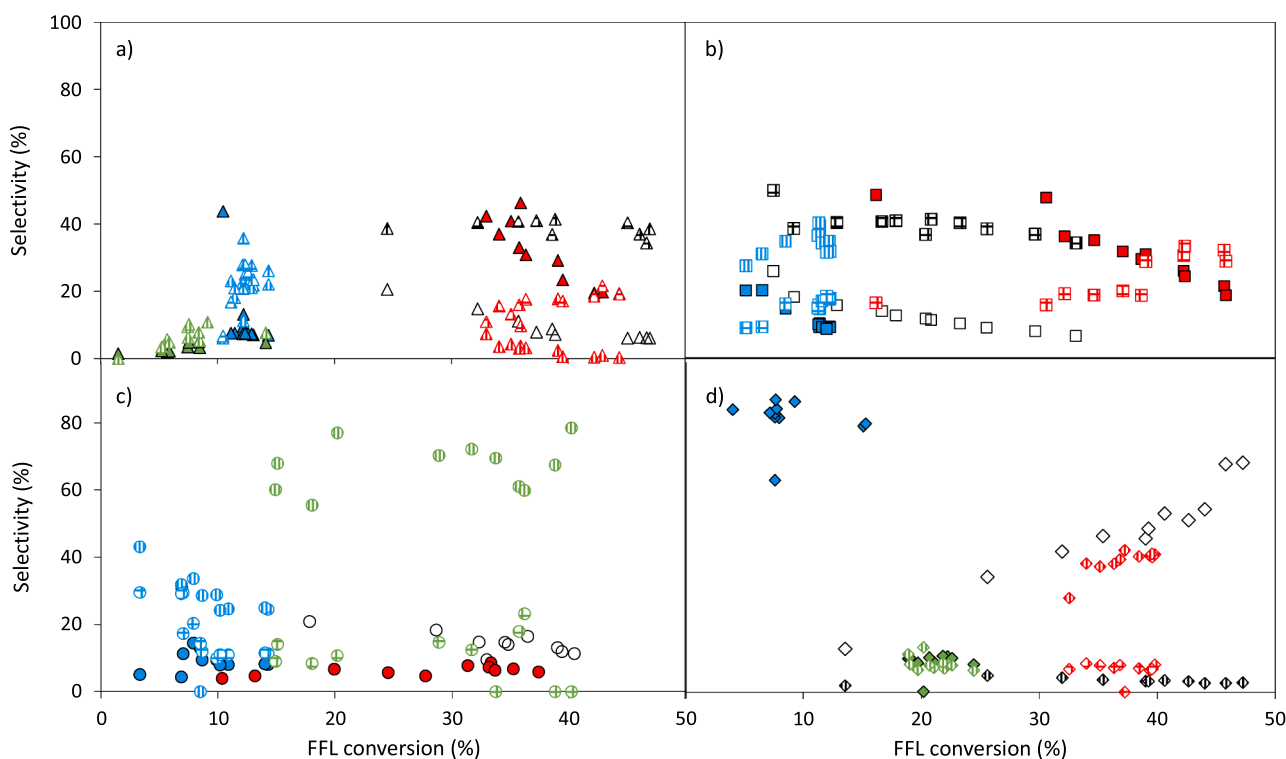


Fig. 6. Conversion vs. selectivity plots for furfural oxidation using H₂O₂ at 50 °C over (a) MgAl-supported, (b) MgZr-supported, (c) CeO₂-supported, and (d) TiO₂-supported catalysts. Red dots correspond to Au-based catalysts, green dots to Pt-based catalysts, blue dots to Pd-based catalysts, and white dots to bulk supports. Solid colors correspond to MA, vertically striped symbols to MAL and squared symbols to BFA.

with a constant MAL production, reaching a final selectivity of 78.5% with almost 28% of FFL conversion. This result could be a synergetic effect of its low basicity (the lowest basicity of all the catalysts tested) and a particular interaction between Pt nanoparticles and the redox surface of CeO₂.

The analysis about the non-carboxylic intermediates is included in the supplementary information (Fig. S16).

3.5. Kinetic study of bifunctional catalysts

All the experimental data were fitted to the proposed kinetic model. The kinetic rates obtained for the heterogeneous contribution are summarized in Table S5 and S6. The correspondence between experimental and fitted values of the best catalysts is shown in Fig. 7, whereas the other materials are included in the Supplementary Information (Fig. S17–S20).

The main conclusions derived from the kinetic study are analyzed in Fig. 8. Except in the case of using CeO₂, all the metal modified materials show higher k_1 values than the parent supports, in good agreement with the higher hydrogen peroxide conversions obtained. The lack of correspondence between the medium-strength acidity and these values suggests the prevalence of the metal activity in the H₂O₂ decomposition over the support one. The positive role of these metals in promoting hydrogen peroxide decomposition has been previously proposed in the literature [54,61].

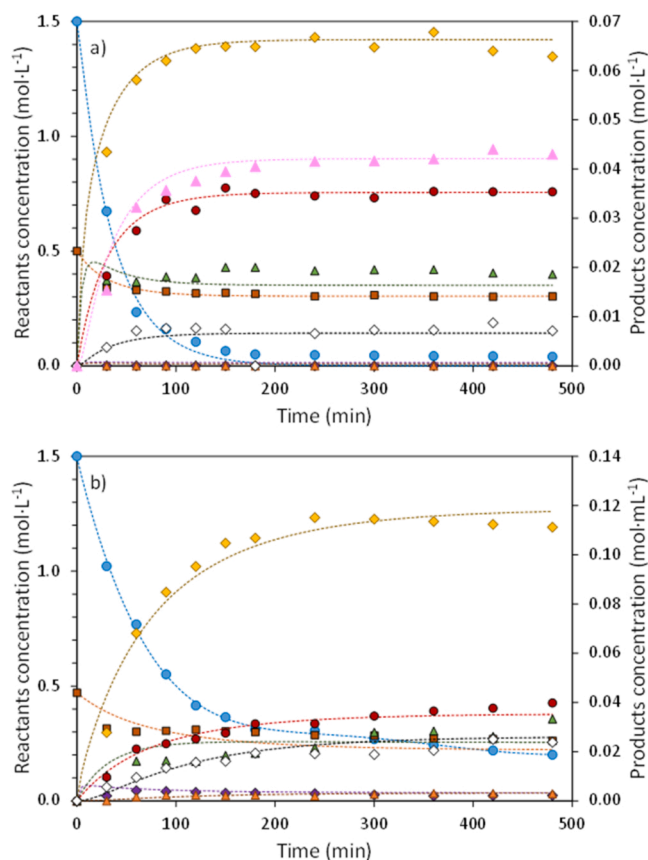


Fig. 7. Furfural oxidation with H₂O₂ at 50 °C in presence of (a) Au/TiO₂ and (b) Au/MgAl. Symbols: H₂O₂ (●); FFL (■); FA (◆); HF (▲); FCA (●); MA (◆); FN (▲); HFN (●); BFA (○); MAL (▲). Broken lines correspond to the kinetic model predictions.

The increment in the H₂O₂ self-decomposition is more notorious than the increase in the rates of the two first steps of the main process, as illustrated in Fig. 8a. This effect is more relevant in those catalysts involving Pd and Pt, whereas this undesired effect is less significant when using Au-modified materials. The presence of metal nanoparticles also affects the dominant oxidizing route. A high prevalence for the furoic route is observed with Pt and Au. In the case of Pt materials, this improvement requires support with redox properties, TiO₂ or CeO₂. On the contrary, the enhancement with Au is observed despite the type of support used, being more significant with mixed oxides (four orders of magnitude) because, with oxides, both steps are promoted, reducing the relative differences.

The effect of using bifunctional catalysts is extended to the undesired oxidations, the different steps that decompose the two primary compounds (FCA and HF), reducing the selectivity and the carbon balance. As observed in Fig. 8c, the relative weight of the FCA decomposition decreases, increasing the relative k_2/k_3 value. This effect is more relevant with Au materials, mainly Au/TiO₂ and Au/MgAl. As to the secondary steps, Au is the only metal that does not produce an increment in these rates (Fig. 8d). The sum of all these secondary kinetic rates is significantly higher with materials containing Pd and Pt, whereas these rates globally decrease with Au-modified catalysts to obtain values lower than those reached with the bulk materials.

These results suggest the coexistence of two different oxidizing mechanisms, the effect of metal nanoparticles (mainly Au) promoting the oxidation by a redox reaction, i.e., the furoic acid production by a selective interaction between furfural and hydrogen peroxide. On the other hand, those oxidation steps that follow a decomposition mechanism, releasing a formic acid molecule are not promoted by these bifunctional catalysts. This hypothesis suggests that the metal particles (mainly Au ones) enhance the simultaneous chemisorption of both reactants required. Thus, the decomposition of H₂O₂ occurs close to the active site where the furfural is adsorbed. On the contrary, the decomposition reactions are less selective and not as sensitive to this proximity as the furoic acid (FCA).

Au is identified as the best metal to maximize FCA production, and the metal dispersion is the most relevant parameter since this determines the frequency of the correct interactions between the active site and the reactants. This hypothesis is corroborated in Fig. 9, where a clear correspondence between the principal kinetic rates and the metal dispersion is observed. Not only the desired step (k_2) is promoted by a high dispersion, but also the hydrogen peroxide decomposition (k_1), the furoic acid decomposition (k_3), and the undesired 2-hydroxyfuran formation (k_4). These last two steps are less influenced than k_1 and k_2 , in agreement with the lower slope of their correlations. Thus, a medium metal dispersion must be considered, trying to reach a selective activation of the target route. Based on this premise, an intermediate dispersion (15–20%) is defined as the optimum one, a range involving Au/TiO₂ and Au/MgAl. A similar analysis with the other metals is not conclusive, no trends for the metal dispersion being observed. This fact reinforces the hypothesis of effective chemisorption required to promote the reaction (sensitive phenomenon).

4. Conclusions

The partial oxidation of furfural using H₂O₂ is a complex reaction in which the conversion and the selectivities are defined by a combination of homogeneous and heterogeneous contributions, including acidity (to promote the oxidation), basicity (to stabilize the organic acids preventing their total decomposition into CO₂), the particular activity of each metal used (Pd, Pt or Au) and a synergetic effect between the metal and the support, mainly when the support has redox properties.

A different balance between these properties and the requirements for each step of the reaction allow proposing an optimum catalyst for each interesting compound. Thus, the 2(5 H) furanone is selectively produced with Pt/MgZr (100%), maleic acid is enhanced by using Pd/

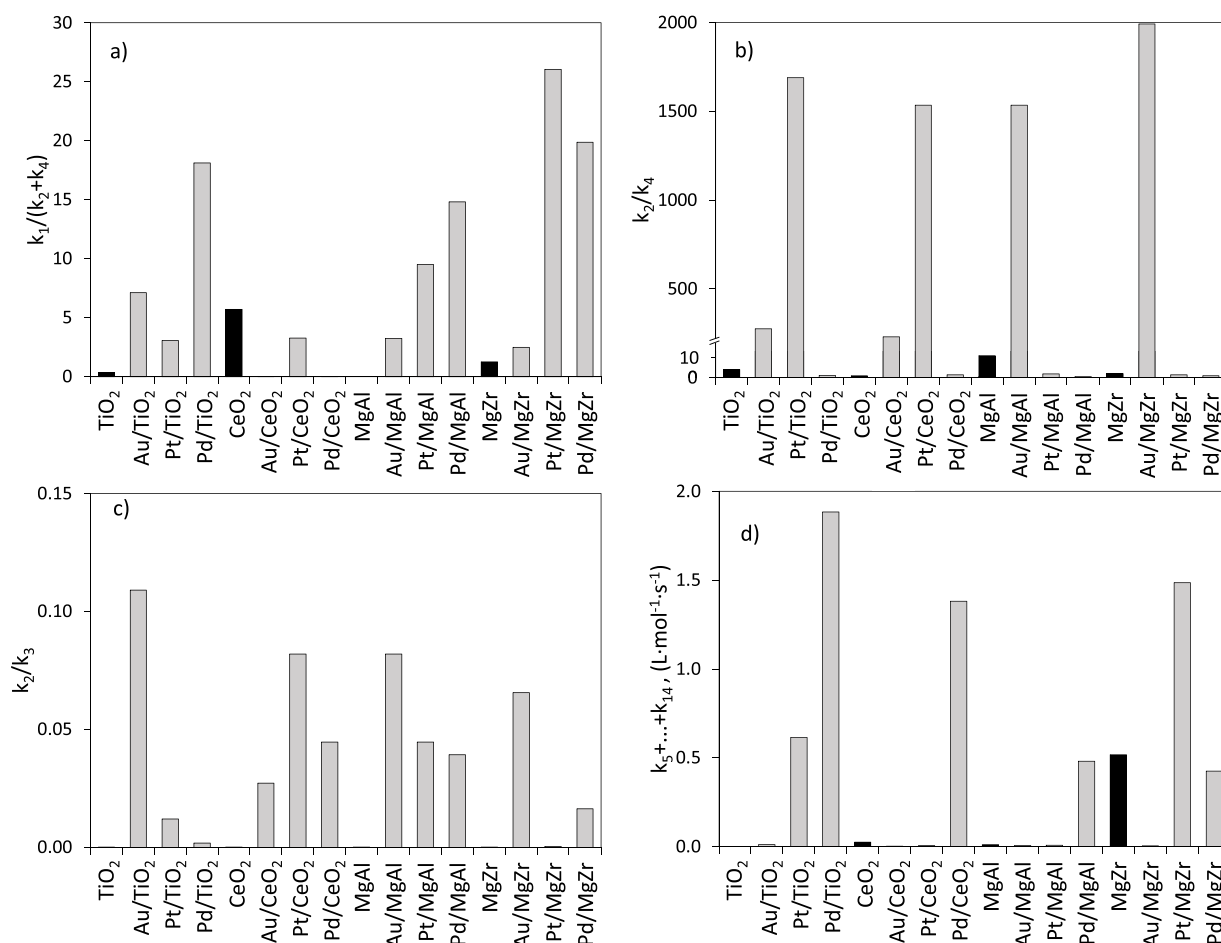


Fig. 8. : Analysis of the kinetic rates as a function of the metal-modified catalyst used.

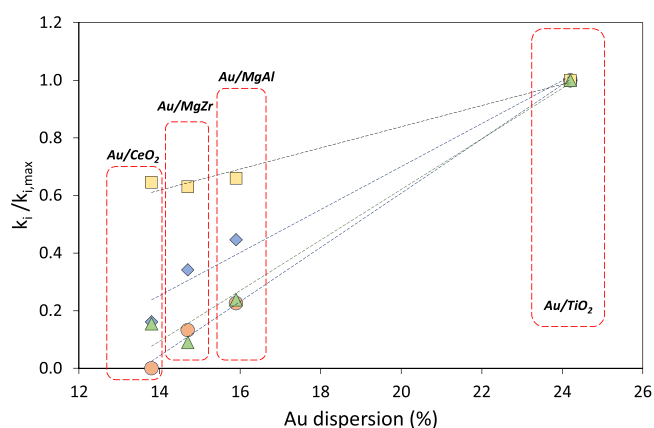


Fig. 9. Normalized evolution of k_1 (●), k_2 (◆), k_3 (■), and k_4 (▲) kinetic rates as a function of the metal dispersion of Au-modified materials. Values obtained with Au/TiO₂ are used as reference values.

TiO₂ (with a stable selectivity of 76.5%), and a 78.5% of selectivity to malic acid is reached with Pt/CeO₂.

As to furoic acid, the maximum selectivity is obtained with Au/TiO₂ (42%). In terms of product yields, Au/MgAl (8.5%) is also a good candidate for its production. The hypothesis that furoic acid is promoted by Au with a secondary role of the support was corroborated, defining and optimum particulate size of 5–7 nm. This size promotes the required

chemisorption of furfural and hydrogen peroxide on the metal particles, reducing the relevance of the parallel reactions (the B-V mechanism).

CRedit authorship contribution statement

Paula Rapado: Investigation, Data curation, Writing – original draft. **Laura Faba:** Methodology, Formal analysis, Writing – review & editing, Supervision. **Salvador Ordóñez:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Electronic supplementary material

E-supplementary data for this work can be found in e-version of this paper online.

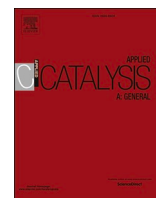
Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.111466](https://doi.org/10.1016/j.jece.2023.111466).

References

- [1] J. Blanco-Cejas, S. Martín, M. Linares, J. Iglesias, J. Moreno, Life cycle assessment applied to bio-based platform molecules: critical review of methodological practices, *J. Clean. Prod.* 414 (2023), 137513, <https://doi.org/10.1016/j.jclepro.2023.137513>.
- [2] S. Takkellapati, T. Li, M.A. González, An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery, *Clean. Technol. Environ. Policy* (7) (2018) 1615–1630, <https://doi.org/10.1007/s10098-018-1568-5>.
- [3] E. Nzediegwu, M. Pérez-Venegas, K. Auclair, M.J. Dumont, Semisynthetic production of hydroxymethylfurfural and furfural: the benefits of an integrated approach, *J. Env. Chem. Eng.* 10 (2022), 108515, <https://doi.org/10.1016/j.jece.2022.108515>.
- [4] T.W. Zhang, W.Z. Li, H.N. Xiao, Y.C. Jin, S.F. Wu, Recent progress in direct production of furfural from lignocellulosic residues and hemicellulose, *Bioresour. Technol.* 354 (2022), 127126, <https://doi.org/10.1016/j.biortech.2022.127126>.
- [5] P. Rapado, L. Faba, S. Ordóñez, Influence of delignification and reaction conditions in the aqueous phase transformation of lignocellulosic biomass to platform molecules, *Biores. Technol.* 321 (2021), 124500, <https://doi.org/10.1016/j.biortech.2020.124500>.
- [6] F. Saleem, P. Müller, K. Eränen, J. Wärnå, D. Yu Murzin, T. Salmi, Kinetics and modelling of furfural oxidation with hydrogen peroxide over a fibrous heterogeneous catalyst: effect of reaction parameters on yields of succinic acid, *J. Chem. Technol. Biotechnol.* 92 (2017) 2206–2220, <https://doi.org/10.1002/jctb.5248>.
- [7] N.K. Gupta, A. Fukuoka, K. Nakajima, Metal-free and selective oxidation of furfural to furoic acid with an N-heterocyclic carbene catalyst, *ACS Sust. Chem. Eng.* 6 (2018) 3434–3442, <https://doi.org/10.1021/acsschemeng.7b03681>.
- [8] P.L. Arias, J.A. Cecilia, I. Gandarias, J. Iglesias, M.L. Granados, R. Mariscal, G. Morales, R. Moreno-Tost, P. Maireles-Torres, Oxidation of lignocellulosic platform molecules to value-added chemicals using heterogeneous catalytic technologies, *Catal. Sci. Technol.* 10 (2020) 271–2757, <https://doi.org/10.1039/d0cy00240b>.
- [9] F. Drault, Y. Snoussi, S. Paul, I. Itabaiara Jr., R. Wojcieszak, Recent advances in carboxylation of furoic acid into 2,5-furandicarboxylic acid: pathways towards bio-based polymers, *ChemSusChem* 13 (2020) 5164–5172, <https://doi.org/10.1002/cssc.202001393>.
- [10] G. Papanikolaou, P. Lanzafame, S. Perathoner, G. Centi, D. Cozza, G. Giorgianni, M. Migliori, G. Giordano, High performance of Au/ZTC based catalysts for the selective oxidation of bio-derivative furfural to 2-furoic acid, *Catal. Commun.* 149 (2021), 106234, <https://doi.org/10.1016/j.catcom.2020.106234>.
- [11] M. Douthwaite, X. Huang, S. Iqbal, P.J. Miedziak, G.L. Brett, S.A. Kondrat, J. K. Edwards, M. Sankar, D.W. Knight, D. Bethell, G.J. Hutchings, The controlled catalytic oxidation of furfural to furoic acid using AuPd/Mg(OH)₂, *Catal. Sci. Technol.* 7 (2017) 5284–5293, <https://doi.org/10.1039/C7CY01025G>.
- [12] Q. Tian, D. Shi, Y. Sha, CuO and Ag₂O/CuO catalyzed oxidation of aldehydes to the corresponding carboxylic acids by molecular oxygen, *Molecules* 13 (2008) 948–957, <https://doi.org/10.3390/molecules13040948>.
- [13] F. Nocito, N. Ditaranto, D. Linsalata, M. Naschetti, R. Comparelli, M. Aresta, A. Dibenedetto, Selective aerobic oxidation of furfural into furoic acid over a highly recyclable MnO₂@CeO₂ core-shell oxide: the role of the morphology of the catalyst, *ACS Sust. Chem. Eng.* 10 (2022) 8615–8623, <https://doi.org/10.1021/acsschemeng.2c02341>.
- [14] C.P. Ferraz, S. Navarro-Jaen, L.M. Rossi, F. Dumeignil, M.N. Ghazzal, R. Wojcieszak, Enhancing the activity of gold supported catalysts by oxide coating: towards efficient oxidations, *Green. Chem.* 23 (2021) 8453–8457, <https://doi.org/10.1039/d1gc02889h>.
- [15] A. Roselli, Y. Carvalho, F. Dumeignil, F. Cavani, S. Paul, R. Wojcieszak, Liquid phase furfural oxidation under uncontrolled pH in batch and flow conditions: the role of in situ formed base, *Catalysts* 10 (2020) 73, <https://doi.org/10.3390/catal10010073>.
- [16] S. Eaimsumang, S. Wongkasemjit, P. Pongstabodee, S.M. Smith, S. Ratanawilai, N. Chollacoop, A. Luengnarumitchai, Effect of synthesis time on morphology of CeO₂ nanoparticles and Au/CeO₂ and their activity in oxidative steam reforming of methanol, *J. Rare Earth* 37 (2019) 819–828, <https://doi.org/10.1016/j.jre.2018.11.010>.
- [17] R. Ciriminna, L. Albanese, F. Meneguzzo, M. Pagliaro, Hydrogen peroxide: a key chemical for today's sustainable development, *ChemSusChem* 9 (2016) 3374–3381, <https://doi.org/10.1002/cssc.201600895>.
- [18] D.Y. Murzin, E. Bertrand, P. Tolvanen, S. Devyatkov, J. Rahkila, K. Eränen, J. Wärnå, T. Salmi, Heterogeneous catalytic oxidation of furfural with hydrogen peroxide over sulfated zirconia, *Ind. Eng. Chem. Res.* 59 (2020) 13516–13527, <https://doi.org/10.1021/acs.iecr.0c02566>.
- [19] Y. Ni, Z.H. Bi, H. Su, L.F. Yan, Deep eutectic solvent (DES) as both solvent and catalyst for oxidation of furfural to maleic acid and fumaric acid, *Green. Chem.* 21 (2019) 1075–1079, <https://doi.org/10.1039/c8gc04022b>.
- [20] M. Rezaei, A.N. Chermahini, H.A. Dabbagh, M. Saraji, A. Shahvar, Furfural oxidation to maleic acid with H₂O₂ by using vanadyl pyrophosphate and zirconium pyrophosphate supported on well-ordered mesoporous KIT-6, *J. Environ. Chem. Eng.* 7 (2019), 102855, <https://doi.org/10.1016/j.jece.2018.102855>.
- [21] C.V. Nguyen, J.R. Boo, C.H. Liu, T. Ahamad, S.M. Alshehri, B.M. Matsagar, K.C. W. Wu, Oxidation of biomass-derived furans to maleic acid over nitrogen-doped carbon catalysts under acid-free conditions, *Catal. Sci. Technol.* 10 (2020) 1498–1506, <https://doi.org/10.1039/c9cy02364j>.
- [22] N. Alonso-Fagúndez, I. Aguirrezabal-Telleria, P.L. Arias, J.L.G. Fierro, R. Mariscal, M.L. Granados, Aqueous-phase catalytic oxidation of furfural with H₂O₂: high yield of maleic acid by using titanium silicalite-1, *RSC Adv.* 4 (2014) 54960–54972, <https://doi.org/10.1039/C4RA11563E>.
- [23] N. Ayoub, J. Toufaily, E. Guénin, G. Enderlin, Catalyst-free process for oxidation of furfural to maleic acid by high frequency ultrasonic activation, *Gren Chem.* 24 (2022) 4164–4173, <https://doi.org/10.1039/d2gc01239a>.
- [24] H.F. Zhang, S.L. Wang, H.X. Zhang, J.H. Clark, F.H. Cao, A biomass-derived metal-free catalyst doped with phosphorus for highly efficient and selective oxidation of furfural into maleic acid, *Green. Chem.* 23 (2021) 1370–1381, <https://doi.org/10.1039/d0gc04205f>.
- [25] A.C. Alba-Rubio, J.L.G. Fierro, L. León-Reina, R. Mariscal, J.A. Dumesic, Oxidation of furfural in aqueous H₂O₂ catalysed by titanium silicalite: deactivation processes and role of extraframework Ti oxides, *Appl. Catal. B* 202 (2017) 269–280, <https://doi.org/10.1016/j.apcatb.2016.09.025>.
- [26] Q. Yu, R.X. Bai, F. Wang, Q.H. Zhang, Y. Zhang, L. Qin, Z.M. Wang, Z.H. Yuan, A sustainable system for maleic acid synthesis from biomass-derived sugar, *J. Chem. Technol. Biotechnol.* 95 (2020) 751–757, <https://doi.org/10.1002/jctb.6260>.
- [27] W. Zhu, F. Tao, S. Chen, M. Li, Y. Yang, G. Lv, Efficient oxidative transformation of furfural into succinic acid over acidic metal-free graphene oxide, *ACS Sust. Chem. Eng.* 7 (2019) 296–305, <https://doi.org/10.1021/acsschemeng.8b03373>.
- [28] Y.N. Palai, A. Bhroti, A. Fukuoka, Selective oxidation of furfural to succinic acid over Lewis acidic Sn-beta, *ACS Catal.* 12 (2022) 3534–3542, <https://doi.org/10.1021/acscatal.1c05348>.
- [29] H. Choudhary, S. Nishimura, K. Ebitani, Metal-free oxidative synthesis of succinic acid from biomass-derived compounds using a solid acid catalyst with hydrogen peroxide, *Appl. Catal. A* 458 (2013) 55–62, <https://doi.org/10.1016/j.apcata.2013.03.033>.
- [30] V. Zvarych, A. Nakonechna, M. Marchenko, O. Khudyi, V. Lubenets, L. Khuda, O. Kushnir, V. Novikov, Hydrogen peroxide oxygenation of furan-2-carbaldehyde via an easy, green method, *J. Agric. Food Chem.* 67 (2019) 3114–3117, <https://doi.org/10.1021/acs.jafc.8b06284>.
- [31] X.M. Xiang, B. Zhang, G.Q. Ding, J.L. Cui, H.Y. Zheng, Y.L. Zhu, The effect of Mg(OH)₂ on furfural oxidation with H₂O₂, *Catal. Commun.* 86 (2016) 41–45, <https://doi.org/10.1016/j.catcom.2016.08.013>.
- [32] X. Li, X. Lan, T. Wang, Selective oxidation of furfural in a bi-phasic system with homogeneous acid catalyst, *Catal. Today* 276 (2016) 97–104, <https://doi.org/10.1016/j.cattod.2015.11.036>.
- [33] J. Thuriot-Roukos, R. Khadraoui, S. Paul, R. Wojcieszak, Raman spectroscopy applied to monitor furfural liquid-phase oxidation catalyzed by supported gold particles, *ACS Omega* 5 (2020) 14283–14290, <https://doi.org/10.1021/acsomega.0c00091>.
- [34] S. Mulk, M. Sajid, L. Wang, F. Liu, G. Pan, Catalytic conversion of sucrose to 5-hydroxymethylfurfural in green aqueous and organic medium, *J. Environ. Chem. Eng.* 10 (2022), 106613, <https://doi.org/10.1016/j.jece.2021.106613>.
- [35] N.D. Shcherban, R.Y. Barakov, S.A. Sergienko, K. Eränen, J. Wärnå, D.Y. Murzin, Furfural oxidation with hydrogen peroxide over ZSM-5 based micro-mesoporous aluminosilicates, *Catal. Lett.* 152 (2022) 2920–2932, <https://doi.org/10.1007/s10562-021-03899-9>.
- [36] C. Ampelli, G. Centi, C. Genovese, G. Papanikolaou, R. Pizzi, S. Perathoner, R. J. van Putten, K.J.P. Schouten, A.C. Gluhoi, J.C. van der Waal, A comparative catalyst evaluation for the selective oxidative esterification of furfural, *Top. Catal.* 59 (2016) 1659–1667, <https://doi.org/10.1007/s11244-016-0675-y>.
- [37] J.T. Pirmohamed, J.M. Dowding, S. Singh, B. Wasserman, E. Heckert, A. S. Karakoti, J.E.S. King, S. Seal, W.T. Self, Nanoceria exhibit redox state-dependent catalase mimetic activity, *Chem. Commun.* 46 (2010) 2736–2738, <https://doi.org/10.1039/B922024K>.
- [38] A. Lolli, R. Amadori, C. Lucarelli, M. Giorgia Cutrufello, E. Rombi, F. Cavani, S. Albonetti, Hard-template preparation of Au/CeO₂ mesostructured catalysts and their activity for the selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, *Microporous Mesoporous Mater.* 226 (2016) 466–475, <https://doi.org/10.1016/j.micromeso.2016.02.014>.
- [39] O. Casanova, S. Iborra, A. Corma, Biomass into chemicals: aerobic oxidation of 5-Hydroxymethyl-2-furfural into 2,5-Furandicarboxylic acid with gold nanoparticle catalysts, *ChemSusChem* 2 (2009) 1138–1144, <https://doi.org/10.1002/cssc.200900137>.
- [40] T. Xie, S. Yue, T. Su, M. Song, W. Xu, Y. Xiao, Z. Yang, C. Len, D. Zhao, High selective oxidation of 5-hydroxymethyl furfural to 5-hydroxymethyl-2-furan carboxylic acid using Ag-TiO₂, *Mol. Catal.* 525 (2022), 112353, <https://doi.org/10.1016/j.mcat.2022.112353>.
- [41] Y. Cao, X. Liu, S. Iqbal, P.J. Miedziak, J.K. Edwards, R.D. Armstrong, D.J. Morgan, J. Wang, G.J. Hutchings, Base-free oxidation of glucose to gluconic acid using

- supported gold catalysts, *Catal. Sci. Technol.* 6 (2016) 107–117, <https://doi.org/10.1039/C5CY00732A>.
- [42] Y.Y. Gorbanev, S. Kegnaes, A. Riisager, Effect of support in heterogeneous ruthenium catalysts used for the selective aerobic oxidation of HMF in water, *Top. Catal.* 54 (2011) 1318–1324, <https://doi.org/10.1007/s11244-011-9754-2>.
- [43] F. Nocito, M. Ventura, M. Aresta, A. Dibenedetto, Selective oxidation of 5-(hydroxymethyl)furfural to DFF using water as solvent and oxygen as oxidant with earth-crust-abundant mixed oxides, *ACS Omega* 3 (2018) 18724–18729, <https://doi.org/10.1021/acsomega.8b02839>.
- [44] L. Faba, E. Díaz, S. Ordóñez, Aqueous-phase furfural-acetone aldol condensation over basic mixed oxides, *Appl. Catal. B* 113 (2012) 201–211, <https://doi.org/10.1016/j.apcatb.2011.11.039>.
- [45] R. López-Asensio, J.A. Cecilia-Buenestado, C. Herrera-Delgado, M.A. Larrubia-Vargas, C. García-Sancho, P.J. Maireles-Torres, R. Moreno-Tost, Mixed oxides derived from Hydrotalcites Mg/Al active in the catalytic transfer hydrogenation of furfural to furfuryl alcohol, *Catalysts* 13 (2023) 45, <https://doi.org/10.3390/catal13010045>.
- [46] J. Quesada, R. Arreola-Sánchez, L. Faba, E. Díaz, V.M. Rentería-Tapia, S. Ordóñez, Effect of Au nanoparticles on the activity of TiO₂ for ethanol upgrading reactions, *Appl. Catal. A* 551 (2018) 23–33, <https://doi.org/10.1016/j.apcata.2017.12.004>.
- [47] L. Faba, J. Cueto, M.A. Portillo, A.L. Villanueva Perales, S. Ordóñez, F. Vidal-Barrero, Effect of catalyst surface chemistry and metal promotion on the liquid-phase ethanol condensation to higher alcohols, *Appl. Catal. A* 643 (2022), 118783, <https://doi.org/10.1016/j.apcata.2022.118783>.
- [48] J. Mazarío, Z. Raad, P. Concepción, C. Cerdá-Moreno, M.E. Domine, Pd supported on mixed oxide as an efficient catalyst for the reductive amination of bio-derived acetol to 2-methylpiperazine, *Catal. Sci. Technol.* 10 (2020) 8049–8063, <https://doi.org/10.1039/d0cy01423k>.
- [49] R. Malathi, R.P. Viswanath, Citral hydrogenation on supported platinum catalysts, *Appl. Catal. A* 208 (2001) 323–327, [https://doi.org/10.1016/S0926-860X\(00\)00715-8](https://doi.org/10.1016/S0926-860X(00)00715-8).
- [50] R. Zanella, S. Giorgio, X.-H. Shin, C.R. Henry, C. Louis, Characterization and reactivity in CO oxidation of gold nanoparticles supported on TiO₂ prepared by deposition-precipitation with NaOH and urea, *J. Catal.* 222 (2004) 357–367, <https://doi.org/10.1016/j.jcat.2003.11.005>.
- [51] C.M. Pichler, M.G. Al-Shaal, D. Gu, H. Joshi, W. Ciptonugroho, F. Schüth, Ruthenium supported on high-surface-area zirconia as an efficient catalyst for the base-free oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid, *ChemSusChem* 11 (2018) 2083–2090, <https://doi.org/10.1002/cssc.201800448>.
- [52] M.A. Hasnat, M.M. Rahman, S.M. Borhanuddin, A. Siddiqua, N.M. Bahadur, M. R. Karim, Efficient hydrogen peroxide decomposition on bimetallic Pt–Pd surfaces, *Catal. Commun.* 12 (2010) 286–291, <https://doi.org/10.1016/j.catcom.2010.10.001>.
- [53] H. Yang, T. Zhang, H. Tian, J. Tang, D. Xu, W. Yang, L. Lin, Effect of Sr substitution on catalytic activity of La_{1-x}Sr_xMnO₃ (0 ≤ x ≤ 0.8) perovskite-type oxides for catalytic decomposition of hydrogen peroxide, *React. Kinet. Catal. Lett.* 73 (2001) 311–316, <https://doi.org/10.1023/A:1014115508872>.
- [54] B. Geng, S. Zhang, X. Yang, W. Shi, P. Li, D. Pan, L. Shen, Cu_{2-x}O@TiO_{2-y} Z-scheme heterojunctions for sonodynamic-chemodynamic combined tumor eradication, *Chem. Eng. J.* 435 (2022), 134777, <https://doi.org/10.1016/j.cej.2022.134777>.
- [55] G. Chen, D. Hong, H. Xia, W. Sun, S. Shao, B. Gong, S. Wang, J. Wu, X. Wang, Q. Dai, Amorphous and homogeneously Zr-doped MnOx with enhanced acid and redox properties for catalytic oxidation of 1,2-Dichloroethane, *Chem. Eng. J.* 428 (2022), 131067, <https://doi.org/10.1016/j.cej.2021.131067>.
- [56] C. Jiménez-Sanchidrián, J.R. Ruiz, The baeyer-villiger reaction on heterogeneous catalysts, *Tetrahedron* (9) (2008) 2011–2026, <https://doi.org/10.1016/j.tet.2007.11.024>.
- [57] D. Zhao, T. Su, Y. Wang, R.S. Varma, C. Len, Recent advances in catalytic oxidation of 5-hydroxymethylfurfural, *Mol. Catal.* 495 (2020), 111133, <https://doi.org/10.1016/j.mcat.2020.111133>.
- [58] H. Kumar, M.W. Fraaije, Conversion of furans by baeyer-villiger monooxygenases, *Catalysts* 7 (2017), <https://doi.org/10.3390/catal7060179>.
- [59] J. Luo, H. Yuan, H. Liu, J. Li, Y. Wang, Y. Wang, J. Yao, H. Li, One-pot Baeyer–Villiger oxidation of cyclohexanone with in situ generated hydrogen peroxide over Sn-Beta zeolites, *Green. Chem. Eng.* 2 (2021) 294–300, <https://doi.org/10.1016/j.gce.2021.03.003>.
- [60] C. Jiménez-Sanchidrián, J.M. Hidalgo, R. Llamas, J.R. Ruiz, Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide/benzonitrile over hydrotalcites as catalysts, *Appl. Catal. A* 312 (2006) 86–94, <https://doi.org/10.1016/j.apcata.2006.06.031>.
- [61] E. Kertalli, J.C. Schouten, T.A. Nijhuis, Effect of hydrogen and propylene on the hydrogen peroxide decomposition over Pt, PtO and Au catalysts, *Appl. Catal. A* 538 (2017) 131–139, <https://doi.org/10.1016/j.apcata.2017.03.023>.



Selective and stable production of furoic acid by furfural aerobic oxidation at controlled mild-pH conditions

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Au/MgAl

ABSTRACT

This study proposes a new and sustainable approach for the aerobic oxidation of furfural to furoic acid, the precursor of 2,5-furandicarboxylic acid (FDCA), a key monomer in the development of green polyethylene terephthalate substitutes. This work presents an alternative method for conducting this reaction utilizing a buffer solution to maintain a constant pH of 8. Au/TiO₂ is identified as the optimal catalyst, its high capacity to activate oxygen being the key factor to explain the favorable results obtained. The mechanistic and kinetic study of experimental results corroborates that the Cannizzaro route (which co-produces furfuryl alcohol) is suppressed. Thus, furoic acid is the only compound detected in the liquid phase when working at temperatures below 120°C and 20 bar O₂. The pH control has also a double positive effect on the stability, with a significant reduction in the humins formation and preventing the catalytic deactivation observed in base-free reactions by the permanent adsorption of the acids obtained. To sum up, this new approach represents a significant improvement in terms of activity, selectivity, and stability. These three aspects are crucial to ensure sustainability and to facilitate the process scale-up.

1. Introduction

There is a high interest in replacing polyethylene terephthalate (PET), one of the most widely used plastics, with a green substitute. Polyethylene 2,5-furandicarboxylate (PEF), the polymer obtained by the polymerization of 2,5-furandicarboxylic acid (FDCA) and ethylene glycol, is the most attractive alternative [1]. The direct route to produce FDCA from renewable resources (biomass) is the oxidation of 5-hydroxymethylfurfural (HMF) [2], the aldehyde obtained by the acidic hydrolysis of hexoses, mainly cellulose. However, the viability of this route is limited by the high cost of the HMF and the competition with other cellulose upgrading strategies. These reasons justify the interest in routes based on furfural, the aldehyde obtained from the hemicellulosic fraction of biomass wastes through well-developed processes, and more than one order of magnitude cheaper than HMF.

The FDCA production via furfural requires an oxidation step to get furoic acid (FCA) [3], obtaining the FDCA by carboxylation. This carboxylation consumes CO₂, with the subsequent negative footprint and the potential benefit in the fight against Climate Change.

As for the first step, the current industrial production of FCA (gas-phase Cannizzaro reaction) falls far short of fulfilling the Principles of

Green Chemistry. It is conducted in strong NaOH media, with all the problems derived from using a homogeneous catalyst [3]. This route involves furfural disproportionation, limiting the maximum selectivity of FCA to 50% since furfuryl alcohol (F-OH) is co-produced. The furfural oligomerization at Cannizzaro conditions (very high pH, 150°C) is also a relevant drawback [4].

A green alternative is the furfural direct oxidation, using H₂O₂, oxygen, or air as oxidizing agents. Studies using H₂O₂ show a complex mechanism, combining oxidations with C-C bond cleavage steps [5–7]. Most of these works are focused on the production of maleic (MA), malic (MAL), or formic acid (FA), and the FCA is obtained as a byproduct with selectivity lower than 5%. The continuous production of acids reduces the pH, enhancing catalytic homogeneous routes (even heterogeneous in the presence of a solid catalyst), and hindering the operation with high selectivities to the target chemical (FCA) [8].

Some authors propose the partial oxidation promoted by O₂. This reaction can be limited by gas-liquid oxygen mass transfer, requiring more severe conditions; and needing heterogeneous catalysts for oxygen activation [9]. To prevent acid-induced catalytic deactivation, these reactions are usually performed in a strong basic medium (NaOH). The presence of NaOH promotes Cannizzaro reactions whereas the solid

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material catalyzes both the direct oxidation of the aldehyde and the sequential oxidation of the furfuryl alcohol to aldehyde and the aldehyde to acid. This approach requires tight temperature control to prevent furfural oligomerization, likely to take place at very basic conditions. Among other works, Verdeguer and co-workers show that high selectivities of FCA (92%) can be achieved in the presence of a PbPt bimetallic catalyst [10]. Dowthwaite et al. reach yields higher than 93% with 1% AuPd/Mg(OH) [9], a value slightly higher than the 76% obtained with Au/MnO [11]. Sha and co-workers achieve high selectivities (92%) to FCA with Ag₂O/CuO [12]. A recent work proposes different Au/Nb₂O₅ catalysts, obtaining moderate conversions (<50%) [13]. As a general conclusion of these works, Au is proposed as the optimum noble metal for the furfural oxidation, more stable in an oxidant aqueous medium than Pt or Pd, and avoiding radical pathways of furfural degradation, with the inherent positive effect on the selectivity and stability of the process [14].

Despite these promising results, this route is still contrary to the Principles of Green Chemistry due to the use of NaOH. An alternative approach considers working in homogeneous base-free conditions (uncontrolled pH). Several works obtain clear improvements concluding that the absence of NaOH must be compensated using basic supports (MgO, CaO, or hydrotalcite-derived materials) to boost the catalytic performance [15,16]. As an alternative to this concept, other authors suggest adding a second metal (bimetallic catalysts), or the development of core-shell materials, with the subsequent increase in the complexity of the catalytic system [17–19].

Despite the promising results in terms of initial conversion and selectivity, there are two relevant drawbacks related to stability: the continuous leaching of the support because of the formation of organic acids [8,20], and the Au deactivation by irreversible formic acid adsorption [16]. Both problems could be minimized using a buffer solution that neutralizes the acids obtained. To our best knowledge, there is no previous literature about this approach, despite the optimum equilibrium between activity, stability, and sustainability that it could represent.

This research proposes the furfural partial oxidation into furoic acid using bifunctional heterogeneous catalysts and substituting the strong basic conditions by a buffer solution. Au is selected as the active metal, considering two different supports, MgAl and TiO₂. When using MgAl, a positive influence is expected due to the basic properties that stabilize the reactants and intermediates [15,16]. In contrast, the use of TiO₂ aims to enhance oxygen activation because oxygen can be adsorbed not only on the Au nanoparticles but also on this reducible support, leading to its dissociation at the interface [21]. The comparison between both materials gives relevant information about the limiting step of the process. The analysis focuses on the main reaction parameters to optimize the selectivity and productivity of the FCA, including catalyst, reaction time, pH, O₂ pressure and temperature. The stability is also assessed through multiple consecutive tests.

2. Experimental section

2.1. Catalysts preparation

The MgAl mixed oxide was synthesized from the parent MgAl hydrotalcite obtained by the co-precipitation of the nitrate salts (1 M) under high saturation conditions (pH 10–12) and vigorous stirring at 85°C, according to the detailed procedure proposed by Larina and co-workers [22]. The suspension was aged at 85°C for 24 h before filtering and washing. The solid was calcined at 700°C in flowing air for 5 h to obtain the desired mixed oxide. Commercial TiO₂ (P25, Sigma Aldrich) was activated in flowing air for 2 h (5 °C·min⁻¹) at 500°C. The CeO₂ was synthesized from an aqueous solution of cetyl trimethyl ammonium bromide (CTAB, Sigma Aldrich, 96%), (NH₄)₂Ce(NO₃)₆ (Sigma Aldrich, 98%), and ammonium hydroxide (VWR, 20%), reaching final concentrations of 0.2, 0.3 and 1.8 M, respectively. The solution was maintained

at 100 °C for 2 h, washed with acetone to remove the CTAB and remnant ions and dried in an oven at 80 °C for 24 h, obtaining the oxide. To activate the oxide surface, the recovered solid was air-treated at 400 °C for 4 h.

Bifunctional materials with 1 wt% of Pd and Pt, were prepared by the incipient wetness impregnation method and Pd(NH₃)₄(NO₃)₂ and Pt(NH₃)₄(NO₃)₂ as precursors (both supplied by Sigma Aldrich, >99.99%). 1 wt% Au was prepared by the deposition-precipitation method, using HAuCl₄·3 H₂O (Sigma Aldrich, 99%) as precursor [23]. These materials were calcined for 3 h at the same temperature as their corresponding bulk materials (i.e., 500 and 700°C for TiO₂ and MgAl, respectively). The catalysts were reduced in H₂ (Air liquid 10 v/v% in Ar) for 4 h, at 300°C (5°C·min⁻¹). The metal content was corroborated by ICP-MS, obtaining differences between the real and the theoretical content lower than 1%.

2.2. Catalyst characterization

Morphological properties (surface area, pore volume) were determined by nitrogen physisorption at -196°C using an ASAP 2020 (Micromeritics) static volumetric apparatus applying the BET and BJH approaches. The metal dispersion was measured by transmission electronic microscopy (TEM), using a JEOL JEL 2100 microscope. Histograms and average particle size were calculated by analyzing at least 100 particles in each sample, using the software Confocal ImageJ.

The metal loading was determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) using a HP 7900 of Agilent. Approximately 50 mg of the sample were dissolved in a mixture of HCl (2.25 mL) and HNO₃ (0.75 mL) using a microwave-assisted Teflon bomb.

The acidity and basicity of the catalysts were analyzed by temperature programmed desorption (TPD) in a Micromeritics 2900 TPD/TPR. 50 mg of solid were pre-treated in He flow and saturated with CO₂ or NH₃ to determine the basicity or acidity, respectively. The evolution of CO₂ and NH₃ signals were followed using a Pfeiffer Vacuum Omnistar Prisma mass spectrometer as well as the temperature was increased at 2.5°C·min⁻¹ from 25 to 550°C. Signals obtained were quantitatively related to the sites concentration after the corresponding calibration of areas obtained.

2.3. Reaction studies

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) equipped with a backpressure regulator and a PID temperature controller. The system was loaded with the catalyst (0.5 g, 50–80 µm) and 0.25 L of a 0.5 M aqueous solution of furfural (Sigma Aldrich, 98%). The pH of the initial furfural solution (4.8) was modified by adding of a buffer solution of KHCO₃ to adjust at pH 8. Air was purged with O₂ (Air Liquid, >99.99%), and the oxidation was carried out with a stirring of 700 rpm. Once reaching the target temperature, samples were taken from the sampling port, filtered using a 0.22 µm nylon syringe filter, and diluted in a 1:4 ratio to prevent saturations of the signal during the analysis. The O₂ pressure and temperature was varied to study their influence on conversion, and the products distribution.

The qualitative and quantitative analyses were done by HPLC (1200 Series, Agilent), using a RI detector, a Hi-Plex H column as the stationary phase, and 0.5 mL·min⁻¹ of 0.5 mM H₂SO₄ (49–51%, VWR) solution as mobile phase. Commercial samples (Sigma Aldrich) of all the compounds detected were used to calibrate the signal, including furoic acid (98%), formic acid (99%), maleic acid (99%), and malic acid (99%).

The analysis of the reaction evolution is presented in terms of conversion, selectivity, yield, and carbon balance closure, according to the following expressions:

$$x \quad (\%) = \frac{C_{FFL,0} - C_{FFL,t}}{C_{FFL,0}} \cdot 100 \quad (1)$$

$$S_i \text{ (%) } = \frac{n_i \cdot C_i}{5 \cdot (C_{FFL,0} - C_{FFL,t})} \cdot 100 \quad (2)$$

$$\text{Yield \text{ (%) } } = \frac{n_i \cdot C_i}{5 \cdot C_{FFL,0}} \cdot 100 \quad (3)$$

$$C.B.(\%) = \frac{\sum (n_i \cdot C_i)}{5 \cdot C_{FFL}} \cdot 100 \quad (4)$$

Where “ C_{FFL} ” is the furfural concentration, “ n_i ” and “ C_i ” are the number of carbons and the molar concentration of each compound.

All the reactions were analyzed twice and discrepancies between analyses were lower than 5%. Due to the complexity of most figures presented, error bars are not included to facilitate the legibility of the plots. Reaction conditions were chosen to guarantee an intrinsic kinetic control, with a small particle size distribution of the catalyst (50–80 μm), and a high stirring speed (700 rpm). This theoretical assumption was corroborated considering the Carberry number (Ca) and the Wheeler-Weisz criteria, obtaining maximum values of $3 \cdot 10^{-9}$ and $2.1 \cdot 10^{-5}$, respectively for the most unfavorable conditions. This analysis is included in the [Supplementary Information \(Table S1\)](#). These values are far from the maximum ones to consider these mass transfers as relevant (0.05 and 0.1) [24]. MATLAB code was used to perform all the calculations and to solve the set of ordinary differential equations (“ode45”). The fitting of the unknown parameters was accomplished by the least-square method using the “lsqcurvefit” function and the Levenberg-Marquardt algorithm.

3. Results and discussion

3.1. Catalyst screening

A blank reaction in the absence of any catalyst was performed at 80°C with 20 bar of O_2 , using KHCO_3 to establish a constant pH (8), to evaluate the relevance of a possible autocatalytic mechanism. No products were detected after 8 h, observing a furfural conversion of 9.4%, a value that directly corresponds to the carbon unbalance (91.5%), suggesting a high relevance of furfural oligomerization. In good agreement with this hypothesis, the initial yellow solution is significantly darker after 8 h, as well as the aspect of the solid catalyst. This undesired effect has been previously observed in the literature [25,26].

The same results were obtained when using different supports (TiO_2 , CeO_2 and MgAl), with total correspondence between conversions of 10.5%, 10.2%, and 9.8%, and carbon balance closure of 89.5%, 89.7%, and 90.1%, for TiO_2 , CeO_2 , and MgAl , respectively. To sum up, these catalysts are not active for the furfural oxidation at these conditions whereas they promote furfural oligomerization. These results are in good agreement with the previous literature [8,16,19], highlighting the high furfural oligomerization trend and the need for a noble metal catalyst to activate the oxygen dissociation required for the oxidation steps. Despite the initial assumption of TiO_2 as an active support to activate the oxygen, these results demonstrate that this activity is only relevant in the metal- TiO_2 interface [21]. Once the need for metal nanoparticles is corroborated, a set of experiments using bifunctional catalysts with different noble metals supported on TiO_2 was performed. The main results after 2 h are summarized in [Fig. 1](#).

FCA or any other products of furfural oxidation are not detected when using Ru or Rh, despite observing furfural conversion with both catalysts. Based on these results, Ru and Rh are discarded for further studies, concluding that they are not active for the target oxidation. The furfural conversions obtained with these materials are mainly caused by adsorption and decomposition into humins, in the same way as when using parent supports.

On the other hand, Pd, Pt, and Au produce furoic acid, FCA selectivity being the highest when using Au (9.6% vs. 5.8% and 4.6% of Pt and Pd after 2 h, respectively). In all the cases, furoic acid is the only

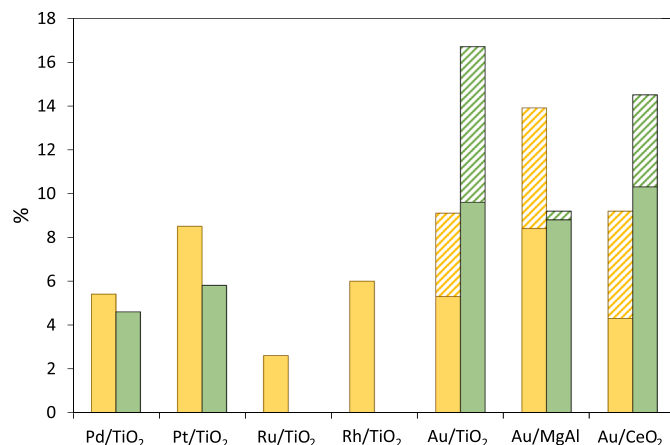


Fig. 1. Furfural conversion (yellow) and FCA selectivity (green) obtained in the furfural oxidation at 80°C with 20 bar of O_2 as a function of the catalyst. Results after 2 h except those shown with diagonal bars that corresponds to 8 h reaction time.

compound detected in the liquid phase. If the selectivity was expressed in terms of the relative distribution of detected products, Pd, Pt, and Au will produce 100% furoic acid. Similar selectivities are only reported when using a very complex catalyst ($\text{Au}(\text{-PVP})/\text{Nb}_2\text{O}_5\text{-AC}$) and NaOH to guarantee a basic medium [9], or in a few works under free-base conditions [19,20]. These results in free-base conditions are limited by a very relevant deactivation, a drawback prevented by this approach, as discussed below.

Although the analysis in terms of total selectivity (based on the furfural conversion and not only on the distribution of the liquid-phase products) could mask the goodness of these results in comparison to other published studies, this parameter allows identifying the relative weight of humins production. To our best knowledge, the only reference with high FCA selectivity that includes the carbon balance indicates values even lower than 10% [17], suggesting a humins production higher than in this approach.

Despite the highest conversion after 2 h is obtained with Pt/TiO_2 (8.5%), the FCA selectivity is almost 40% lower than the one obtained with Au/TiO_2 . Thus, Au/TiO_2 shows the best compromise between activity and FCA selectivity, reaching almost double selectivity than the one obtained with Pd/TiO_2 , despite the same conversion. This result suggests that this catalyst minimizes humins production.

According to this screening, Au is selected as the most promising metal. Its activity is also analyzed using other supports, such as MgAl or CeO_2 . The highest conversion after 2 h reaction time is obtained for Au/MgAl (8.4%). However, this catalyst presents low FCA selectivity (8.8%), with almost 93% of the converted furfural being transformed into degradation products (humins). Similar FCA selectivities are reached with Au/TiO_2 and Au/CeO_2 (9.6% and 10.3%, respectively), observing slightly higher conversion in the case of Au/TiO_2 (5.3% vs. 4.3%). Since no conclusive results were obtained by this screening, the activity of these materials was compared at longer reaction times (8 h).

The relative increase in the furfural conversion after 8 h reaction time is quite similar in all the cases, obtaining almost double values (9.1%, 13.9%, and 9.2%, for Au/TiO_2 , Au/MgAl , and Au/CeO_2 , respectively). As to the FCA production, Au/TiO_2 is highlighted as the most selective one (16.7%), followed by Au/CeO_2 (14.5%) and, finally, Au/MgAl (9.2%). With the two first catalysts, the carbon balance closure remains over 92%, whereas a lower value (88.6%) is reached with Au/MgAl , suggesting a higher relevance of humins formation since no other product was detected in the liquid phase.

According to the literature, the metal dispersion and, subsequently, the metal nanoparticle size are the key parameters to activate the oxygen [27]. Considering the characterization results summarized in

Table 1

Summary of the main characterization properties of the different catalysts.

	Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore Volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Metal dispersion (%)	Acidity ($\mu\text{molNH}_3\cdot\text{g}^{-1}$)	Basicity ($\mu\text{molCO}_2\cdot\text{g}^{-1}$)
Pd/TiO ₂	66	0.4	13.1	104.3	68.6
Pt/TiO ₂	54	0.4	11.0	153.9	66.3
Ru/TiO ₂	48	0.4	21.0	186.2	19.3
Rh/TiO ₂	55	0.3	42.7	175.1	26.3
Au/TiO ₂	62	0.7	24.2	130.0	25.2
Au/MgAl	196	0.4	15.9	338.3	315.8
Au/CeO ₂	115	0.2	13.8	195.9	50.5

Table 1, the best Au dispersion corresponds with Au/TiO₂, a result that could justify the highest FCA selectivity reached with this material (16.7%, 100% if considering only the products in the liquid phase). However, there is not a good correlation between these two parameters, with significant discrepancies in terms of FCA selectivity despite the similar metal dispersion of Au/MgAl and Au/CeO₂. These results suggest that the catalyst performance cannot be explained in terms of structure sensitiveness, with surface reactivity playing a key role in the selectivity evolution. Thus, the high surface acidity of MgAl is suggested as the responsible for its high humins production. The relevant role of these

active sites in humins formation has been demonstrated in the literature [28–30].

To maximize the FCA production and to evaluate the relative relevance of the different active sites, the influence of reaction conditions (O₂ pressure and temperature) has been studied, considering two catalyst with opposite properties: Au/TiO₂ (the highest metal dispersion and the lowest concentration of acidic and basic sites) because of its high FCA production, and Au/MgAl (the material with the highest concentration of acidic and basic sites) because of its high furfural conversion. If active sites related to the support are not of key relevance, working at

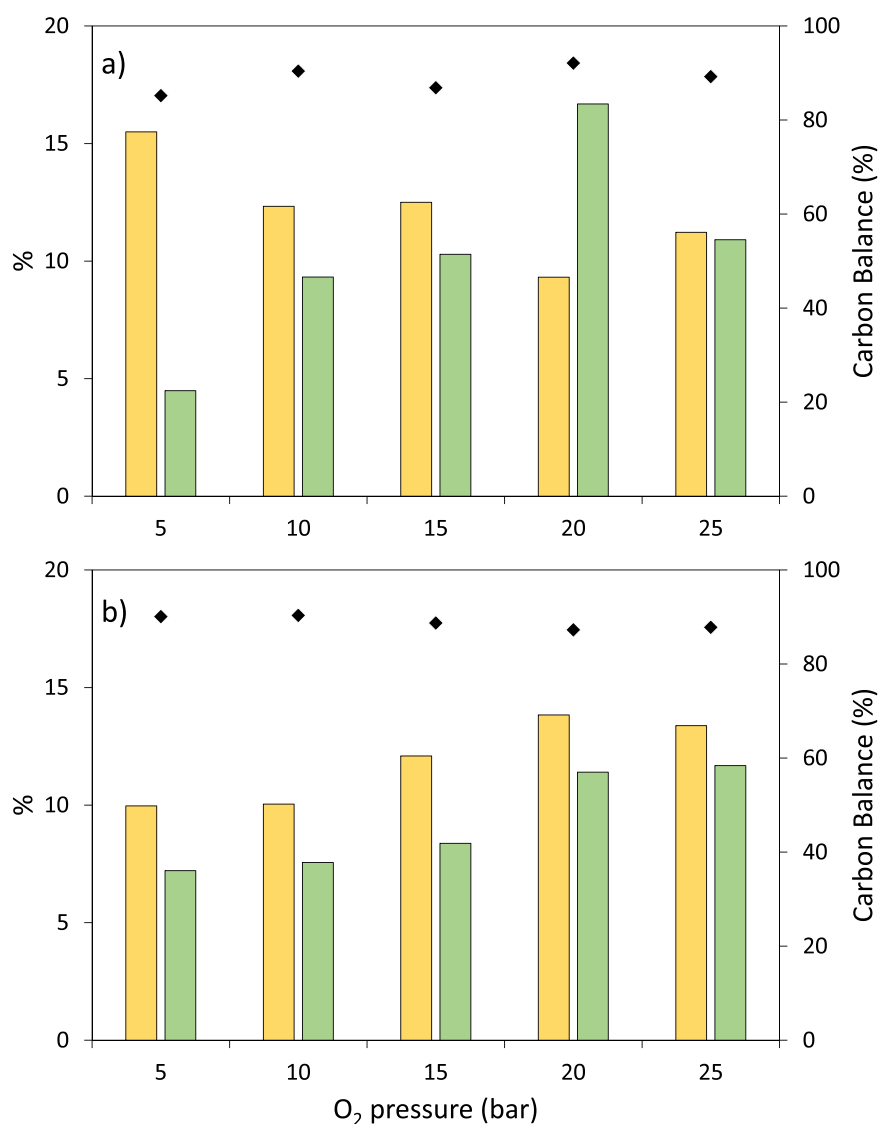


Fig. 2. Furfural conversion (yellow), FCA selectivity (green) and carbon balance closure (◆, right axis) obtained after 8 h of furfural oxidation at 80°C as a function of the O₂ pressures using (a) Au/TiO₂ and, (b) Au/MgAl as catalyst.

higher pressures and temperatures could improve the results by a faster O_2 activation. On the other hand, the evaluation of these results when using Au/MgAl could be relevant to evaluate the different kinetics and mechanisms of humins formation and furfural oxidation.

3.2. Influence of the oxygen partial pressure

The influence of O_2 pressure was studied from 5 to 25 bar of O_2 , keeping constant the temperature at 80°C. A different effect is observed when working with Au/TiO₂ or Au/MgAl, as shown in Fig. 2.

Reaction conditions are chosen to guarantee that experimental results are not limited by oxygen availability. In reactions at 10, 15, 20, and 25 bar, the oxygen (from 0.34 to 0.85 M) is higher than the stoichiometric one (furfural requires 0.5 M of oxygen to be transformed into FCA). The fast stirring ensures a good mixture between the liquid and the gas phases, leading to the effective oxygen saturation of the liquid phase (concentrations in the liquid phase of 0.005, 0.008, 0.104, and 0.013 M, at 10, 15, 20, and 25 bar, respectively). As to the experiment at 5 bar, the O_2 concentration (0.17 M) is slightly lower than the stoichiometric one, but the conversion obtained is significantly lower than the maximum that could be obtained at these conditions. Thus, all the results can be explained based on the activity of the catalyst.

In both cases, very different behaviours are observed below and above 20 bar, although with different trends depending on the catalyst. When using Au/TiO₂, the highest conversion (15.5%) is obtained at the lowest pressure (5 bar), observing a clear decreasing trend with the pressure, reaching a minimum at 20 bar (9.3%). At 25 bar, a slight increase in conversion is observed (11.3%). As to the target product, its selectivity strongly increases from 5 to 20 bar (from 4.5% to 16.7%), with a relevant decrease (10.9%) at 25 bar. These results suggest a positive effect of the O_2 pressure on the control of the main reaction explained suggesting that the surface oxygen concentration can be limiting for this step. Thus, most of the furfural converted at low pressure is transformed into humins since the low surface oxygen concentration promotes those routes that do not require oxygen (mainly oligomerization to humins). Once the availability of the oxygen

increases, humins production is hindered, increasing the selectivity for partial oxidation. The decrease in FCA selectivity observed at 25 bar is explained because the excess of O_2 and the subsequent promotion of secondary reactions degrade the FCA released in the reaction. The final product of these reactions is CO₂ (not analysed) but its intermediates in the oxidation process, maleic and formic acid, are, mainly at intermediate times (1.5% after 3.5 h). In good agreement, the maximum FCA selectivity is obtained after 3 h (11.4%), its degradation being more favourable than its production for longer times.

As for Au/MgAl, from 5 to 20 bar, there is a clear correspondence between the O_2 pressure, the furfural conversion (from 10% to 13.8%, values that correspond to activities from 12.5 to 17.3 mmol/g·h) and the FCA concentration (from 7.2% to 11.4%), suggesting that the surface concentration of oxygen is somewhat limiting the catalyst performance (opposite behavior than Au/TiO₂). At 25 bar, the FCA selectivity slightly increases (from 11.4% to 11.8%) but the furfural conversion decreases (from 13.8% to 13.4%), suggesting that the presence of oxygen is changing the properties of the metal sites or that there is a competitive adsorption between furfural and oxygen. With this catalyst, maleic and formic acid are not detected and the carbon balance obtained is only due to the presence of humins production, a process insensitive to the pressure.

3.3. Influence of the temperature

To study the influence of temperature, furfural oxidation was studied in the range 80–150°C keeping 20 and 25 bar of O_2 pressure and using the KHCO₃ buffer to guarantee a constant pH of 8. The main results obtained with both catalysts are shown in Fig. 3, comparing the furfural conversion, carbon balance closure, and product distribution in selectivity terms.

Furfural conversion strongly increases when increasing the temperature, at both pressures and catalysts tested. These increments are more relevant when working at 20 bar, reaching maximum values of 85% and 69.5%, for Au/TiO₂ and Au/MgAl, respectively. The corresponding maximum values at 25 bar are 45.4% and 41%, respectively.

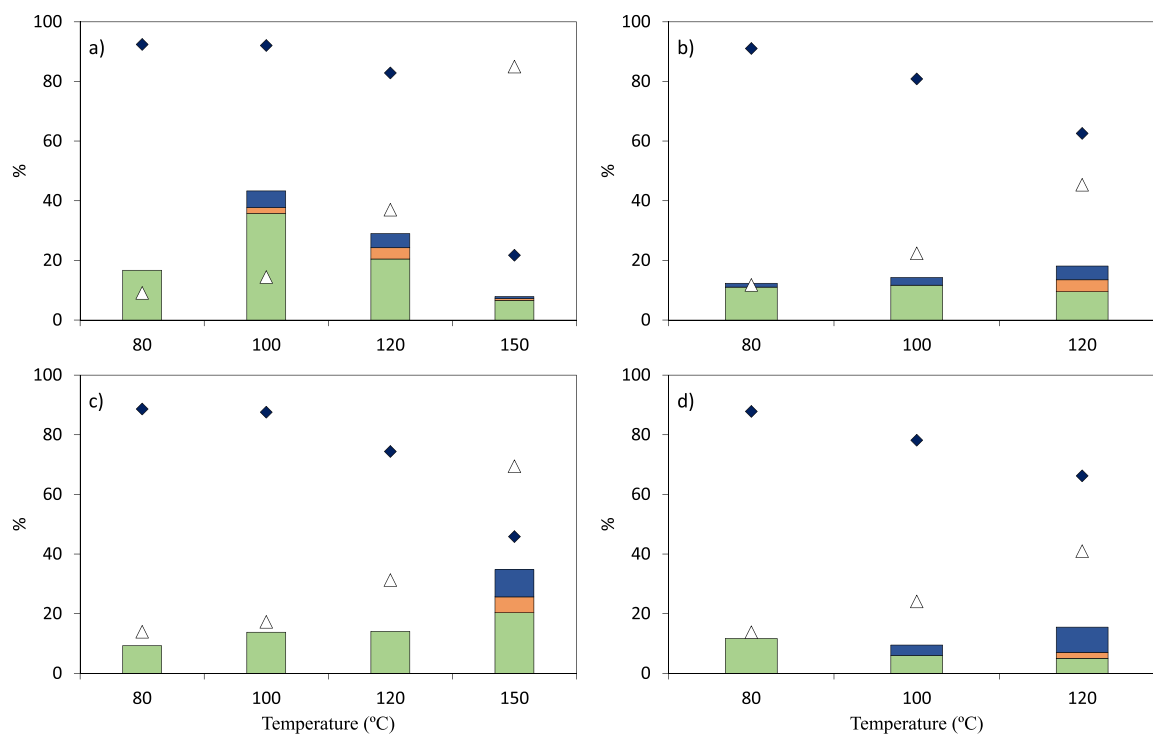


Fig. 3. Furfural conversion (Δ), carbon balance (◆) and selectivity distribution (bars) obtained in the furfural oxidation at different temperatures (80–150°C) for Au/TiO₂ at (a) 20 and (b) 25 bar, and Au/MgAl at (c) 20 and (d) 25 bar. Legend: FCA (green), MA (orange), FA (blue).

These rising trends match with a decrease in the carbon balance, being in both cases more relevant when working at 25 bar. Considering the low carbon balance at 120°C (62.6% and 41% for Au/TiO₂ and Au/MgAl, respectively), this pressure was not tested at 150°C. At the same temperature, when working at 20 bar, the carbon balance obtained were 83% and 74%, respectively. The carbon unbalance increase suggests that, at these conditions, a relevant fraction of the furfural converted is not transformed into the target compound (FCA). On the contrary, it undergoes oligomerization, producing insoluble humins not detected in the liquid phase.

The presence of these humins determines the selectivity distribution since, according to the selectivity equation (Eq. (2)), these undesired compounds are also considered for the calculus (parameter based on the total furfural disappearance). However, this is not the only aspect to explain the carbon balance depletion. The presence of FCA oxidation compounds, such as maleic and formic acid, involves the release of CO₂, a compound involved in the carbon balance that cannot be detected with our experimental system. Moreover, the temporal profiles of these compounds (discussed in the kinetic section) suggest that the severity of the reaction is high enough to lose control of the main reaction, producing the total oxidation of these organics into CO₂.

Looking at the effect of temperature and pressure on catalyst performance, the optimum conditions must be established by analysing the FCA selectivity and yield. In general, Au/TiO₂ presents higher oxidation activity than Au/MgAl, not only because of the higher conversion but also since maleic and formic acids are detected in relevant amounts in all the cases, except when working at 80°C and 20 bar. Thus, mild conditions are the optimum to maximize FCA production. In good agreement, the maximum selectivity is reached at 100°C and 20 bar (35.8%), observing a decrease in selectivity when increasing the temperature. This effect is not so well observed when working at 25 bar because the increase in conversion masks the global result. As to the production, the maximum FCA yield is obtained at 120°C and 20 bar (7.6%). In this case, the selectivity decrease is compensated with a conversion increase. Similar selectivities are obtained at 100°C and 150°C, with yields of 5.3%. As to the results obtained at 25 bar, the selectivity is always significantly lower, as well as the yield, reaching the maximum value at 120°C (4.3%).

The lower oxidation activity of Au/MgAl produces lower FCA selectivities (maximum value of 20.4 at 150°C and 20 bar of O₂ pressure) but this compound is the only one detected in the liquid phase (i.e. the selectivity in the liquid phase is 100% for FCA) except when working at 150°C or 25 bar. In yield terms, 120°C and 20 bar are the optimum conditions for this catalyst, reaching 4.4% of FCA yield. However, this value is more than 40% lower than the optimum with Au/TiO₂ (same conditions).

As conclusion of this reaction conditions screening, the oxygen activation (promoted by Au/TiO₂) is identified as the key aspect to perform the furfural oxidation whereas no relevant problems related to the stability of the adsorption of reaction intermediates (aspect in which the acidic/basic properties of Au/MgAl could be crucial) is not so important.

3.4. Kinetics studies

To elucidate the reaction mechanism, identify all the possible routes for the furfural transformation, and discern if the same mechanism explains the results obtained by the two catalysts, Fig. 4 illustrates the evolution of the selectivities with conversion for the most representative experiments (those in which a larger number of compounds are involved). At milder conditions, FCA is obtained with almost 100% selectivity in the liquid phase.

FCA, the target product, is an oxidation primary product, being the main reaction product at low conversions, and following a marked decreasing trend as the conversion increases. This conclusion is the same despite the catalyst and the reaction conditions. At low conversions, the

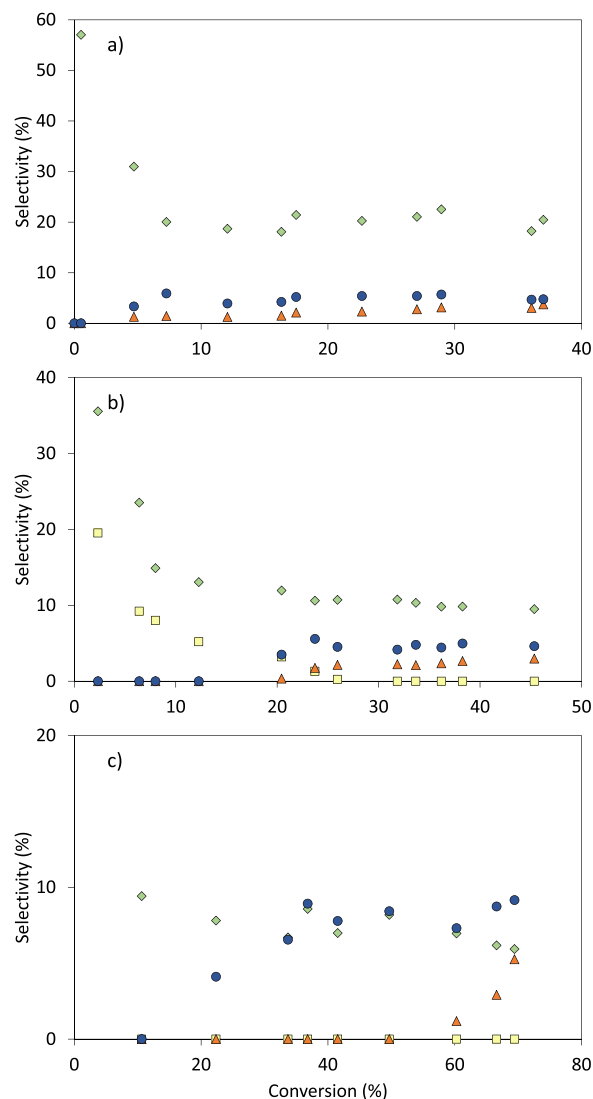


Fig. 4. Selectivity evolution as a function of conversion. Data corresponding to: (a) Au/TiO₂ at 120°C and 20 bar, (b) Au/TiO₂ at 120°C and 25 bar, and (c) Au/MgAl at 150°C and 20 bar. Symbols: FCA (◆), HFN (□), FA (●), MA (▲).

FCA decrease coincides with the appearance of formic and maleic acid (FA and MA, respectively).

In the same way, the FCA profile reaches a flat evolution, more noticeable in the case of the reaction catalyzed with Au/TiO₂ at 120°C and 20 bar. According to these results, the furfural oxidation into FCA and the subsequent degradation into MA and FA is identified as the main route, being common for both catalysts tested.

Results obtained with Au/TiO₂ at 25 bar and 120°C demonstrate the presence of a parallel route, producing 2-hydroxy-2(5H)furanone (henceforth, HFN) as a primary product. The well-marked selectivity decrease observed for HFN indicates that its degradation is a fast process. This second route is identified as relevant only for the most severe pressure and temperature conditions tested using Au/TiO₂, i.e., at 120 and 150°C and 20 bar, and at 100 and 120°C with 25 bar of O₂. The detailed profiles are included in the [Supplementary Information](#) (Fig. S1–S6). On the contrary, this compound is not observed in any case when working with Au/MgAl.

It should be noted that FA selectivities are always higher than the MA ones, suggesting that FA is produced from more than one route. This fact is more evident in the case of using Au/MgAl. In this case, MA is only

detected when the furfural conversion is higher than 65%, whereas FA is relevant from 20%. This observation suggests a third parallel route in which furfural is directly oxidized into formic acid, obtaining a very unstable intermediate that is only observed at trace levels at low conversions (2-hydroxyfuran, HF).

These conclusions allow defining the reaction mechanism illustrated in Scheme 1, where compounds in grey color are required to complete the carbon balance, but they are not quantitatively detected at working conditions (only in traces at the most severe ones).

Based on this mechanism, a preliminary fit of the experimental data considering all the steps were carried out for both materials and all the conditions. Experimental results were fitted to different kinetic models, the best results being obtained when considering an evolution type Langmuir-Hinshelwood for the main reactions, and a potential and independent behavior for the oligomerization and the total oxidation into CO₂. This model is congruent with the furfural and FCA adsorptions previously discussed, a hypothesis that could be extended to all the organics involved since they have the same functional groups. Considering that O₂ is continuously provided by gas-liquid interphase transport, the concentration of this reactant can be considered constant and embedded in the apparent kinetic rate values.

The temporal evolution of all the compounds obtained with both catalysts at the different conditions tested was fit to the proposed mechanism applying the corresponding mass balances, considering the reactor as an ideal stirred batch reactor. All the equations as well as the kinetic rates and the adsorption constants are included in the Supplementary Information (Eq. S1-S6, Table S2-S7). In the same way, all the temporal profiles comparing the experimental points with the fitted data are also included in the Supplementary Information (Fig. S1-S6).

Relevant conclusions can be drawn from this comprehensive study, allowing a significant simplification of this complex model. The values obtained for “k₂” (HFN formation step) are systematically lower than those values obtained for “k₁” (FCA formation step), being zero in most of the cases and more than two orders of magnitude lower than “k₁” in the other cases. Moreover, the “k₅” (HFN decomposition) values are significantly higher than the “k₂” ones. In the same way, “k₆” (HF decomposition) values are one or two orders of magnitude higher than “k₃” (HF formation). In fact, this last constant has null values for all the reactions carried out with Au/MgAl. With this context and considering the negligible concentration of HF and HFN intermediates, the

production of maleic and formic acid can be assimilated to a primary step, being directly obtained from furfural, without distinguishing if the particular formation route is from HF or HFM. With this simplification, “K_{ads,HFN}” and “K_{ads,HF}” are also neglected in the simplified model.

The profiles of the FCA discard a relevant decomposition of this compound when using Au/TiO₂. In good agreement, negligible values for “k₄” and “K_{ads,FCA}” were obtained. However, to define a common mechanism for both catalysts, the FCA decomposition into MA and FA is considered. Based on the conclusions of this detailed study, the reaction mechanism can be simplified to the one shown in Scheme 2, and the kinetic model can be expressed according to the following equations (Eq. 5 – Eq. 8), in which only the relevant kinetic steps and adsorption processes are considered.

$$\frac{dC_{FFL}}{dt} = \frac{-k'_1 \cdot K_{ads,FFL} \cdot C_{FFL} - k'_2 \cdot K_{ads,FFL} \cdot C_{FFL}}{1 + K_{ads,FFL} \cdot C_{FFL}} - k'_3 \cdot C_{FFL} \quad (5)$$

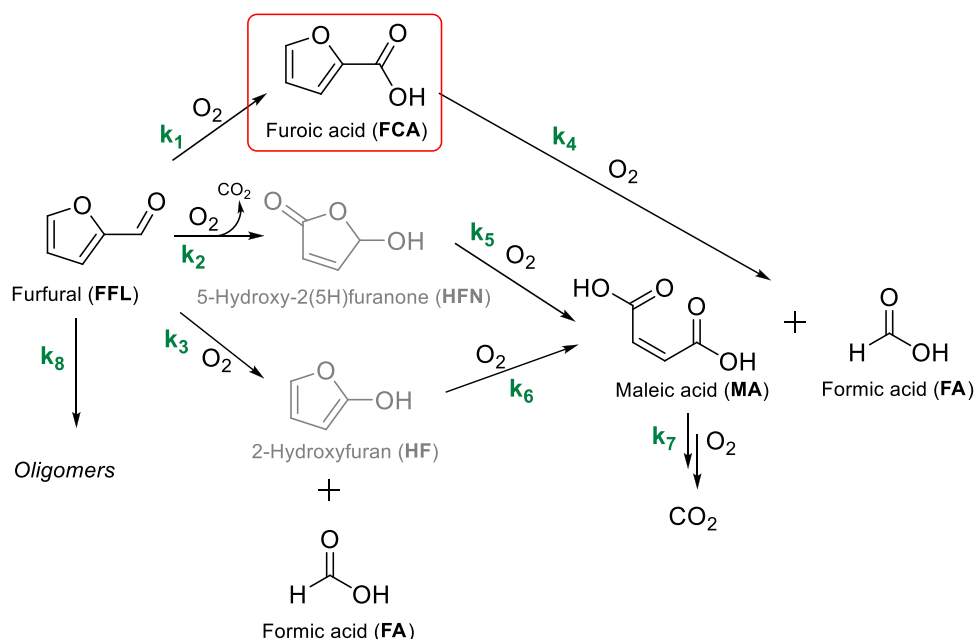
$$\frac{dC_{FCA}}{dt} = \frac{k'_1 \cdot K_{ads,FFL} \cdot C_{FFL}}{1 + K_{ads,FFL} \cdot C_{FFL}} - k'_5 \cdot C_{FCA} \quad (6)$$

$$\frac{dC_{MA}}{dt} = \frac{k'_2 \cdot K_{ads,FFL} \cdot C_{FFL}}{1 + K_{ads,FFL} \cdot C_{FFL}} - k'_4 \cdot C_{MA} + k'_5 \cdot C_{FCA} \quad (7)$$

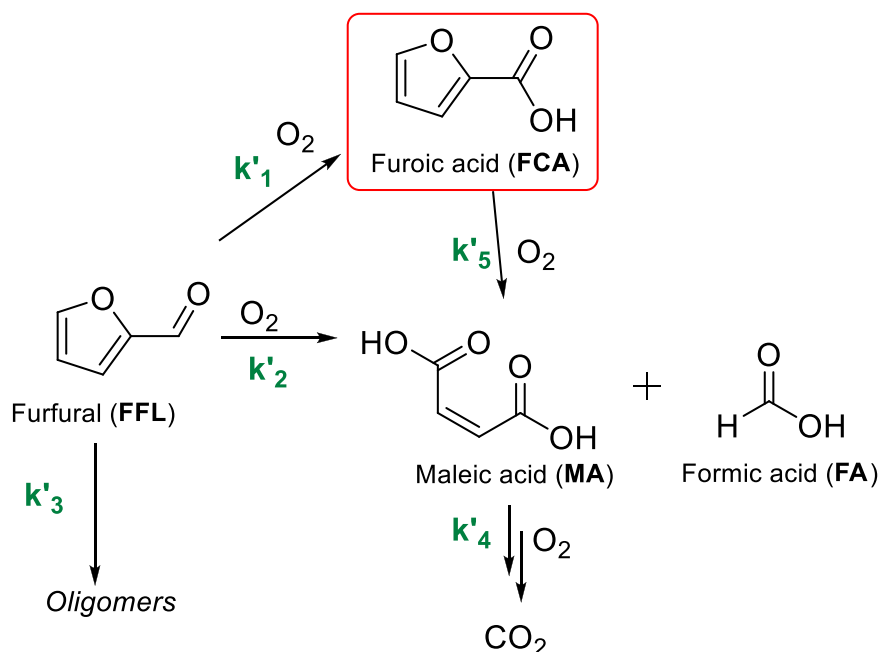
$$\frac{dC_{FA}}{dt} = \frac{k'_2 \cdot K_{ads,FFL} \cdot C_{FFL}}{1 + K_{ads,FFL} \cdot C_{FFL}} \quad (8)$$

After comparing different types of kinetics and analyzing the fit of all the reactions tested, some steps are considered with a Langmuir-Hinshelwood model, whereas other steps follow first-order behavior. For the adsorption processes, the best fit was obtained considering that both oxidation routes involving furfural require the adsorption of this reactant on the same type of active sites. In all the cases, apparent rates are considered, involving in these constants the oxygen concentration, since, as commented before, oxygen concentration will be constant throughout each entire experiment.

The kinetic constants obtained for Au/TiO₂ are summarized in Table 2. This model represents the temporal evolution of all the compounds obtained in reactions at the most severe conditions whereas, for all the reactions at 80°C (and most of those at 100°C), the presence of only one product (FCA) reduces the number of steps involved, with null values for k'₂, k'₄ y k'₅. The corresponding values for Au/MgAl are



Scheme 1. Reaction mechanism of furfural oxidation using O₂ as oxidizing agent.



Scheme 2. Simplified reaction mechanism of furfural oxidation using O_2 as oxidizing agent according to the preliminary analysis of the complex mechanism.

Table 2

Reaction rate constants based on the simplified reaction mechanism for Au/TiO₂ catalyst as function of different O_2 pressures and reaction temperatures.

P (bar)	T (°C)	k'_1 [s^{-1} mol $^{-1}$]	k'_2 [s^{-1} mol $^{-1}$]	k'_3 [s^{-1}]	k'_4 [s^{-1}]	k'_5 [s^{-1}]	$K_{ads, FFL}$ (L·mol $^{-1}$)	r^2
5	80	0.0017	-	$8.3 \cdot 10^{-6}$	-	-	0.00036	0.9999
	80	0.0015	-	$5.5 \cdot 10^{-6}$	-	-	0.00034	0.9999
15	80	0.0017	-	$5.2 \cdot 10^{-6}$	-	-	0.00030	0.9995
	80	0.0017	-	$4.3 \cdot 10^{-6}$	-	-	0.00029	0.9998
25	80	0.0017	-	$3.9 \cdot 10^{-6}$	-	-	0.00028	0.9999
	100	0.0142	0.012	$7.4 \cdot 10^{-6}$	0.105	$8 \cdot 10^{-8}$	0.00015	0.9999
25	100	0.0110	0.010	$5.1 \cdot 10^{-6}$	0.141	$1.7 \cdot 10^{-6}$	0.00012	0.9984
	120	0.0944	0.140	$1.4 \cdot 10^{-5}$	0.111	$1.2 \cdot 10^{-6}$	$4 \cdot 10^{-5}$	0.9996
25	120	0.0750	0.101	$8.9 \cdot 10^{-6}$	0.250	$2.2 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	0.9977
	150	0.2148	0.414	$3.8 \cdot 10^{-5}$	0.240	$5 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	0.9942

shown in Table 3, observing slightly higher values for almost all the kinetic rate constants.

Figs. 5 and 6 show the good fit of experimental values to those predicted by the model for the most representative experiments, with Au/TiO₂ and Au/MgAl, respectively. The adjustment of each reaction is shown in the supplementary information (Fig. S7-S10).

As analyzed in Fig. 7, using Au/TiO₂ at the lowest temperature (80°C), the direct production of FCA from furfural (k'_1) does not depend on the oxygen pressure, obtaining very similar rate constant values at all the studied pressures. This fact suggests that oxygen surface

concentration is large enough for not being a limiting reactant, and does not lead to any kind of inhibition or modification of furfural adsorption sites. However, different trend was observed at higher temperatures (100–120°C), observing that total pressure negatively affects this step (Table 2). This result suggests that oxygen hinders the oxidation reaction at these conditions, that could be at first insight, unexpected for an oxidation reaction. This apparent contradiction can be explained by two different causes: a competitive adsorption of oxygen and furfural at higher temperatures (plausible if temperature has a more marked negative effect on furfural adsorption than for oxygen adsorption) or

Table 3

Reaction rate constants based on the simplified reaction mechanism for Au/MgAl catalyst as function of different O_2 pressures and reaction temperatures.

P (bar)	T (°C)	k'_1 [s^{-1} mol $^{-1}$]	k'_2 [s^{-1} mol $^{-1}$]	k'_3 [s^{-1}]	k'_4 [s^{-1}]	k'_5 [s^{-1}]	$K_{ads, FFL}$ (L·mol $^{-1}$)	r^2
5	80	0.0051	-	$7.6 \cdot 10^{-6}$	-	-	$1.0 \cdot 10^{-5}$	0.9999
10	80	0.0073	-	$7.3 \cdot 10^{-6}$	-	-	$1.4 \cdot 10^{-5}$	0.9996
15	80	0.0082	-	$6.0 \cdot 10^{-6}$	-	-	$1.4 \cdot 10^{-5}$	0.9997
20	80	0.0090	-	$6.6 \cdot 10^{-6}$	-	-	$9.2 \cdot 10^{-6}$	0.9997
25	80	0.0011	-	$5.9 \cdot 10^{-6}$	-	-	$1.1 \cdot 10^{-5}$	0.9998
20	100	0.0012	-	$8.1 \cdot 10^{-6}$	-	-	$1.3 \cdot 10^{-5}$	0.9992
	100	0.0039	0.0046	$1.7 \cdot 10^{-5}$	0.030	$3.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-6}$	0.9979
20	120	0.0035	-	$9.3 \cdot 10^{-6}$	-	-	$1.5 \cdot 10^{-6}$	0.9953
25	120	0.0099	0.0764	$2.8 \cdot 10^{-5}$	0.076	$8.0 \cdot 10^{-5}$	$1.6 \cdot 10^{-6}$	0.9986
20	150	0.0156	0.0886	$1.6 \cdot 10^{-5}$	0.018	$5.3 \cdot 10^{-6}$	$0.8 \cdot 10^{-6}$	0.9998

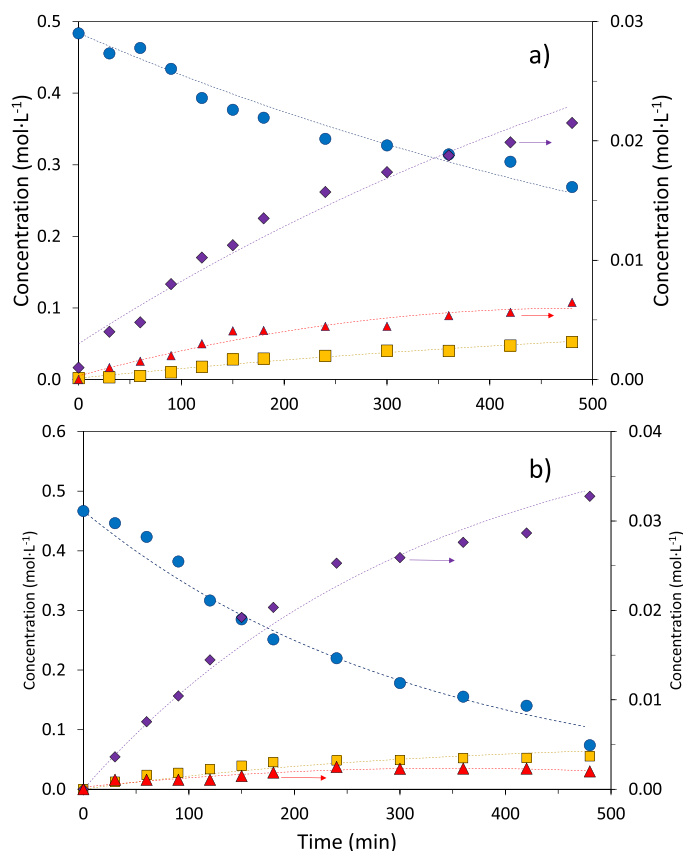


Fig. 5. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of all the compounds involved in the furfural oxidation catalyzed by Au/TiO₂ at (a) 120°C and 25 bar, and (b) 150°C and 20 bar. Symbols: FFL (●), FCA (◆), MA (▲), and FA (■).

that higher oxygen concentrations at the highest studied temperatures can lead to an overoxidation of the Au atoms, decreasing its intrinsic activity for this reaction.

A decreasing trend with total oxygen pressure is observed for the furfural oligomerization (k_3). According to the initial comparison of results in the absence of a catalyst and using the different supports, the furfural oligomerization has a relevant homogeneous component, but the solid catalysts also contribute to this reaction (mainly catalysts with acid properties). Both mechanisms have been previously identified in the literature [26,27,31]. The evolution of k_3 (constant that involves both mechanisms) with the pressure indicates that the furfural oligomerization is inhibited by the presence of oxygen. If this analysis is extended to higher temperatures, the comparison between kinetic rates obtained at 20 and 25 bar demonstrates that the role of oxygen concentration cannot be discarded. Thus, minor discrepancies are obtained, with slightly higher values at 20 bar in comparison to the same step at 25 bar and the same temperature. In global terms, working with high pressure enhances the selective FCA production with k_1/k_3 ratios from 206 to 430, at 5 and 25 bar, respectively.

In the case of the reactions catalyzed with Au/MgAl, the kinetic study demonstrates a positive effect of the oxygen pressure enhancing the target reaction, with increasing k_1 values with increasing O₂ pressures at all the studied temperatures. This trend is the opposite of that observed for Au/TiO₂ catalysts and suggests that oxygen surface concentration can be limiting for this step when working with Mg-Al supported catalysts. It should be noted that the absence of redox properties of the MgAl support hinders oxygen mobility from metal sites where O₂ is activated to the support (several authors suggest that furfural can be adsorbed in basic sites of the support in this kind of materials [32]). This fact makes surface oxygen concentration more limiting and justifies that

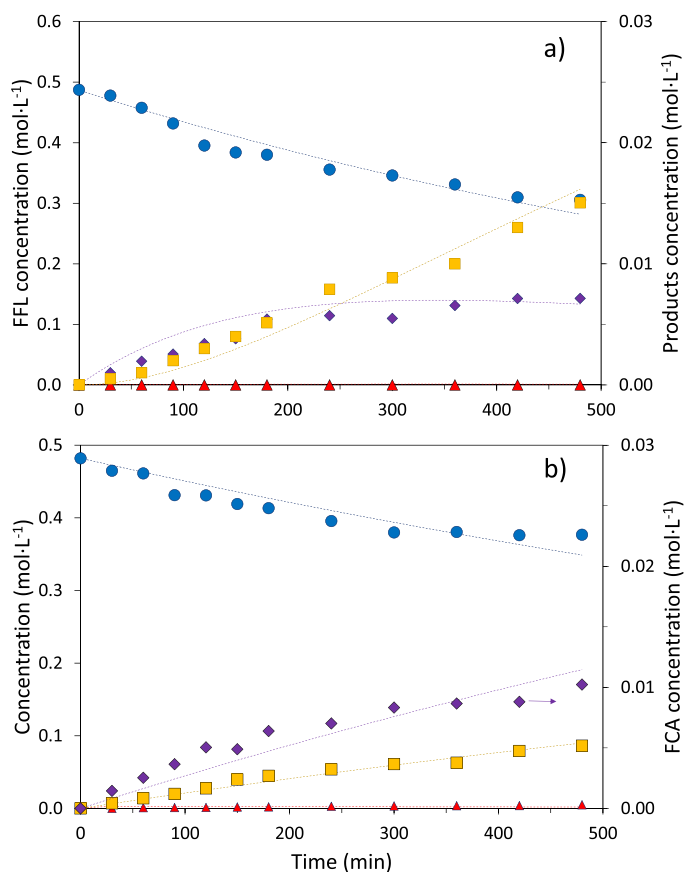


Fig. 6. Comparison between experimental (symbols) and fit values (broken lines) obtained for the temporal evolution of all the compounds involved in the furfural oxidation catalyzed by Au/MgAl at (a) 100°C and 25 bar, and (b) 120°C and 25 bar. Symbols: FFL (●), FCA (◆), MA (▲), and FA (■).

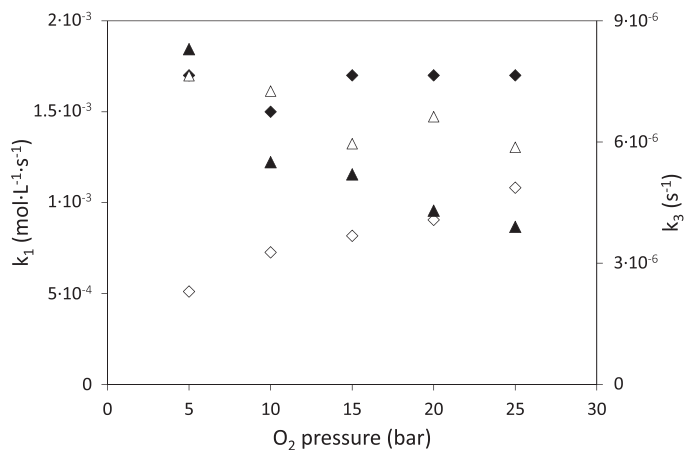


Fig. 7. Evolution of k_1 (diamonds) and k_3 (triangles) with the O₂ pressure. Data corresponding to Au/TiO₂ (black) and Au/MgAl (white).

increasing pressures lead to higher reaction rates. The chemical differences between Mg-Al oxide (with a higher concentration of basic sites that can promote furfural adsorption but inactive for activating oxygen) and TiO₂ (which has a lower affinity for furfural adsorption but higher electron mobility that can promote overoxidation of the metal sites at the highest temperatures) appear to be responsible for the differential effect of oxygen pressure.

Regarding the furfural oligomerization, the second relevant reaction with this material, the decreasing trend defined for Au/TiO₂ is also

observed, with slightly higher values. This result is in good agreement with the role of acid sites promoting oligomerization [33]. With this catalyst, the other steps are only significant when working in the most severe conditions, not obtaining data enough to complete a deep analysis.

As to the influence of the temperature, both at 20 and 25 bar, kinetic rates demonstrate a clear increasing trend, coherently with an Arrhenius dependence. This correspondence verifies the initial assumptions considered when deciding which steps follow an exponential model and which adsorption constants are relevant (opposite behavior of kinetic rates and adsorption constants with the temperature). Although not all the steps are relevant at mild conditions, all the rates obtained were adjusted to the Arrhenius model, obtaining the activation energies summarized in Fig. 8. Although the activation energy should be independent of the pressure, it must be noted that the analysis is done considering the apparent kinetic constants, which involve the oxygen pressure.

The highest activation energy is obtained for the FCA decomposition (k'_5), in good agreement with the fact that this step is only relevant at the most severe conditions. No relevant differences were obtained with the two parallel steps involving the furfural to produce FCA and MA (k'_1 and k'_2 , respectively), with typical values of catalytic reactions. Quite similar activation energies are also obtained for the FFL oligomerization (k'_3) and MA total oxidation (k'_4), but in this case with values congruent with a non-catalytic character of these steps.

The activation energies obtained with this material are lower than those obtained with Au/TiO₂. These results suggest that the slower kinetics obtained are due to significantly lower values of the pre-exponential constants, values related to the probability of constructive interactions between both reactants.

To sum up, the oxygen availability in the vicinity of adsorbed furfural is suggested as the main factor controlling the kinetics of the furfural oxidation to produce furoic acid when using Au/MgAl, obtaining significantly better results when working with Au/TiO₂ because of the higher oxygen mobility in the support. Thus, at the same conditions, FCA productions 160% higher than those obtained with Au/MgAl are

reached when using TiO₂ as support.

3.5. Catalyst reusability

Activity studies performed with Au/TiO₂ working under controlled pH conditions (buffered solution) demonstrate that this new approach allows obtaining a relevant increase in terms of furoic acid selectivity (100% in the liquid phase except when working at too high temperatures) concerning previous literature at pH 14 [9,13]. Moreover, the relevance of humins production is reduced. However, to compare this configuration with the base-free one, stability is a key factor to consider. Literature under uncontrolled pH demonstrates a high FCA selectivity but a strong deactivation due to the permanent adsorption of this acid and the catalytic leaching due to the low pH [8,15,16,20].

To study the catalytic stability, the catalyst after the reaction with Au/TiO₂ at 100°C and 20 bar was recovered by filtration, washed with water, and introduced in subsequent cycles with fresh solutions of furfural without any previous reactivation. Results obtained after 8 h of reaction are summarized in Fig. 9, in terms of furfural conversion, furoic acid selectivity, and carbon balance closure. Strong stability is observed, with negligible decreases in the furfural conversion (14.6% after the fourth cycle) and constant furoic acid selectivities of 35%. The slight increase in the carbon balance closure suggests that the humins formation is slightly hindered, maybe because of the permanent adsorption of these solids on the active catalytic sites.

These results demonstrate that the catalytic leaching and the deactivation by permanent adsorption of FCA are prevented by working with a buffer solution at pH 8. This strong stability contrasts with the results published when working under uncontrolled pH, which is a clear advantage of this configuration.

4. Conclusions

We propose a new approach for obtaining furoic acid by aqueous-phase partial oxidation of furfural working with a buffer solution at controlled pH = 8 and using a low catalytic loading. Different catalysts

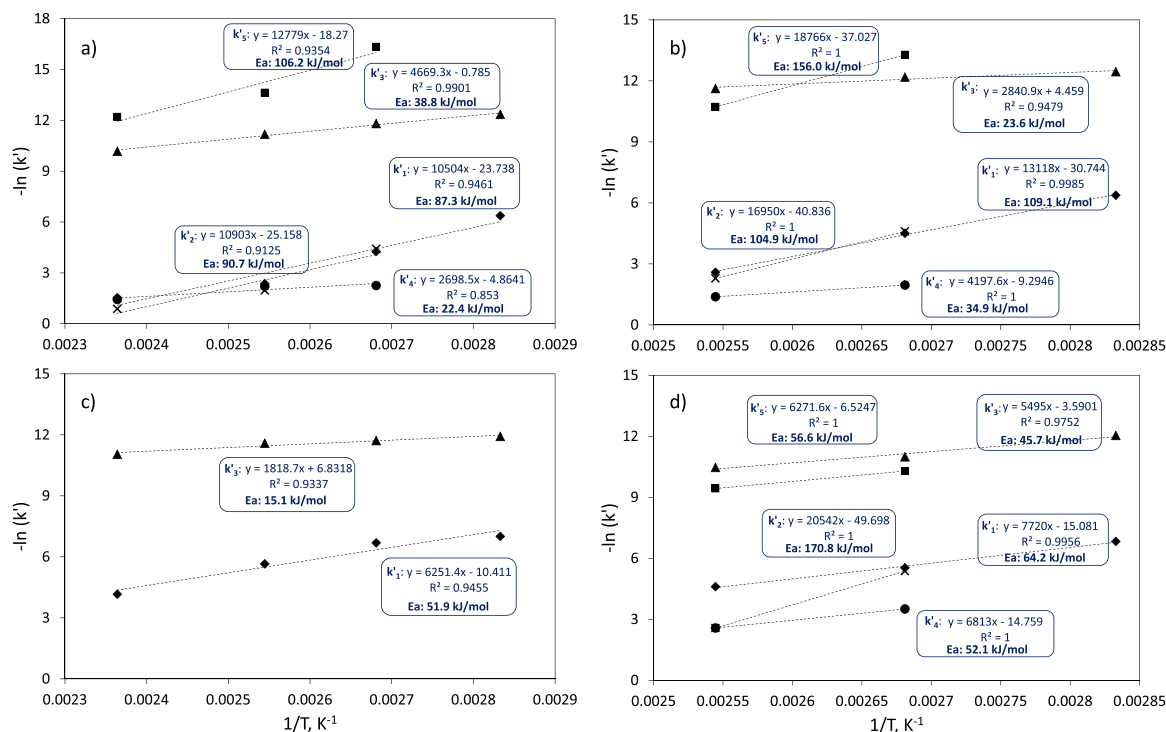


Fig. 8. Activation energy (Ea) values according to the Arrhenius model (N/A = non available). Data corresponding to (a) Au/TiO₂ 20 bar; (b) Au/TiO₂ 25 bar; (c) Au/MgAl 20 bar; (d) Au/MgAl 25 bar. Symbols: k'_1 (◆); k'_2 (×); k'_3 (▲); k'_4 (●); k'_5 (■).

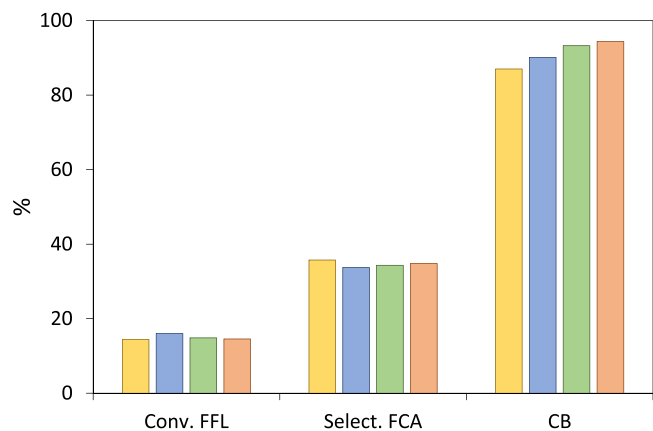


Fig. 9. Stability results obtained with Au/TiO₂ at 100°C and 20 bar. Results corresponding to data after 8 h with the first (yellow), second (blue), third (green), and fourth (orange) cycle.

were tested, involving supports (TiO₂, MgAl, and CeO₂) and active metals (Au, Pd, Pt), with a thorough screening of reaction conditions. Experimental results demonstrate the high oxidation activity of Au, as well as a synergetic effect with TiO₂ to activate the oxygen, obtaining the most promising results when working at 100°C and 20 bar: 100% of furoic acid selectivity in the liquid phase, 16% of furfural conversion, and 35.8% of furoic acid total selectivity, reducing the humins production. All these results were fit to a common reaction mechanism conditioned by furfural adsorption, concluding that temperature and the support properties play a key role in furoic acid production.

This study introduces a very promising path to obtain polymer precursors by a sustainable route, obtaining a good equilibrium between the advantages of the previous configurations proposed in the literature (strong pH using NaOH and uncontrolled pH) and reducing the drawbacks of both procedures. Thus, furoic acid can be selectively produced at mild conditions (a clear improvement with respect to the Cannizzaro mechanism obtained when working at pH 14), the relevance of humins production is significantly reduced, and very interesting results in terms of catalytic stability are obtained (a very relevant drawback of the free-base configuration).

CRediT authorship contribution statement

Rapado Paula: Writing – original draft, Software, Investigation, Data curation. **Ordóñez Salvador:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Faba Laura:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcata.2023.119536](https://doi.org/10.1016/j.apcata.2023.119536).

References

- [1] T. Kim, J. Bamford, U.R. Gracida-Alvarez, P.T. Benavides, Life cycle greenhouse gas emissions and water and fossil-fuel consumptions for polyethylene furanate and its coproducts from wheat straw, *ACS Sust. Chem. Eng.* 10 (2022) 2830–2843, <https://doi.org/10.1021/acssuschemeng.1c08429>.
- [2] A. Lolli, S. Albonetti, L. Utili, R. Amadori, F. Ospitali, C. Lucarelli, F. Cavani, Insights into the reaction mechanism for 5-hydroxymethylfurfural oxidation to FDCA on bimetallic Pd-Au nanoparticles, *Appl. Catal. A* 504 (2015) 408–419, <https://doi.org/10.1016/j.apcata.2014.11.020>.
- [3] F. Deng, A.S. Amarasekara, Catalytic upgrading of biomass derived furans, *Ind. Crop. Prod.* 159 (2021), 113055, <https://doi.org/10.1016/j.indcrop.2020.113055>.
- [4] I. Sádaba, M. Ojeda, R. Mariscal, J.L.G. Fierro, M.L. Granados, Catalytic and structural properties of co-precipitated Mg-Zr mixed oxides for furfural valorization via aqueous aldol condensation with acetone, *Appl. Catal. B* 101 (2011) 638–648, <https://doi.org/10.1016/j.apcatb.2010.11.005>.
- [5] D.Yu. Murzin, E. Bertrand, P. Tolvanen, S. Devyatkov, J. Rahkila, K. Eränen, J. Wärnå, T. Salmi, Heterogeneous catalytic oxidation of furfural with hydrogen peroxide over sulfated zirconia, *Ind. Eng. Chem. Res.* 59 (2020) 13516–13527, <https://doi.org/10.1021/acs.iecr.0c02566>.
- [6] F. Saleem, P. Müller, K. Eränen, J. Wärnå, D. Yu Murzin, T. Salmi, Kinetics and modelling of furfural oxidation with hydrogen peroxide over a fibrous heterogeneous catalyst: effect of reaction parameters on yields of succinic acid, *J. Chem. Technol. Biotechnol.* 92 (2017) 2206–2220, <https://doi.org/10.1002/jctb.5248>.
- [7] P. Rapado, L. Faba, S. Ordóñez, Role of the different catalytic sites in the H₂O₂-mediated aqueous-phase furfural partial oxidation, *J. Env. Chem. Eng.* 11 (2023), 111466, <https://doi.org/10.1016/j.jece.2023.111466>.
- [8] A. Roselli, Y. Carvalho, F. Dumeignil, F. Cavani, S. Paul, R. Wojcieszak, Liquid phase furfural oxidation under uncontrolled pH in batch and flow conditions: the role of in situ formed base, *Catalysts* 10 (2020) 73–84, <https://doi.org/10.3390/catal10010073>.
- [9] M. Douthwaite, X. Huang, S. Iqbal, P.J. Miedziak, G.L. Brett, S.A. Kondrat, J. K. Edwards, M. Sankar, D.W. Knight, D. Bethell, G.J. Hutchings, The controlled catalytic oxidation of furfural to furoic acid using AuPd/Mg(OH)₂, *Catal. Sci. Technol.* 7 (2017) 5284–5293, <https://doi.org/10.1013/c7cy01025g>.
- [10] P. Verdeguer, N. Merat, L. Rigal, A. Gaset, Optimization of experimental conditions for the catalytic oxidation of furfural to furoic acid, *J. Chem. Technol. Biotechnol.* 61 (1994) 97–102, <https://doi.org/10.1002/jctb.280610203>.
- [11] C.P. Ferraz, A.G.M. Da Silva, T.S. Rodrigues, P.H.C. Camargo, S. Paul, R. Wojcieszak, Furfural oxidation on gold supported on MnO₂: influence of the support structure on the catalytic performances, *Appl. Sci.* 8 (2018) 1246–1258, <https://doi.org/10.3390/app8081246>.
- [12] Q. Tian, D. Shi, Y. Sha, CuO and Ag₂O/CuO catalyzed oxidation of aldehydes to the corresponding carboxylic acids by molecular oxygen, *Molecules* 13 (2008) 948–956, <https://doi.org/10.3390/molecules13040948>.
- [13] M. Lin, C. Mochizuki, T. Ishida, Y. Zhang, M. Haruta, T. Murayama, Effect of poly (N-vinylpyrrolidone) ligand on catalytic activities of Au nanoparticles supported on Nb₂O₅ for CO oxidation and furfural oxidation, *Catal. Today* 410 (2023) 143–149, <https://doi.org/10.1016/j.cattod.2022.03.034>.
- [14] R. Wojcieszak, C.P. Ferraz, J. Sha, S. Houde, L.M. Rossi, S. Paul, Advances in base-free oxidation of bio-based compounds on supported gold catalysts, *Catalysts* 7 (2017) 352–374, <https://doi.org/10.3390/catal7110352>.
- [15] Z. Ren, Y. Yang, S. Wang, X. Li, H. Feng, L. Wang, Y. Li, X. Zhang, M. Wei, Pt atomic clusters catalysts with local charge transfer towards selective oxidation of furfural, *Appl. Catal. B* 295 (2021), 120290, <https://doi.org/10.1016/j.apcatb.2021.120290>.
- [16] C.P. Ferraz, S. Narvarro-Jaén, L.M. Rossi, F. Dumeignil, M.N. Ghazzal, R. Wojcieszak, Enhancing the activity of gold supported catalysts by oxide coating: towards efficient oxidations, *Green. Chem.* 23 (2021) 8453–8457, <https://doi.org/10.1039/d1gc02889h>.
- [17] C.P. Ferraz, N.J.S. Costa, E. Teixeira-Neto, A.A. Teixeira-Neto, C.W. Liria, J. Thuriot-Roukos, M.T. Machini, R. Froidevaux, F. Dumeignil, L.M. Rossi, R. Wojcieszak, 5-Hydroxymethylfurfural and furfural base-free oxidation over AuPd embedded bimetallic nanoparticles, *Catalysts* 10 (2020) 75–90, <https://doi.org/10.3390/catal10010075>.
- [18] Y. Wu, Z.L. Guo, C.X. Sun, Y.D. Yang, Q. Lii, Integrated experimental and DFT analysis on the efficient and green upgrading of agroforestry biomass derived furan chemicals over NiMoO₄-CNTs-CF electrocatalyst with bi-catalytic sites, *Ind. Crop. Prod.* 187 (2022), 115492, <https://doi.org/10.1016/j.indcrop.2022.115492>.
- [19] F. Nocito, N. Ditaranto, D. Linsalata, M. Naschetti, R. Comparelli, M. Aresta, A. Dibenedetto, Selective aerobic oxidation of furfural into furoic acid over a highly recyclable MnO₂@CeO₂ core-shell oxide: the role of the morphology of the catalyst, *ACS Sust. Chem. Eng.* 10 (2022) 8615–8623, <https://doi.org/10.1021/acssuschemeng.2c02341>.
- [20] C.P. Ferraz, M. Zielinski, M. Pietrowski, S. Heyte, F. Dumeignil, L.M. Rossi, R. Wojcieszak, Influence of support basic sites in green oxidation of biobased substrates using Au-promoted catalysts, *ACS Sust. Chem. Eng.* 6 (2018) 16332–16340, <https://doi.org/10.1021/acssuschemeng.8b03330>.

- [21] A. Stephen, K. Hashmi, Gold-catalyzed organic reactions, *Chem. Rev.* 107 (2007) 3180–3211, <https://doi.org/10.1021/cr000436x>.
- [22] O. Larina, K.V. Valihura, P.I. Kyriienko, N.V. Vlasenko, D.Y. Balakin, I. Khalakhan, T. Cendat, S.O. Soloviev, S.M. Orlyk, Successive vapour phase Guerbet condensation of ethanol and 1-butanol over Mg–Al oxide catalysts in a flow reactor, *Appl. Catal. A* 588 (2019) 117265, <https://doi.org/10.1016/j.apcata.2019.117265>.
- [23] J. Quesada, R. Arreola-Sánchez, L. Faba, E. Díaz, V.M. Rentería-Tapia, S. Ordóñez, Effect of Au nanoparticles on the activity of TiO₂ for ethanol upgrading reactions, *Appl. Catal. A* 551 (2018) 23–33, <https://doi.org/10.1016/j.apcata.2017.12.004>.
- [24] J.J. Carbery, A boundary-layer model of full-particle mass transfer in fixed beds, *AIChE J.* 6 (1960) 460–463, <https://doi.org/10.1002/aic.690060323>.
- [25] C.P. Ferraz, M.A.S. Garcia, E. Teixeira-Neto, L.M. Rossi, Oxidation of benzyl alcohol catalyzed by gold nanoparticles under alkaline conditions: weak vs. strong bases, *RSC Adv.* 6 (2016) 25279–25285, <https://doi.org/10.1039/c6ra01795a>.
- [26] A. Sadier, S. Paul, R. Wojcieszak, R. Selective oxidation of furfural at room temperature on a TiO₂-supported Ag catalyst, *Catalysts* 12 (2022) 805–814, <https://doi.org/10.3390/catal12080805>.
- [27] V.P. Santos, S.A.C. Carabineiro, P.B. Tavares, M.F.R. Pereira, J.J.M. Órfao, J. L. Figueiredo, Oxidation of CO, ethanol and toluene over TiO₂ supported noble metal catalysts, *Appl. Catal. B* 99 (2010) 195–205, <https://doi.org/10.1016/j.apcatb.2010.06.020>.
- [28] I.V. Zandvoort, Y. Wang, C.B. Rasrendra, E.R.H. van Eck, P.C.A. Bruijninx, H. J. Heeres, B.M. Weckhuysen, Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions, *ChemSusChem* 6 (2013) 1745–1758, <https://doi.org/10.1002/cssc.201300332>.
- [29] H. Shen, H. Shan, L. Liu, Evolution process and controlled synthesis of humins with 5-hydroxymethylfurfural (HMF) as model molecule, *ChemSusChem* 13 (2020) 513–519, <https://doi.org/10.1002/cssc.201902799>.
- [30] S. Liu, Y. Zhu, Y. Liao, H. Wang, Q. Liu, L. Ma, C. Wang, Advances in understanding the humins: formation, prevention and application, *Appl. Energ. Comb. Sci.* 10 (2022), 100062, <https://doi.org/10.1016/j.jaecs.2022.100062>.
- [31] L. Filiciotto, A.M. Balu, J.C. Van der Waal, R. Luque, Catalytic insights into the production of biomass-derived side products methyl levulinate, furfural and humins, *Catal. Today* 302 (2018) 2–15, <https://doi.org/10.1016/j.cattod.2017.03.008>.
- [32] H.R. Xing, P. Hu, S.L. Li, Y.G. Zuo, J.Y. Han, X.J. Hua, K.S. Wang, F. Yang, P. Feng, T. Chang, Adsorption and diffusion of oxygen on metal surfaces studied by first-principle study: a review, *J. Mater. Sci. Technol.* 62 (2021) 180–194, <https://doi.org/10.1016/j.jmst.2020.04.063>.
- [33] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, How catalyst and experimental conditions determine the selective hydroconversion of furfural and 5-hydroxymethylfurfural, *Chem. Rev.* 118 (2018) 11023–11117, <https://doi.org/10.1021/acs.chemrev.8b00134>.



Biomass to plastics: From HMF to fructose for the synthesis of 2,5-furandicarboxylic acid over Au/TiO₂

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ABSTRACT

This study focuses on the catalytic synthesis of 2,5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF). The influences of temperature, O₂ pressure, initial HMF concentration (i.e., catalytic loading), and NaOH:HMF ratio are studied. A minimum temperature is required to promote oxidation, but it also favors the humins formation. The HMF degradation is identified as the bottleneck of this approach, requiring working with a minimum O₂ pressure and a high catalytic loading to prevent the humins formation. At 80°C, a NaOH:HMF ratio of 2:1, and 25 bar oxygen pressure, FDCA selectivity reached 87 % after 8 hours, with minimal humins formation. This result represents an improvement in the sustainability of typical conditions proposed in the literature, mainly because of the minimum NaOH excess used. Additionally, the study explored a one-pot process integrating fructose dehydration and HMF oxidation. While promising, challenges arose in preventing HMF degradation during the process. Nonetheless, these findings highlight viable pathways for sustainable FDCA production, emphasizing the importance of optimizing reaction conditions to balance FDCA yield and humins prevention.

1. Introduction

Polyethylene terephthalate (PET) is one of the most widely used plastics, its worldwide market volume has a continuously increasing trend, reaching 25.5 million metric tons (MMT) in 2022, with a forecast of more than 35.7 MMT for 2030, if the current trend is not altered [1]. Due to the well-known environmental drawbacks of using non-renewable and non-biodegradable polymers, their replacement by a biomass-derived substitute is of crucial interest. Polyethylene 2,5-furandicarboxylate (PEF), the polymer obtained by the polymerization of 2,5-furandicarboxylic acid (FDCA) and ethylene glycol [2], with similar properties as polyethylene terephthalate, is the most attractive alternative for this substitution [3,4]. According to current statistics, the market value of FDCA is anticipated to reach about 770 million euros in 2025 [5].

FDCA can be produced by two different routes: (1) via the carboxylation of furoic acid, and (2) by the oxidation of the 5-hydroxymethylfurfural (HMF) [6,7]. The furoic acid route requires a cascade process involving the hemicellulose hydrolysis and dehydration to produce furfural (FFL) [8], its partial oxidation to produce furoic acid [9], and the subsequent carboxylation of this acid to FDCA [10]. Currently, furoic

acid is obtained by the gas-phase Cannizzaro reaction (strong basic conditions), the maximum FCA yield being limited because of the co-production of furfuryl alcohol (FOH) [11]. Although its production working with buffer solutions at pH 8 and heterogeneous catalysts has been demonstrated as feasible using both, H₂O₂ and O₂ as oxidizing agents [12,13], the FCA selectivity is always a weak point of these routes because of the relevant number of side reactions and humins formation. Additionally, the carboxylation step is a complex gas-solid reaction that is far to be optimized from the sustainability viewpoint [14].

The synthesis from HMF has been primarily studied through electrochemical and photochemical routes using Co, Ni, Ti, V, and Mo oxides as catalysts [15–18]. Among these studies, Au/TiO₂ highlighting as one of the most promising catalysts because of its high activity, stability, and remarkable selectivity resulting from its ability to activate the oxygen and to adsorb HMF [19,20]. As to the thermocatalytic route, it has been studied using molecular oxygen in the presence of Pt, Pd, or Ru-based heterogeneous catalysts. However, these systems have insufficient stability or selectivity [21–23]. Gold catalysts, including Au/TiO₂, are active and more stable than Pt and Pd, reaching almost total selectivity with HMF conversions higher than 80 % [24,25]. Extensive studies have been conducted on optimizing the active phase and metal-support

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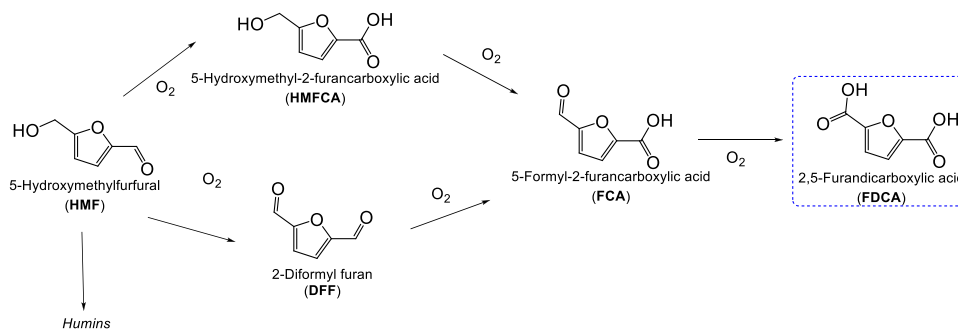
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Scheme 1. General mechanism of HMF oxidation to produce FDCA [28].

interaction [26], yet further optimization of reaction conditions is still required.

Based on the literature, the catalytic oxidation of HMF is defined as a two-step process, see Scheme 1, that follows two different mechanisms as a function of the functional group that suffers the first oxidation, reaching 5-hydroxymethyl-2-furancarboxylic acid (HMFA) in case of being the aldehyde group, or 2,5-diformyl furan (DFF) if it is the case of the hydroxyl one. The prevalence of HMFA or DFF routes is conditioned by different factors, such as the metal used (Au promoting the HMFA pathway, other noble metals promoting the DFF route [24]) and the solvent (aprotic polar organic solvents promote the DFF route, water and basic environment enhances the HMFA one) [23,27].

Previous studies demonstrate the positive effects of homogeneous base addition on the performance of HMF oxidation, both activating the HMF to produce the HMFA [29,30] and increasing the solubility of the reaction products. However, the basic environment leads to the formation of by-products that cannot be easily identified, generally known as humins, with the subsequent negative effect on the selectivity and, in the case of using a heterogeneous catalyst, on the stability [31]. Despite the expected influence of reaction conditions in the humins formation, there is a relevant gap in the literature about these aspects. The only studies addressing humin prevention in HMF oxidation suggest the use of organic solvents [32], raising concerns about the sustainability of the process.

The economic feasibility is another bottleneck of this route since it is restricted by the difficulty of isolating the HMF from biomass hydrolysis streams (unstable aldehyde in an aqueous medium, decomposing into levulinic and formic acids as final products [33,34]). The development of a one-pot process that allows in situ HMF oxidation would be of great interest, preventing its decomposition and reducing the costs of the process. However, the opposite catalytic properties required for sugar hydrolysis (an acid-catalyzed process [35,36]) and HMF oxidation (redox catalysis, enhanced at alkaline conditions) make this approach difficult. Some authors propose a biphasic system where the dehydration of sugars takes place in aqueous media and HMF is extracted to an organic phase where oxidation is carried out, implying complex reactor developments and difficult process control [37–39]. In addition, most of these studies propose complex catalytic systems [40], or the oxidation is limited to produce DFF instead of FDCA [41].

This study aims to conduct a comprehensive analysis of the impact of various reaction conditions (including temperature, oxygen pressure, NaOH:HMF ratio, and HMF initial concentration) on the oxidation of HMF to FDCA over Au/TiO₂ catalysts. The objective is to identify the optimal conditions that achieve a balance between activity, selectivity, and sustainability. Subsequently, we evaluate the feasibility of directly producing FDCA from fructose in a one-pot configuration. This evaluation involves assessing whether the conclusions drawn from the study using commercial HMF remain applicable when using biomass-related feedstocks.

2. Materials and methods

2.1. Catalyst preparation and characterization

Au was deposited at 1 wt% into TiO₂ P25 commercial support (Sigma Aldrich, 99 %) by deposition-precipitation with urea method (DPU) using HAuCl₄·3 H₂O (Sigma Aldrich, 99 %) as precursor [42]. The material was calcined for 3 h at 500°C. The catalyst was reduced in H₂ (Air liquid 10 v/v% in Ar, flow rate: 20 mL·min⁻¹) for 4 h, at 300°C reached with a slope of 5°C·min⁻¹. This catalyst has been deeply characterized in previous work [14], highlighting its mesoporous character (63 m²/g, 35.9 nm of average particle size), as well as the high Au dispersion (24.2 %).

2.2. Reaction studies

Reactions were performed in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE seal) equipped with a back-pressure regulator and a PID temperature controller. For the oxidation of pure HMF, the system was loaded with the catalyst (0.5 g Au/TiO₂, 50–80 μm) and 0.25 L of an aqueous solution of HMF and NaOH (Sigma Aldrich, 99 %) with different concentrations (from 0.1 to 0.01 M) and relative ratios (from 4:1–1:1) as a function of the experiment (see results section). Air was purged with O₂ (Air Liquid, >99.99 %) three times before pressurizing the system at the desired O₂ pressure (see results section). Oxidations were performed under fast stirring (700 rpm) to ensure the correct suspension of the catalyst, maximize the liquid-gas contact, and minimize the mass transfer limitations, ensuring kinetic control.

For a one-pot system, the reactor was loaded with 0.2 L of an aqueous solution of 0.125 M of fructose (Sigma Aldrich, 98 %) at the desired acid initial concentration (0.25 M HCl). After 3 hours, 50 mL of a NaOH solution (1.65 M) and 0.5 g of Au/TiO₂ were added to promote the oxidation. Samples were filtered using a 0.22 μm Nylon syringe filter, and diluted water in a 1:4 ratio before their analysis by HPLC (1200 Series, Agilent) equipped with a RI detector and a Hi-Plex H column, using 0.5 mL·min⁻¹ of 5 mM H₂SO₄ solution as mobile phase. Commercial standards were used for calibration. The analyses of the reactions are present in terms of conversion, selectivity, yield, and carbon balance closure, according to the following expressions:

$$x \text{ (%) } = \frac{C_{i,0} - C_{i,t}}{C_{i,0}} \cdot 100 \quad (1)$$

$$S_i \text{ (%) } = \frac{n_j \cdot C_j}{(C_{i,0} - C_{i,t})} \cdot 100 \quad (2)$$

$$C.B. \text{ (%) } = \frac{\sum (n_j \cdot C_j)}{\sum (n_i \cdot C_i)} \cdot 100 \quad (3)$$

Where " n_i " and " C_i " are the number of carbons and the molar concentration of reactant (HMF or fructose) and " n_j " and " C_j " are the number of

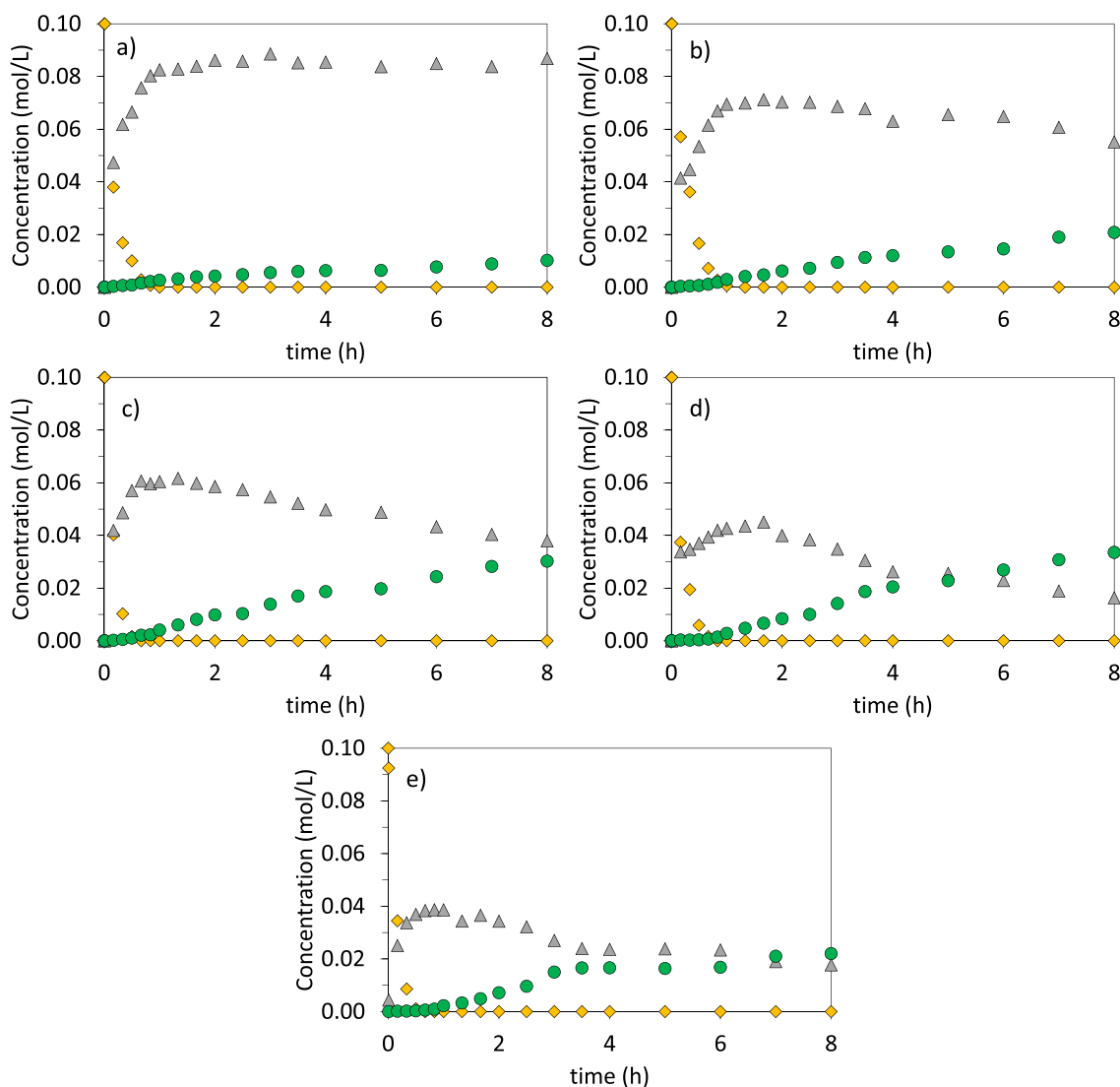


Fig. 1. Temporal evolution of all the compounds involved in the 0.1 M HMF oxidation as a function of temperature at 20 bar and NaOH:HMF 4:1 ratio over Au/TiO₂ (2 g·L⁻¹). Legend: (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C, and (e) 100°C. Symbols: HMF (◆), HMFCFA (▲), and FDCA (●).

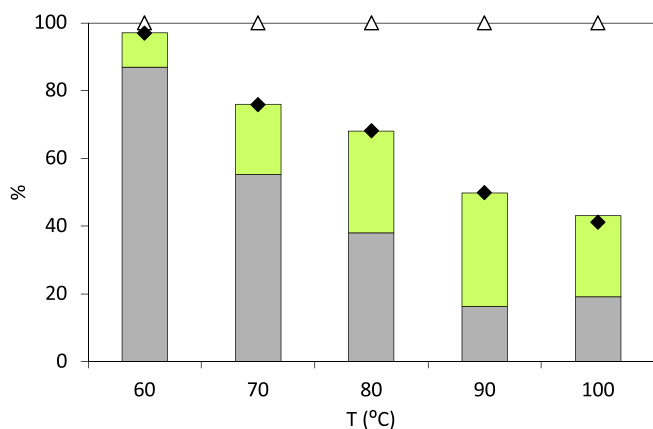


Fig. 2. HMF conversion (△), carbon balance (◆), and selectivity distribution (bars) obtained after 8 h of 0.1 M HMF oxidation at different temperatures (60–100°C) over Au/TiO₂ (2 g·L⁻¹) at 20 bar and 4:1 molar ratio NaOH:HMF. Legend: HMFCFA (grey) FDCA (green).

carbons and the molar concentration of each involved compound.

Reaction conditions were chosen to guarantee an intrinsic kinetic control, with a small particle size distribution of the catalyst (50–80 µm), and a high stirring speed (700 rpm). This stirring speed was chosen after comparing the results obtained with a model catalytic test (Au/TiO₂, 80°C, 20 bar, 4:1 NaOH/HMF, 0.1 M HMF) at different stirring speeds (600, 1400 rpm) not observing discrepancies in the results (differences in conversion <2 %). Based on these results, external mass transport limitations are discarded. MATLAB code was used to perform all the kinetic calculations using the least-squares method, employing the "lsqcurvefit" function and the Levenberg-Marquardt algorithm.

3. Results and discussion

As preliminary studies, the possible HMF oxidation and/or degradation promoted by basic conditions has been tested considering two different configurations, both in the absence of any solid catalyst. On the one hand, the HMF self-degradation was evaluated at room temperature and at atmospheric pressure using the most basic conditions considered in this work (0.04 M NaOH, 4:1 NaOH/HMF). After 24 h, more 50 % of the initial HMF disappears but no products are detected, with the subsequent decrease in the carbon balance (47.5 %). The dark color of the

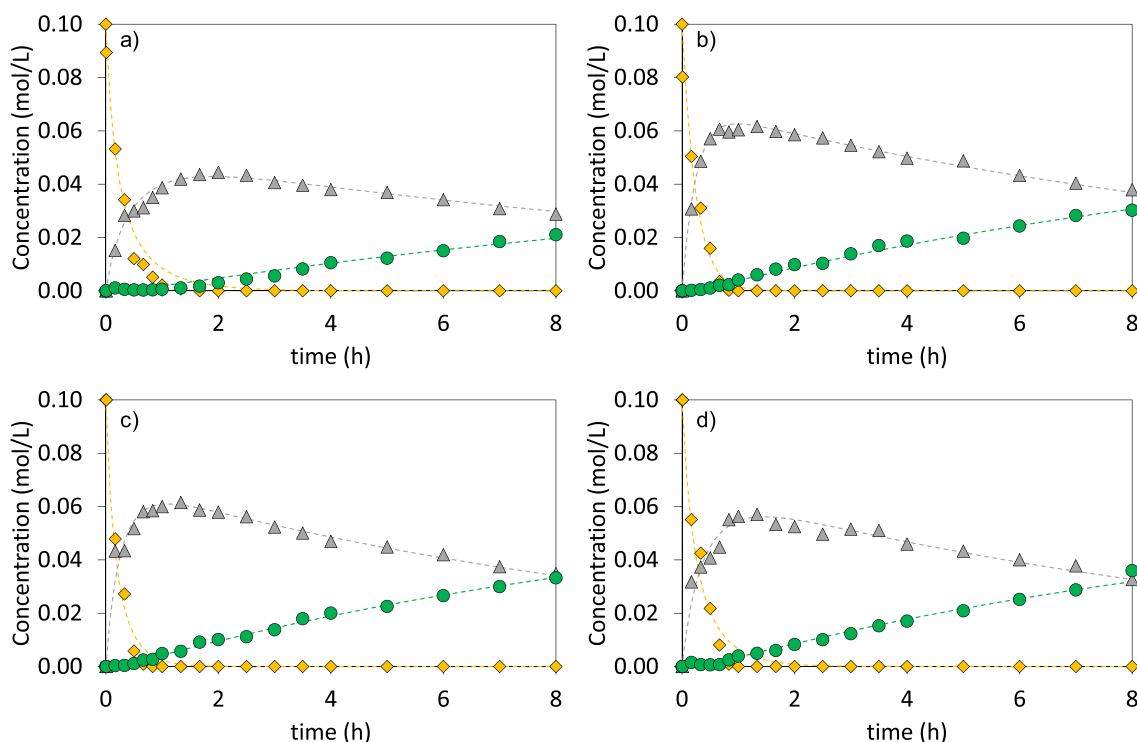


Fig. 3. Temporal evolution of all the compounds involved in the HMF oxidation as a function of pressure at 80°C and 4:1 ratio NaOH:HMF. Legend: (a) 15 bar, (b) 20 bar, (c) 25 bar, and (d) 30 bar. Symbols: HMF (◆), HMFCFA (▲), and FDCA (●). Broken lines represent the kinetic model.

solution is congruent with these results, suggesting a high HMF polymerization trend (humins formation), even in the absence of oxidizing conditions. Humins remain soluble at high pH levels due to their coiled conformations, which are cross-linked by weak forces such as Van der Waals bonds [31,36].

The same experiment was also performed under oxidizing condition (20 bar of O₂). After 1 h, 98.4 % of HMF conversion is reached, but the carbon balance decreases to 6.8 %, suggesting that the HMF oligomerization, the only reaction taking place at these conditions, is significantly promoted by oxidizing conditions. No products were detected by increasing the temperature to 80°C.

Both experiments indicate the need for a metal catalyst to steer the reaction toward the production of FDCA by activating the oxygen dissociation required for oxidation steps [31,43–45]. The systematic study about the reaction conditions that allow reaching the maximum FDCA yield with the minimum severity is then studied using in all the cases Au/TiO₂ (2 g·L⁻¹).

3.1. Influence of the reaction temperature on the HMF oxidation

Fig. 1 shows the temporal profiles obtained in the aerobic oxidation of a 0.1 M HMF solution as a function of the temperature (range studied 60–100°C). The high O₂ pressure chosen (20 bar) ensures the theoretical excess of this reactant, whereas the fast stirring (700 rpm) promotes the oxygen transfer from the gas to the liquid phase, discarding mass transfer limitations as relevant in the discussion of the results. The NaOH:HMF ratio (4:1) has been chosen considering the literature [43] to promote the reaction and to keep the humins soluble, preventing their precipitation on the catalyst surface, with the subsequent catalytic deactivation by pore blockage.

Total HMF conversion is reached in less than 1 h, regardless of the temperature. HMFCFA is the first component detected, discarding the parallel route of DFF. This intermediate has the typical profile of a primary reaction product, reaching its maximum in less than one hour, with concentrations that correspond to more than 80 % of the HMF

converted at 60°C. As the temperature increases, the maximum decreases (70 % at 70°C, 67 % at 80°C, 44 % at 90°C, 38 % at 100°C), suggesting a higher relevance of humins formation. Reaction at 60°C has not severity enough to promote the second oxidation step, FDCA being obtained in traces (<10 % after 8 h). Increasing the temperature, HMFCFA decreases because of the formation of FDCA. There is total correspondence between the HMFCFA disappeared and the FDCA formation, which suggests that HMF is the only humins precursor. Consequently, the carbon balance has been constant since the first hour, obtaining a well-marked decreasing trend with the temperature, from 97 % at 60°C to 40 % at 100°C. This parameter, as well as the selectivity distribution obtained after 8 h are compared in Fig. 2.

The comparison after 8 h reaction time reflects that the second oxidation is not enough promoted at temperatures below 80°C, being the solution enriched in HMFCFA. The maximum FDCA selectivity is observed at 90°C (33.5 % of the total HMF converted, a value that represents 67.3 % of the products detected in the liquid phase). However, the carbon balance (49.8 %) obtained at this temperature indicates that these conditions are also favourable for the humins formation. This effect is even more relevant at 100°C. The balance between maximizing the activity and minimizing the humins formation seems to be obtained at 80°C. Although after 8 h the relative selectivity of FDCA is only 44 %, the higher carbon balance closure (67 %) and the temporal profiles suggest that longer times could significantly improve this value with a limited humins formation. These conditions are considered as the base case for further studies. This study allows concluding some relevant aspects that condition the following studies: (1) humins are generated by the polymerization of HMF but other oxidized compounds are not involved; (2) although temperature promotes both reactions, humins formation is more sensitive to this factor than the oxidation steps, being required to modify other parameters to maximize the FDCA yield, and (3) Minimizing humins formation should be prioritized over maximizing FDCA yield as the primary criterion when selecting optimum conditions to prevent catalytic deactivation (decreasing as much as possible the NaOH usage for avoiding humins precipitation).

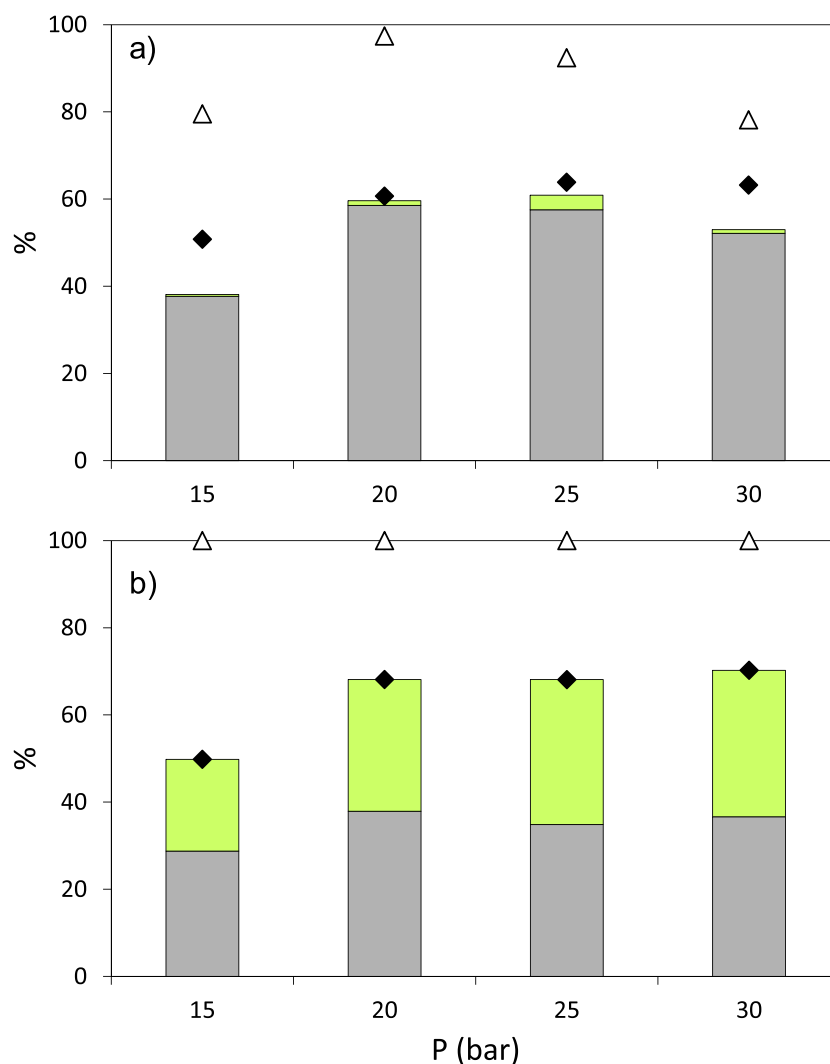


Fig. 4. HMF conversion (△), carbon balance (◆), and selectivity distribution (bars) obtained after (a) 0.5 h and (b) 8 h of 0.1 M HMF oxidation at 80°C as a function of the O₂ pressures using Au/TiO₂ and a NaOH:HMF molar ratio of 4:1. Legend: HMFA (grey) FDCA (green).

Table 1

Apparent reaction rate constants based on reaction mechanism for Au/TiO₂ catalyst (2 g·L⁻¹) as a function of different O₂ pressures when using 0.1 M of initial HMF concentration and a 4:1 NaOH:HMF ratio.

P (bar)	k ₁ (h ⁻¹)	k ₂ (h ⁻¹)	k ₃ (L·mol ⁻¹ ·h ⁻¹)	r ²
15	1.52	0.065	25.9	0.9892
20	2.76	0.080	28.3	0.9893
25	2.96	0.088	32.5	0.9913
30	1.98	0.090	25.2	0.9871

3.2. Influence of O₂ pressure on the HMF oxidation

The optimization of O₂ pressure is interesting because of two opposite aspects. On the one hand, since 20 bar of O₂ represents a high excess concerning the theoretical consumption required to promote the complete oxidation of HMF, trying to minimize the pressure would represent an effort to improve the economy of the process. On the contrary, higher O₂ pressure could enhance the interaction of this molecule with the metal sites, promoting oxygen dissociation and, subsequently, the oxidation pathway over the humins formation. The influence of O₂ pressure was studied from 15 to 30 bar of O₂, keeping constant the optimum temperature at 80°C. Temporal profiles, shown in Fig. 3,

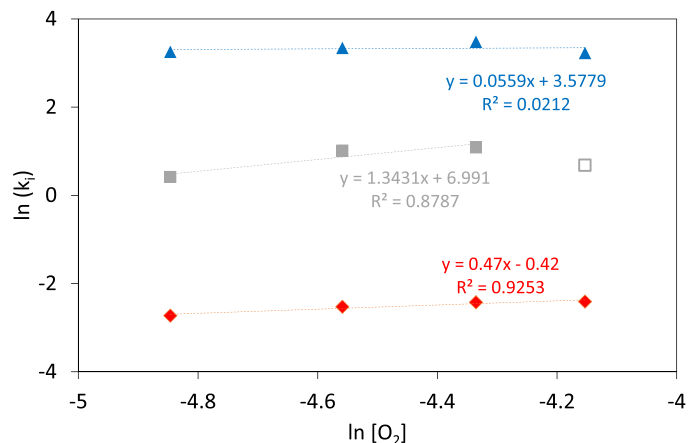


Fig. 5. Evolution of kinetic constants with the O₂ when performing the HMF oxidation with 2 g·L⁻¹ of Au/TiO₂ at 80°C with a NaOH:HMF ratio of 4:1. Legend: (■) k₁; (◆) k₂; (▲) k₃.

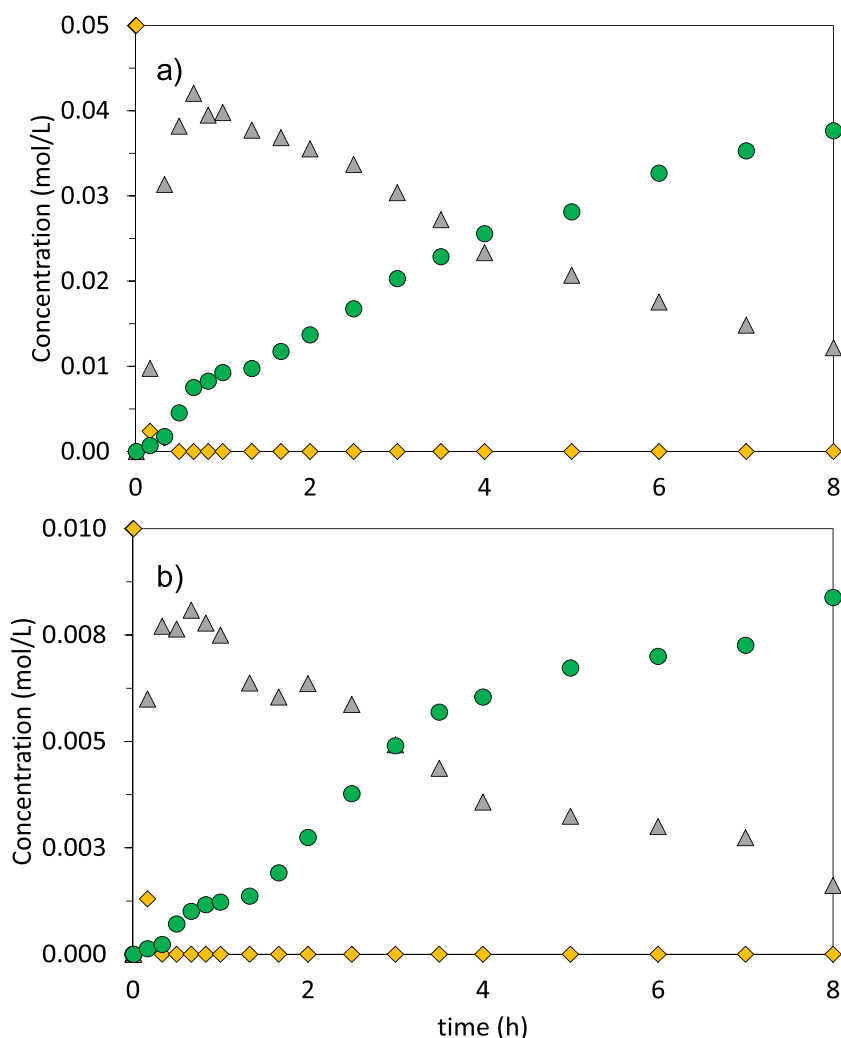


Fig. 6. Temporal evolution of all the compounds involved in the HMF oxidation at 25 bar, 80°C, and 4:1 ratio NaOH:HMF as a function of HMF concentration. Legend: (a) 0.05 M HMF, and (b) 0.01 M HMF. Symbols: HMF (◆), HMFCa (▲), and FDCA (●).

demonstrate that the reaction mechanism remains unaltered. Thus, total HMF conversion is reached after 1 h and HMFCa is the only intermediate detected. However, the product distribution changes significantly, also affecting the carbon balance, which indicates that the pressure of oxygen plays a key role in the process, despite the large excess theoretically used in all the cases.

To facilitate the discussion of this effect results after 0.5 h (before reaching total HMF conversion) and 8 h are compared in Fig. 4.

As anticipated, the decrease in the carbon balance occurs during the first 0.5 h of the reaction, no observing more evolution once the HMF conversion is complete. This fact indicates that HMF plays a crucial role in humins formation. From 15–25 bar, results after 0.5 h indicate a positive effect of O_2 pressure tuning the reaction to the desired oxidation, reducing the humins formation, and observing an increase in the carbon balance from 50 % to 63 %. Considering the short reaction time evaluated, the almost total selectivity of the HMFCa is explained by its character as a primary compound (not enough time to promote the second step). Results obtained at 30 bar suggest a possible inhibition effect that could indicate that all the Au sites are covered by O_2 molecules, disturbing the HMF adsorption. Thus, there is less HMF adsorbed, reducing the frequency of interaction between the two reactants (lowest HMF conversion). This effect would be more relevant at increasing pressures, discarding this approach.

The expected evolution to the second step is observed after 8 h. The

analysis of these results suggests a lower effect of O_2 pressure on the second step, and the ratio FDCA/HMFCa increases from 0.4 at 15 bar to 0.5 at 25 bar. As in the previous analysis, this trend is not observed at 30 bar, reinforcing the inhibition.

Comparing the results at 0.5 and 8 h, a slight increase in the carbon balance is observed, except when working at 15 bar: from 60.7 % to 68.1 %, from 63.9 % to 68.4 %, and from 63.2 % to 70.2 %, respectively. Reversible HMF adsorption is discarded as the main reason for this effect since the increase is more relevant at 30 bar, conditions at which the O_2 adsorption competes with the HMF one. Then, this fact suggests certain reversibility of the oligomers formation. The decomposition of soft humins under an oxidizing atmosphere at mild conditions has been previously considered in the literature [46]. Thus, once there is no more HMF in the reaction medium (1 h), the HMFCa is still produced by the decomposition of these “weak” oligomers. This hypothesis is supported by several pieces of evidence, mainly at 30 bar: (1) there is no correspondence between the HMF disappearance and the HMFCa maximum, this point being displaced to 80 minutes, and (2) the total yield of HMFCa and FDCA increases with the time, suggesting a continuous incorporation of more HMFCa, and not only the transformation observed in the other cases.

To reinforce this discussion, a simplified kinetic analysis of results obtained at different pressures has been performed. The experimental results are consistent with a reaction mechanism composed of two

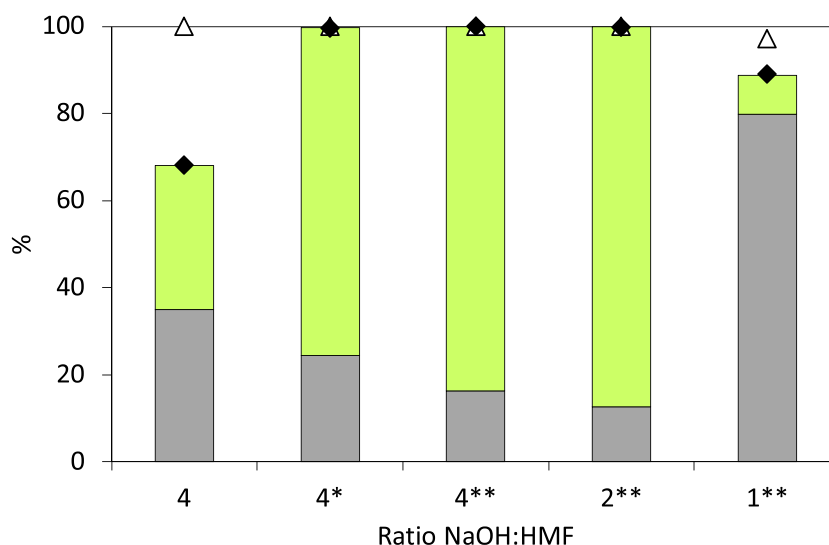


Fig. 7. HMF conversion ($\triangle$), carbon balance ($\blacklozenge$), HMFCFA selectivity (grey bars), and FDCA selectivity (green bars) obtained after 8 h of HMF oxidation at 80°C over Au/TiO₂ (2 g·L⁻¹) with 25 bar of O₂ as a function of the NaOH:HMF ratio. (*) initial HMF concentration 0.05 M; (**) initial HMF concentration 0.01 M. Base case (4): 80°C, 25 bar, 0.1 M of HMF and NaOH:HMF 4:1.

consecutive oxidation steps, with HMFCFA being the unique intermediate detected in the FDCA formation. An irreversible first-order kinetics has been observed for both successive steps. The high excess of oxygen in all the experiments (the fast stirring and the pressure excess guarantees the saturation) allows considering constant oxygen concentration in each experiment, the effect of oxygen on reaction kinetic being embedded in the apparent kinetic rate constant. With these established premises, the kinetic modelling was performed using the following mass balance equations:

$$\frac{d[\text{HMF}]}{dt} = -k_1 \cdot [\text{HMF}] - k_3 \cdot [\text{HMF}]^2 \quad (4)$$

$$\frac{d[\text{HMFCFA}]}{dt} = k_1 \cdot [\text{HMF}] - k_2 \cdot [\text{HMFCFA}] \quad (5)$$

$$\frac{d[\text{FDCA}]}{dt} = k_2 \cdot [\text{HMFCFA}] \quad (6)$$

In these equations, the effect of undesired consumptions because of the HMF transformation into insoluble compounds (humins) is considered in the “ k_3 ” term, proposing a second-order reaction, which corresponds to a bimolecular process. First-order oligomerization kinetics was also evaluated, obtaining a poorer model prediction. Table 1 summarizes the apparent kinetic rate constants obtained for experiments at different pressures, as well as the corresponding regression coefficients. The high values obtained (>0.98 in all the cases) indicate good correspondence between the theoretical model proposed and the experimental data. This fact is also corroborated by the good fit observed in all the graphs including temporal profiles (Fig. 3), the theoretical values being plotted with broken lines.

Since all the experiments were performed at the same temperature and oxygen is at large excess (close to saturation concentration), oxygen concentration can be considered as a constant at a given pressure. However, this concentration increases as operation pressure increases, allowing to correlate reactivity trends with oxygen concentration. The significant differences observed corroborate the role of this reactant, with different impacts in three evaluated reactions. Thus, each apparent kinetic constant can be expressed as a function of the oxygen concentration according to this expression, estimating oxygen concentration with the Henry law for the oxygen-water system:

$$k_i = k'_i \cdot [\text{O}_2]^n \quad (7)$$

The linearization of this expression is shown in Fig. 5. The value of k_1 obtained at 30 bar was excluded from this analysis since experimental results demonstrate an inhibition effect of the oxygen adsorbed when working at so high pressure, shielding the effect on the reaction rate.

Results indicate a more relevant effect of the oxygen in the first step of the reaction (HMFCFA formation), whereas the HMFCFA oxidation is less sensitive to oxygen concentration. Considering the few points available for fitting the first step (complete conversion in 1 h), the kinetic order of the second step (0.5) is considered more robust than the corresponding one for the first step (1.3 which could correspond to a real 1.5). In both cases, the oxygen adsorption and subsequent dissociation seem to be relevant, explaining these reaction orders. As suggested in the discussion of experimental results, a negligible role of oxygen in the humins formation is demonstrated. The intrinsic kinetic rate values obtained ($k_1 = 1090 \text{ L}^{1.5} \cdot \text{mol}^{-1.5} \cdot \text{h}^{-1}$; $k_2 = 0.66 \text{ L}^{0.5} \cdot \text{mol}^{-0.5} \cdot \text{h}^{-1}$; and $k_3 = 36 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$) are in good agreement with the literature [7,47]. Thus, the first step is significantly faster than the second one, being promoted by NaOH (the direct comparison is not possible because of the different kinetic orders).

3.3. Influence of NaOH and HMF concentration

Results at different pressures and temperatures suggest that longer times could improve the FDCA yield. However, longer times could increase the complexity of humins, resulting in heavy compounds insoluble even at high pH values. This fact is a potential inconvenience that discourages this option, highlighting the importance of optimizing other operating conditions that may prevent the original formation of these humins.

Strategies to reduce their formation require analyzing the effect of working at different initial HMF concentrations (in good agreement with the second reaction order of the humins formation step, reducing the HMF concentration could decrease the relative weight of their formation) or NaOH:HMF ratios (a relevant effect would suggest that humins formation is homogeneously catalyzed).

The effect of the HMF concentration has been studied considering two reactions with lower initial HMF concentration (0.05 and 0.01 M) but keeping constant the NaOH:HMF ratio (4:1). This study was

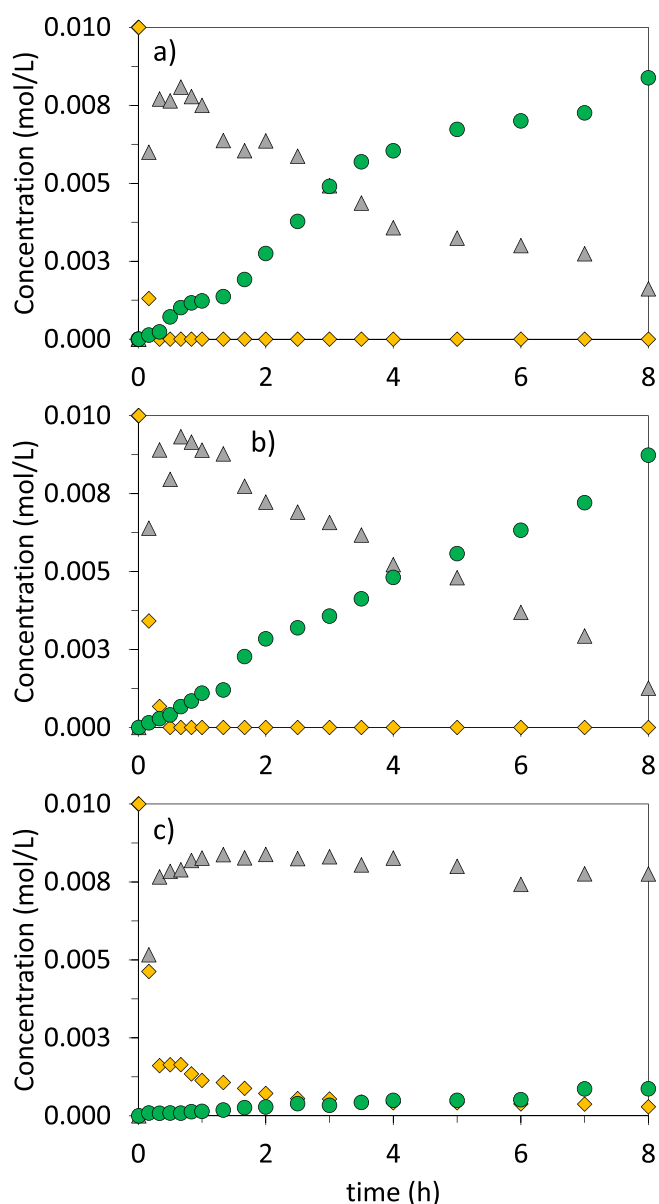


Fig. 8. Temporal evolution of the compounds involved in the HMF oxidation as a function of NaOH concentration over Au/TiO₂ (2 g·L⁻¹) at 25 bar O₂, 80°C, and 0.01 M HMF. Legend: (a) 0.04 M, (b) 0.02 M, and (c) 0.01 M. Symbols: HMF (◆), HMFCa (▲), and FDCA (●).

performed at 80°C and under 25 bar of O₂. Temporal profiles are detailed in Fig. 6.

As anticipated, total HMF conversion was reached at shorter times, after 30 and 20 minutes, respectively, times that correspond to the maximum HMFCa. Longer times are required to transform this intermediate into the FDCA, obtaining a continuous increase and final yields after 8 h of 75.3 % and 83.8 %, respectively, see Fig. 7.

The most relevant result of this study is the total disappearance of humins, with carbon balances higher than 99.7 % during all the experiments. This fact is congruent with a predominance of oxidation over oligomerization at diluted conditions (higher oxygen/HMF ratios), promoting oxidative pathways. In the same way, lower HMF concentrations also lead to lower humins formation (second-order dependence).

Based on these results, the role of NaOH in promoting the humins is clear. However, the literature indicates that an alkaline pH is required to

promote oxidation stabilizing the intermediates. Considering that the use of alkaline solutions is against the Principles of Green Chemistry because of the wastewater generated, the possibility of reducing the excess of NaOH is considered a good practice. For this study, an initial concentration of HMF of 0.01 M was used, due to the maximum FDCA yield obtained with these diluted conditions. Temporal profiles working with 4:1, 2:1, and 1:1 ratios (values that correspond to initial pH of 14, 14, and 10, respectively) are plotted in Fig. 8, whereas results after 8 h are summarized in Fig. 7 for a better comparison.

In terms of the HMF evolution, a negligible effect of reducing the NaOH excess from 4:1–2:1 is observed, with total conversion in 20 minutes. However, working with equimolar amounts of both compounds significantly reduces the HMF oxidation rate, requiring more than 3 h to obtain more than 90 % of conversion. Even after 8 h, traces of HMF are detected (97 % of conversion). HMFCa and FDCA are the only compounds detected, discarding a different mechanism because of the different pH. At 2:1 condition, the carbon balance remains close to 100 % during all the reactions, and more than 87 % of FDCA is reached after 8 h. On the contrary, at 1:1, the low alkalinity prevails in the second oxidation step, HMFCa being the main product detected (80 % after 8 h). At these conditions, there is a soft but continuous decrease in the carbon balance, with final values of 89 %. This result could be explained by the permanent adsorption of HMFCa or FDCA on the catalytic surface because the pH is not alkaline enough to promote their desorption.

Based on these results, 80°C and 25 bar of O₂, working with an initial HMF concentration of 0.01 M and a NaOH:HMF ratio of 2:1 are defined as the optimal conditions when using pure HMF as a reactant. However, isolating HMF from sugar hydrolysis is quite complex because of the high HMF reactivity that promotes its rehydration into levulinic and formic acid. Considering this bottleneck, the possibility of integrating as a one-pot reaction the hydrolysis and oxidation was evaluated. It is expected that promoting the HMF oxidation limits its degradation. Obtaining good results in this approach could imply a relevant improvement in the economic feasibility of the process, considering the cost savings derived from the one-pot configuration.

3.4. One-pot synthesis of FDCA from fructose

Fructose is used as the model sugar to evaluate the one-pot configuration. This sugar is present in biomass, can be obtained from cellulose through hydrolysis and inversion reactions, and is the direct precursor of HMF. There are many references analyzing the dehydration of fructose to obtain HMF, mainly using HCl as a catalyst [48–50]. Based on our previous studies, a one-pot approach is proposed considering a first step under dehydration conditions of 3 h (time at which the maximum HMF was reached) [48]. After 3 h at 120°C under an inert atmosphere (20 bar of N₂), a solution of NaOH was added to the reaction medium to neutralize the previous acidic conditions and to reach a 2:1 theoretical ratio (based on the expected HMF concentration). In this solution, the required amount of Au/TiO₂ was suspended to guarantee the presence of Au nanoparticles required to promote the oxidation. The temperature is then decreased to 80°C, introducing an oxidizing atmosphere of 25 bar of O₂. The main results are summarized in Fig. 9.

After 1 h, there is a total correspondence between fructose conversion and carbon balance closure (2.7 % and 97.5 %). However, no products in the liquid phase were detected, suggesting a partial fructose oligomerization. After 3 h (still under hydrolytic conditions), fructose conversion reaches 64 % and HMF is obtained with more than 59 % selectivity. This time was chosen to switch to oxidizing conditions since levulinic acid is already obtained with 25 % of selectivity and longer times are expected to increase this value. The carbon balance at this point is 90 %, which is congruent with the lack of signal of formic acid (the acid that is simultaneously produced with levulinic acid). It is suggested that this acid could be decomposed or incorporated into the sugar oligomer's structure as a part of the humins precursor.

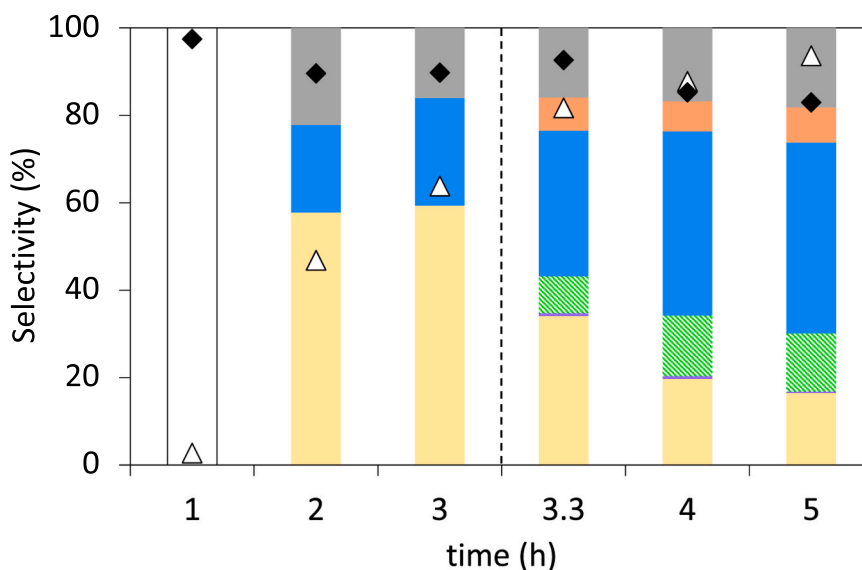


Fig. 9. Fructose conversion ($\triangle$), carbon balance ($\blacklozenge$), and selectivity distribution of products obtained in dehydration of fructose combined with oxidation of HMF. Legend: HMF (yellow), HMFCFA (purple), FDCA (dashed green), LA (blue), FA (orange), and others (grey). The broken line indicates the change from dehydration to oxidation conditions.

Once under oxidizing conditions, only traces of HMFCFA are observed (selectivity lower than 1 % during all the reaction), but the total oxidation is observed, yielding 14 % of FDCA after 4 h. Longer times do not improve this selectivity because of the formation of levulinic and formic acids, reaching up to 44 % and 9 %, respectively. The effect of high pH promoting levulinic acid formation has been previously reported in the literature [49].

The kinetic model proposed for HMF oxidation does predict FDCA concentration obtained in the one-pot experiment (0.014 mol/L vs. 0.012 mol/L, theoretical vs. experimental value), with quite good correspondence during all the reaction. However, relevant differences are observed when comparing expected and experimental values for HMF and HMFCFA. On the one hand, the kinetic model predicts total HMF conversion, whereas experimental data demonstrate a significant HMF concentration due to the continuous incorporation of more HMF by fructose dehydration. In addition, the kinetic model predicts a stream enriched in the HMFCFA intermediate, whereas this compound is negligible in the real sample. This result indicates a different interaction between the reactants (HMF and oxygen) and the catalyst, promoting the step less sensitive to the oxygen adsorbed (HMFCFA oxidation to FDCA). This fact could be explained by the high salinity obtained when neutralizing the initial HCl and possible interaction with the oxidizing catalyst, by the interaction of fructose and primary derivatives with the active phase, or by a different nature of the fructose-derived humins leading to a more severe deactivation.

According to these results, the one-pot fructose hydrolysis and HMF oxidation process is feasible, but the optimum conditions proposed for HMF oxidation are not applicable in this system, requiring a particular study to maximize the FDCA yield, promoting the first oxidation step and reducing the relevance of levulinic acid production.

4. Conclusions

This study demonstrates the critical influence of reaction conditions on the catalytic synthesis of 2,5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF). Temperature significantly influences the reaction kinetics, mainly the second oxidation step, requiring a minimum of 80°C to obtain FDCA as the main product. This selectivity increases with the temperature, but the humins formation prevails over the oxidizing route. A high excess of O_2 pressure is required to guarantee the oxygen dissociative adsorption on the total amount of Au

nanoparticles, a fact which reduces the humins formation enhancing the oxidation. Humins are mainly produced by a homogeneous catalytic route, reducing the HMF initial concentration. Working with a low NaOH excess is crucial to reduce their relevance and to increase the sustainability character of this route. At 80°C, using a NaOH:HMF ratio of 2:1 and 25 bar oxygen pressure, FDCA selectivity reached 87 % after 8 hours, with negligible humins formation, as confirmed by carbon balance analysis. Furthermore, the study explored a one-pot process integrating fructose hydrolysis and HMF oxidation, showing feasibility (14 % of FDCA obtained after 9 h of reaction) but highlighting challenges in preventing HMF degradation.

Author contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

CRediT authorship contribution statement

Paula Rapado: Writing – original draft, Methodology, Formal analysis, Data curation. **Cristina Lois:** Investigation, Data curation. **Marina Cano:** Methodology, Investigation. **Laura Faba:** Writing – original draft, Supervision, Formal analysis, Data curation, Conceptualization. **Salvador Ordonez:** Writing – review & editing, Visualization, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgment

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References

- [1] PET market volume worldwide 2015-2030 | Statista (<https://www.statista.com/statistics/1245264/polyethylene-terephthalate-market-volume-worldwide/>) Accessed March 2024.
- [2] E. de Jong, H.A. Visser, A.S. Dias, C. Harvey, G.-J.M. Gruter, *Polymers* 14 (2022) 943, <https://doi.org/10.3390/polym14050943>.
- [3] S. Singhal, S. Agarwal, M.P. Mudoi, N. Singhal, R. Singh, *Biomass. Convers. Biorefinery* 13 (2023) 15619–15636, <https://doi.org/10.1007/s13399-021-01871-6>.
- [4] T. Kim, J. Bamford, U.R. Gracida-Alvarez, P.T. Benavides, *ACS Sustain. Chem. Eng.* 10 (2022) 2830–2843, <https://doi.org/10.1021/acssuschemeng.1c08429>.
- [5] C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, *Chem. Soc. Rev.* 49 (2020) 4273–4306, <https://doi.org/10.1039/D0CS00041H>.
- [6] A. Banerjee, G.R. Dick, T. Yoshino, M.W. Kanan, *Nature* 531 (2016) 215–219, <https://doi.org/10.1038/nature17185>.
- [7] H. Cong, H. Yuan, Z. Tao, H. Bao, Z. Zhang, Y. Jiang, D. Huang, H. Liu, T. Wang, *Catalysts* 11 (2021) 1113, <https://doi.org/10.3390/catal11091113>.
- [8] Y. Luo, Z. Li, X. Li, X. Liu, J. Fan, J.H. Clark, C. Hu, *Catal. Today* 319 (2019) 14–24, <https://doi.org/10.1016/j.cattod.2018.06.042>.
- [9] X. Wu, H. Guo, L. Jia, Y. Xiao, B. Hou, D. Li, *Catalysts* 13 (2023) 663, <https://doi.org/10.3390/catal13040663>.
- [10] X. Han, Y. Wang, G. Liu, M. Wang, C. Guo, J. Shen, *J. CO₂ Util.* 75 (2023) 102572, <https://doi.org/10.1016/j.jcou.2023.102572>.
- [11] P. Bhojaraj, M. Harley, Rajamathi, *Appl. Clay Sci.* 174 (2019) 86–89, <https://doi.org/10.1016/j.clay.2019.03.028>.
- [12] P. Rapado, L. Faba, S. Ordóñez, *J. Environ. Chem. Eng.* 11 (2023) 111466, <https://doi.org/10.1016/j.jece.2023.111466>.
- [13] P. Rapado, L. Faba, S. Ordóñez, *Appl. Catal. A-Gen.* 670 (2024) 119536, <https://doi.org/10.1016/j.apcata.2023.119536>.
- [14] L. Faba, P. Rapado, S. Ordóñez, *Greenh. Gases* 13 (2023) 227–244, <https://doi.org/10.1002/ghg.2175>.
- [15] C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, *Chem. Soc. Rev.* 49 (2020) 4273–7306, <https://doi.org/10.1039/d0cs00041h>.
- [16] Y.C. Yang, T.C. Mu, *Green. Chem.* 23 (2021) 4228–4254, <https://doi.org/10.1039/d1gc00914a>.
- [17] H. Luo, J. Barrio, N. Sunny, A. Li, L. Steier, N.I. Shah, I.E.L. Stephens, M.M. Titirici, *Adv. Energ. Mat.* 11 (2021) 2101180, <https://doi.org/10.1002/aenm.202101180>.
- [18] X. Wu, Z. Zhai, J. Wu, K. Tan, Z. Li, S. Yin, *Chem. Eng. J.* 485 (2024) 149774, <https://doi.org/10.1016/j.cej.2024.149774>.
- [19] W. Yu, Y. Wang, H. Zhang, Q. Zhang, S. Wang, Z. Liu, G. Yang, F. Peng, *ACS Sustain. Chem. Eng.* 11 (2023) 13116–13125, <https://doi.org/10.1021/acssuschemeng.3c03289>.
- [20] H. Li, S. Wang, M. Wang, Y. Gao, J. Tang, S. Zhao, C. Li, *Angew. Chem. -Int. Ed.* 134 (2022) e202204272, <https://doi.org/10.1002/anie.202204272>.
- [21] X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, Y. Wang, *ACS Catal.* 4 (2014) 2175–2185, <https://doi.org/10.1021/cs5003096>.
- [22] S. Hameed, L. Lin, A. Wang, W. Luo, *Catalysts* 10 (2020) 120, <https://doi.org/10.3390/catal10010120>.
- [23] P. Verdeguer, N. Merat, A. Gaset, *J. Mol. Catal. A Chem.* 85 (1993) 327–344, [https://doi.org/10.1016/0304-5102\(93\)80059-4](https://doi.org/10.1016/0304-5102(93)80059-4).
- [24] A. Villa, M. Schiavoni, S. Campisi, G.M. Veith, L. Prati, *ChemSusChem* 6 (2013) 609–612, <https://doi.org/10.1002/cssc.201200778>.
- [25] C.A. Antonyraj, N.T.T. Huynh, S.-K. Park, S. Shin, Y.J. Kim, S. Kim, K.-Y. Lee, J. K. Cho, *Appl. Catal. A-Gen.* 547 (2017) 230–236, <https://doi.org/10.1016/j.apcata.2017.09.012>.
- [26] S. Albonetti, A. Lolli, V. Morandi, A. Migliori, C. Lucarelli, F. Cavani, *Appl. Catal. B* 163 (2015) 520–530, <https://doi.org/10.1016/j.apcatb.2014.08.026>.
- [27] L. Yu, H. Chen, Z. Wen, M. Jin, Z. Ma, X. Ma, Y. Sang, M. Chen, Y. Li, *Catal. Today* 367 (2021) 9–15, <https://doi.org/10.1016/j.cattod.2020.10.037>.
- [28] Z. Li, L. Zhao, B. Li, S. Bian, J. Wang, H. Zhang, C. Zhao, *Catal. Today* 408 (2023) 64–72, <https://doi.org/10.1016/j.cattod.2022.09.002>.
- [29] B.N. Zope, D.D. Hibbitts, M. Neurock, R.J. Davis, *Science* 330 (2010) 74–78, <https://doi.org/10.1126/science.1195055>.
- [30] T. Mallat, A. Baiker, *Chem. Rev.* 104 (2004) 3037–3058, <https://doi.org/10.1021/cr0200116>.
- [31] D. Yan, J. Xin, Q. Zhao, K. Gao, X. Lu, G. Wang, S. Zhang, *Catal. Sci. Technol.* 8 (2018) 164–175, <https://doi.org/10.1039/C7CY01704A>.
- [32] S. Liu, Y. Zhu, Y. Liao, H. Wang, Q. Liu, L. Ma, C. Wang, *Appl. Energ. Comb. Sci.* 10 (2022) 100062, <https://doi.org/10.1016/j.jaecs.2022.100062>.
- [33] P. Rapado, D. Garcés, L. Faba, S. Ordóñez, *Ind. Crop. Prod.* 212 (2024) 118309, <https://doi.org/10.1016/j.indcrop.2024.118309>.
- [34] R. Wojcieszak, I. Itabiana, *Catal. Today* 354 (2020) 211–217, <https://doi.org/10.1016/j.cattod.2019.05.071>.
- [35] Q.N.B. Nguyen, H.A.N. Le, P.D. Ly, H.B. Phan, P.H. Tran, *Chem. Commun.* 56 (2020) 13005–13008, <https://doi.org/10.1039/D0CC05582D>.
- [36] W. Wei, G. Lyu, W. Jiang, Z. Chen, S. Wu, *J. Colloid Interface Sci.* 602 (2021) 146–158, <https://doi.org/10.1016/j.jcis.2021.05.161>.
- [37] M. Kröger, U. Prüße, K.-D. Vorlop, *Top. Catal.* 13 (2000) 237–242, <https://doi.org/10.1023/A:1009017929727>.
- [38] W.N.P. van der Graaff, K.G. Olvera, E.A. Pidko, E.J.M. Hensen, *J. Mol. Catal. A Chem.* 388–389 (2014) 81–89, <https://doi.org/10.1016/j.molcata.2013.11.013>.
- [39] G. Yi, S.P. Teong, Y. Zhang, *ChemSusChem* 8 (2015) 1151–1155, <https://doi.org/10.1002/cssc.201500118>.
- [40] F. Wang, L. Jiang, J. Wang, Z. Zhang, *Energ. Fuels* 30 (2016) 5885–5892, <https://doi.org/10.1021/acs.energyfuels.6b01148>.
- [41] Z. Yang, W. Qi, R. Su, Z. He, *ACS Sustain. Chem. Eng.* 5 (2017) 4179–4187, <https://doi.org/10.1021/acssuschemeng.7b00175>.
- [42] J. Quesada, R. Arreola-Sánchez, L. Faba, E. Díaz, V.M. Rentería-Tapia, S. Ordóñez, *Appl. Catal. A* 551 (2018) 23–33, <https://doi.org/10.1016/j.apcata.2017.12.004>.
- [43] T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J.A. Lopez-Sanchez, M. Sankar, Q. He, C.J. Kiely, G.J. Hutchings, F. Cavani, *Green. Chem.* 13 (2011) 2091–2099, <https://doi.org/10.1039/C1GC15355B>.
- [44] A. Piccolo, P. Conte, A. Cozzolino, *Eur. J. Soil Sci.* 50 (1999) 687–694, <https://doi.org/10.1046/j.1365-2389.1999.00276.x>.
- [45] S.E. Davis, L.R. Houk, E.C. Tamargo, A.K. Datye, R.J. Davis, *Catal. Today* 160 (2011) 55–60, <https://doi.org/10.1016/j.cattod.2010.06.004>.
- [46] S.G. Maerten, D. Voß, M.A. Liauw, J. Albert, *ChemistrySelect* 2 (2017) 7296–7302, <https://doi.org/10.1002/slct.201701553>.
- [47] F. Neaut, R.S. Marin, M. Florea, N. Petrea, O.D. Pavel, V.I. Părvulescu, *Appl. Catal. B* 180 (2016) 751–757, <https://doi.org/10.1016/j.apcatb.2015.07.043>.
- [48] D. Garcés, E. Díaz, S. Ordóñez, *Ind. Eng. Chem. Res.* 56 (2017) 5221–5230, <https://doi.org/10.1021/acs.iecr.7b00952>.
- [49] D. Garcés, L. Faba, E. Díaz, S. Ordóñez, *ChemSusChem* 12 (2019) 924–934, <https://doi.org/10.1002/cssc.201802315>.
- [50] X. Liu, D.C.Y. Leong, Y. Sun, *Green. Chem.* 22 (2020) 6531–6539, <https://doi.org/10.1039/D0GC02315A>.

Carboxylation reactions for integrating CO₂ capture with the production of renewable monomers

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Abstract: Research advances in carboxylation reactions using CO₂ and light organic molecules of renewable origin are reviewed in this work, especially considering chemical catalytic approaches. Carboxylation, one of the most promising carbon capture and utilization (CCU) technologies, has a double environmental benefit, reducing greenhouse gas emissions by developing sustainable processes for commodity synthesis. The industrial interest is based on its potential use in the synthesis of biopolymer precursors from bioplatfrom molecules such as ethanol or furfural. Acrylic acid is obtained from ethylene (after ethanol dehydration), by a liquid phase reaction activated by organometallic catalysts. Promising yields are reported for different ligands and solvents, but a practical and sustainable implementation of these reactions is still challenging. On the other hand, the furoic acid carboxylation (furoic acid obtained by oxidation of furfural) is a solid-gas reaction that produces 2,5furandicarboxylic acid in presence of alkaline carbonates. In this case, the economic feasibility is the main bottleneck to solve for scaling-up, and efforts should be focused on substituting the most active alkaline carbonate (Cs) by more available alternatives. © 2022 The Authors. *Greenhouse Gases: Science and Technology* published by Society of Chemical Industry and John Wiley & Sons Ltd.

Keywords: ethylene; acrylic acid; furoic acid; 2,5dicarboxylic acid; biomass

Introduction

Carbon dioxide emissions have exponentially increased in the last decades, with over 34 billion tons emitted each year quantified in 2020.¹ Considering the high relevance of this problem, controlling CO₂ concentration in the atmosphere is a worldwide issue that needs to be solved urgently. In the last two decades, the CO₂ capture and storage/sequestration (CCS) strategies have focused the

main research attention on developing a plethora of physical and chemical technologies.^{2–6} Nowadays, high efficiencies are obtained but their industrial implementation is hindered because of the high costs required for the transportation and stable storage of the recovered CO₂, as well as the technical limitations to guarantee the security and viability of these approaches.

With these perspectives, the ambitious targets of the European Union require the development of other

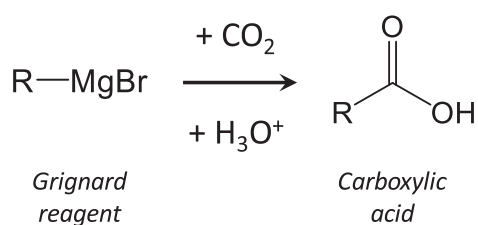
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Scheme 1. Reaction of Grignard with CO₂.

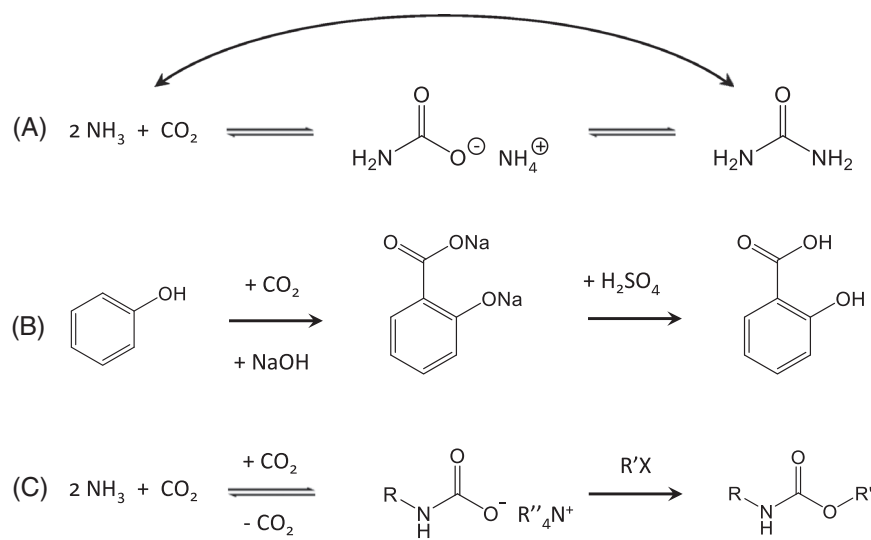
techniques, not only for CO₂ capture, but also its use as a chemical feedstock (CCU technologies). This strategy considers CO₂ as an activated molecule, a feedstock to synthesize value-added chemicals. From the process sustainability point of view, CO₂ is the most attractive C₁ carbon source (renewable and overly abundant), destined to be the substitute for common C₁ precursors, such as methane, formaldehyde, methyl halides, or carbon monoxide in coupling reactions. On the other hand, CO₂ insertion into organic molecules lead to formation of carboxylic functions, key functional groups in further chemical processing (active sites for polymerization reaction, tuning chemicals biocompatibility, etc.). The ideal approach must consider its upgrading reactions at mild temperatures and low pressures, according to the principles of the green chemistry. These conditions can be achieved by enzymatic, biochemical and chemical routes. In this review, only the chemical routes are considered, with a clear approach to highlight the main relevant aspects from a chemical engineering point of

view, issues that are relevant for a future scale-up to the industrial application.

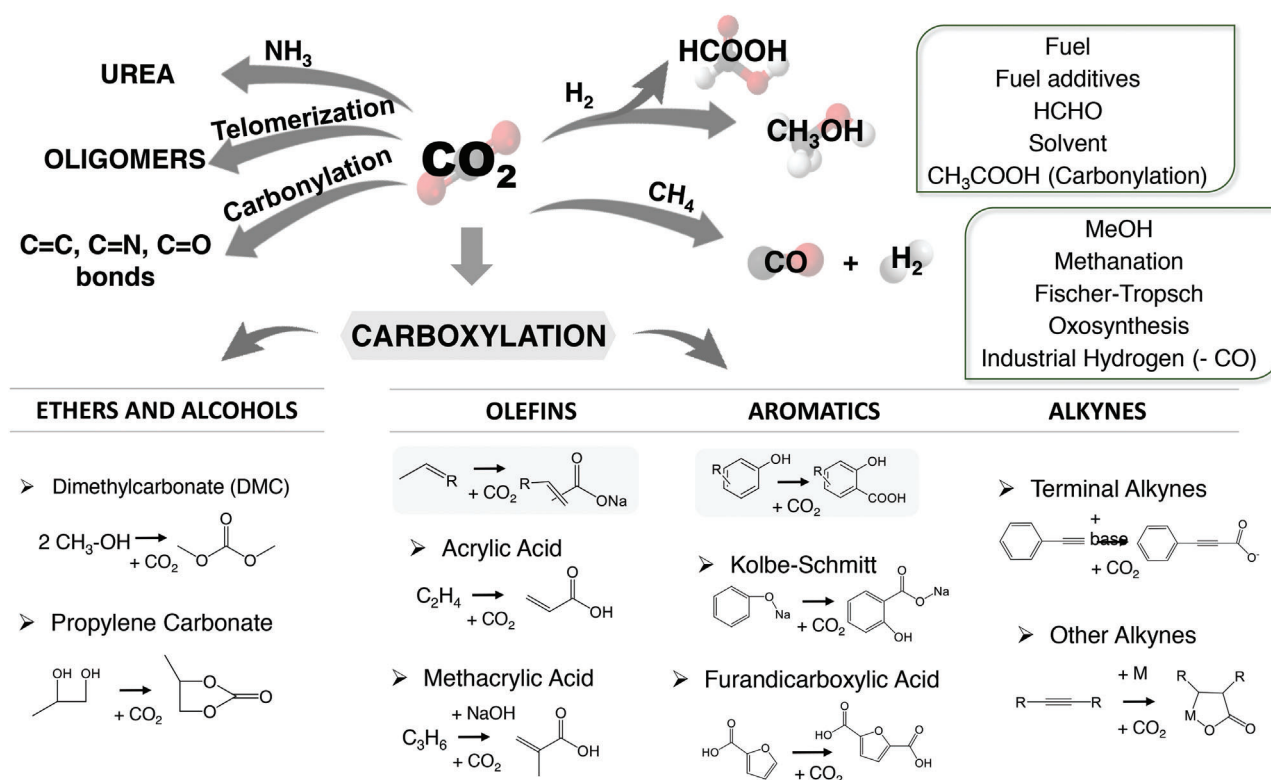
The incorporation of CO₂ into organic molecules was first proposed more than 100 years ago, as a particular application of the reaction of Grignard (see Scheme 1).⁷ However, the limited availability of the parent reagents, as well as their chemical reactivity and complex manipulation makes CO₂ fixation by this method unattractive for industrial implementation.

Currently, there are many organic reactions involving carbon dioxide. Nevertheless, the CO₂ thermodynamic stability and kinetic inertness (high oxidation state of carbon atom, linear geometry) restrict the industrial applicability to a very limited number of processes, highlighting the synthesis of urea and its derivatives,⁸ such as the Kolbe–Schmitt process to produce salicylic acid and other aromatic hydroxy acids⁹ and, in the last years, the production of organic carbonates, replacing phosgene as the C₁ building unit.^{10–15} These mechanisms are illustrated in Scheme 2.

Strong research efforts are devoted to developing alternative and effective processes to activate CO₂ and open the range of possibilities for its utilization. At present, several reaction systems have been proposed in the literature considering CO₂ as a reactant for synthesizing high-molecular polymers and fine chemicals, including carbonylations, cycloadditions, telomerizations, methylations, etc.^{16–21} The most promising ones are reviewed in Scheme 3. Except for the previously mentioned processes, most of these



Scheme 2. Schemes of CO₂ industrial processes: (A) urea production; (B) salicylic acid production by Kolbe–Schmitt process; (C) production of organic carbamates.



Scheme 3. Summary of the most promising chemical routes for the CO₂ valorization, highlighting carboxylation, the objective of this work.

alternatives are still at the lab scale, requiring stronger research efforts to make them attractive for a scale-up. In most of them, the development of active and selective catalysts is still the weakest point. Moreover, effective contact between CO₂ (gas) and the reactants (solids in many cases) and their chemical activation is also a relevant challenge, observing weak equilibria to overcome the thermodynamic barrier without compromising the stability of any of the reagents or intermediates involved.

A large part of the research efforts has focused on the development of technologies that allow a suitable and sustainable conversion of CO₂ to liquid fuels such as methanol, ethanol, dimethyl ether and other hydrocarbons. Relevant reviews analyze the state-of-art of these studies.²¹ The direct transformation of CO₂ into methanol (Eqn 1) has attracted much attention, mainly using Cu/ZnO/Al₂O₃ as the catalyst.^{22–28} The kinetics of the reaction significantly decrease in presence of CO/CO₂/H₂ mixtures, a situation for which theoretical calculations (using Density Functional Theory, DFT) demonstrate a high activity of materials based on molybdenum phosphides.²⁹ In any case, the direct CO₂ transformation into methanol

is technically hindered by the role of water as an inhibitor on the catalyst^{30,31} and economically limited nowadays by the availability and cost of hydrogen. The improvements of the manufacture of renewable hydrogen increases its availability and significantly reduces its cost. For the water inhibition, most of the approaches suggest the two-step process, with previous partial hydrogenation to obtain carbon monoxide by the reverse water-gas shift (RWGS) reaction (Eqn 2).



RWGS is an endothermic reversible reaction. Its main drawback is the development of active catalyst (usually based on copper or ceria oxides) at temperatures low enough to prevent the severe limitation by equilibrium. Since most of the catalysts studied require a temperature above 400°C,^{32–34} the equilibrium constant is low, requiring different methodologies to increase this conversion, such as working with high H₂ pressure, removing water vapor or using selective membranes.

Once the carbon monoxide is obtained, there is a huge of well-established process to produce not only methanol (by second hydrogenation) but also other interesting compounds and fuels, such as dimethyl ether, light alkanes, ethanol or formic acid, including catalytic, photochemical and electrochemical routes.^{35–38} These technologies are out of the scope of this work since, once the CH_4 is obtained, the subsequent steps are already implemented at an industrial scale.

Among the alternative routes, carboxylation deserves a special attention. It can be used to produce the precursors different kinds of polymers (mainly plastics). Nowadays these materials are produced from petroleum, with relevant drawbacks derived from this non-renewable origin and their slow biodegradation. The need to replace non-bio and nonrenewable plastics is clearly stated but, nowadays, bioplastics only represent 1% of the 368 million tons of plastic produced worldwide each year.³⁹ This percentage is expected to increase by 50% in the next 25 years,³⁹ a goal that requires strong efforts in development of efficient, sustainable and cheap industrial processes for manufacturing the appropriate monomers.

Biomass has become the most effective substitute of petroleum to obtain polymers precursors. This complex and renewable resource is composed of different extractives and natural polymers, which could be isolated and transformed (via chemical or enzymatic routes) into a plethora of platform molecules, some of them relevant in this context.⁴⁰ Among these compounds, bioethanol or cellulose-derived aldehydes (as furfural or hidroxymethylfurfural) play a key role as bioplatfrom molecules.

The production of bioethanol by sugar fermentation is a well-known process, already stablished at industrial scale. In addition to its use as fuel, ethanol is a promising precursor of many commodities, such as butanol and heavier alcohols.⁴¹ Moreover, its dehydration produces ethylene, a widely used hydrocarbon, one of the most typical monomer in the plastic industry, and also a promising reactant for CO_2 upgrading. On the other hand, the aqueous phase hydrolysis of hemicellulosic fractions produces cyclic aldehydes, highlighting 5hydroxymethylfurfural (5HMF) and furfural, from hexoses and pentoses, respectively.⁴² Their carboxylic functionalization is the starting point of the synthesis of polyethylene 2,5-furandicarboxylate (PEF), the renewable substitute of the most used plastic (PET).

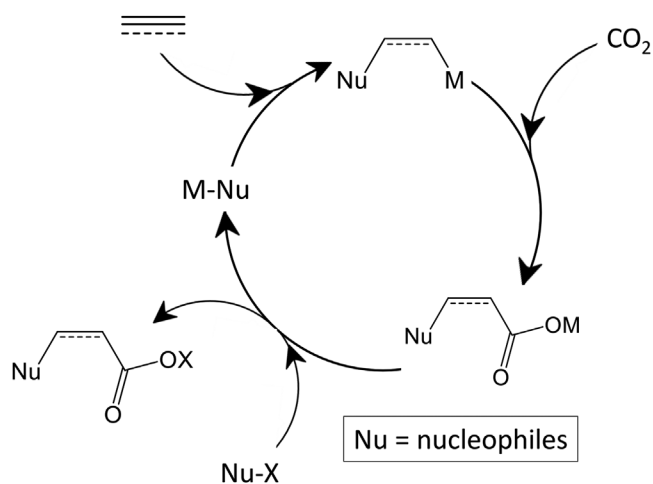
This brief review is intended to provide an overview of the research progress in chemical carboxylation, one of the most promising new routes to both functionalize and increase the carbon-chain length of different compounds by the insertion of a carbon dioxide molecule, directly preparing mono- and di-carboxylic acids and other derivatives.^{43,44} After an initial exposition of the main concepts and general mechanisms of carboxylation, the application of this approach to different platform molecules is considered, with special interest in molecules of renewable origin, analyzing the main systems proposed in the literature, the reaction conditions and the main drawbacks linked to each process.

Chemical carboxylation mechanisms

Carboxylic acids are important building blocks in the chemical industry for manufacturing rubbers, plastics, cosmetics, detergents, dyes, surfactants, among others.⁴⁵ Most of these chemicals are nowadays produced by different oxidation processes, reactions carried out at severe conditions (high temperature for gas phase reactions or strong acidity for liquid phase processes). On the other hand, these oxidation reactions are characterized by very low selectivities to the target carboxylic acid, an important fraction of the carbon atoms of the parent molecule being transformed into carbon oxides.^{46,47} The substitution of these routes by the direct carboxylation using CO_2 could also improve the sustainability and atom economy of these industrial processes.

Due to the thermodynamic stability of CO_2 , its incorporation into an organic molecule requires demanding activation steps, resulting into different approaches: the biochemical, the electrocatalytic, the photocatalytic and the chemocatalytic one. The last one can take place by two different mechanisms: (1) in liquid phase, at soft temperatures using organometallic intermediates (homogeneous catalysis); (2) or at higher temperatures, with a solvent-free configuration, using inorganic salts as precursors.

According to the first one, the formation of a carboxylic acid by CO_2 carboxylation takes place through the nucleophilic addition of (transition) metal ligand species (label as M-Nu) to the unsaturated bond of a substrate molecule, followed by the insertion of CO_2 into the resulting organometallic intermediate (usually considered as the real homogeneous catalyst).



Scheme 4. Typical reaction patterns of transition metal promoted carboxylation of unsaturated substrates with CO₂ (adapted from Ref. 49).

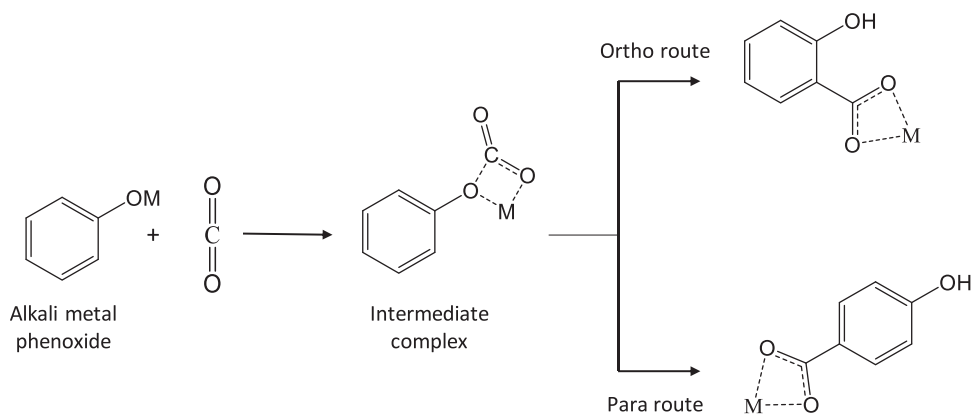
The general pathway is depicted in Scheme 4. This route has been proposed using several transition metals, such as Ni, Cu, Co, Ni, Pd, Au and Ru, and some noble metals, such as Rh, Pd.^{48–50} The reaction takes place in the liquid phase at low pressure (15 bar of CO₂) and low temperatures (from –70 to 60°C) using different solvents to dissolve the organics.

This mechanism can be applied to different unsaturated organic compounds, including alkynes, alkenes, allenes and aldehydes, both cyclic and acyclic compounds, resulting in a huge diversity of potential reactants. Despite the chemical potential, this route has significant drawbacks from the sustainability point of view, which hinders its applicability at industrial scale. The lack of heterogeneous catalysts reduces the

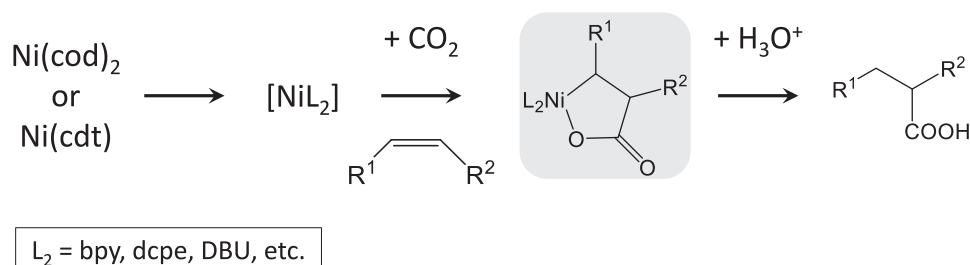
possibility of reusability and hamper the stream purification. Moreover, most of the organic solvents (THF, dioxane),^{51–54} ligands (trialkylboranes, metallactones),⁵⁵ and metal precursors ((IPr)CuCl, Ni(cod)₂, bis(amidine))^{51–53} used in the reaction are expensive and have a clear toxic character. Thus, their cost and stoichiometric consumption could reduce the economic feasibility and produce relevant environmental drawbacks in case of an incomplete stream purification.

An alternative carboxylation pathway (second mechanism, illustrated in Scheme 5) considers the direct coupling between aromatics and CO₂ without requiring the presence of an external organometallic nucleophile. This route was firstly proposed in 1860,⁵⁶ when salicylic acid was prepared by heating a mixture of phenol and sodium in the presence of carbon dioxide at atmospheric pressure. Further studies demonstrated that higher yields are obtained using phenolic salts and under enhanced pressure, developing the process currently known as the Kolbe–Schmitt reaction. This reaction is defined as a heterogeneous gas–solid reaction that enables synthesizing aromatic hydroxycarboxylic acids via carboxylation of a phenol salt of an alkali metal under severe reaction conditions at 125°C and 4–7 atm carbon dioxide pressure.^{5,57}

Nowadays, this mechanism is well established, for example, in the industry for the salicylic acid production. Its application to different aromatics opens a new route to obtain biopolymer precursors without the use of organic solvents and organometallic catalysts, preventing the previously mentioned environmental problems derived from the first mechanism. Most of the reported studies are



Scheme 5. Kolbe–Schmitt reaction pathway. In the scheme, “M” represents an alkali metal (adapted from Markovic *et al.*, 2007⁹).



Scheme 6. Carboxylation of olefins using Ni organometallic complexes as catalysts (adapted from Ref. 59).

performed in the absence of any solvent, the main requirement to establish a good contact between the salt and the CO₂ is to guarantee the melting state of the solid without its decomposition. This fact establishes different temperatures and metals as a function of the original aromatic to be transformed.

Liquid phase carboxylation of unsaturated molecules using organometallic complexes

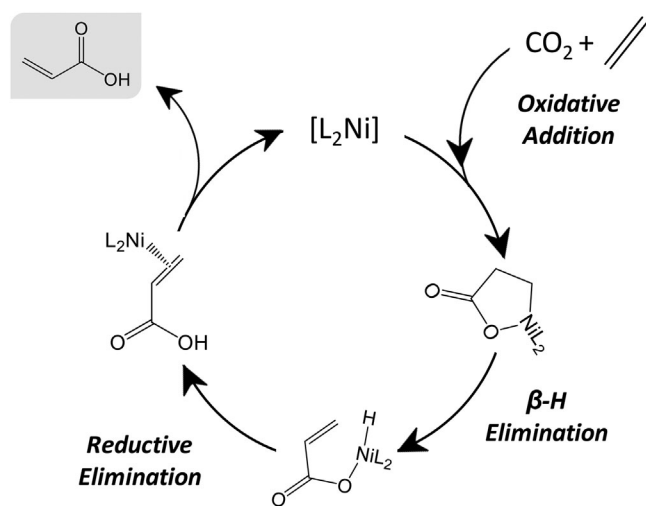
The reaction of alkenes with CO₂ was reported for the first time in the 1980s, using nickel complexes (lactones, homogeneous catalysis) to stabilize the reaction intermediates, Scheme 6.⁵⁸ Despite the plethora of alkenes that could be used as reactant, the most interesting studies are focused on the valorization of the lightest alkenes, ethylene and propylene, since they are the raw materials necessary to obtain industrial interesting carboxylic acids, such as malonic, succinic, acrylic and methacrylic acid.

In 1987, the first studies focused on the reactivity of ethylene proposed using homogeneous iron salts as metal catalyst. FeCl₂ was dissolved in THF at very low temperatures (−78°C), the solution was then saturated in ethylene, obtaining a complex (metal lactone) once the corresponding ligand is added. This complex stabilized the ethylene, allowing the carboxylation (C=C bond) when treated the solution with a CO₂ stream at 1 bar.⁵⁹ This study suggests for the first time the strong influence of the ligand of the position of the new C=C bond, obtaining succinic or methylmalonic acid as a function of if bidentate or monodentate ligands are used. In both cases, a double CO₂ addition is produced, obtaining C4 carboxylates that could be transformed into the corresponding acids by hydrolysis.

From ethylene to acrylic acid

The direct acrylic acid production from ethylene and CO₂ is a desired but challenging reaction due to relevant thermodynamic limitations ($\Delta G_0 = 42.7$ kJ/mol). Acrylic acid has an essential value as monomer (50% of the total esters) and as an intermediate to produce paints and coatings, adhesives, construction chemicals and hygienic products, among other examples. Currently, this acid is industrially synthesized by the oxidation of propylene (non-renewable resource), a two-step reaction with acrolein as intermediate. This route has relevant drawbacks from the environmental point of view, highlighting the strong material requirements for the reactors (due to the high corrosive reaction conditions) and the low E-factor derived from the production of acetic acid and CO₂ as side-product. Despite the thermal optimization to reduce these undesired products, this process has a global warming potential of 2.3–2.5 kg CO₂/kg acrylic acid.⁶⁰ Thus, in the context of the circular economy and sustainability, there is a high interest in developing a sustainable and economical alternative process, with the ethylene carboxylation being one of the most promising alternatives.

The first studies date from the first decade of the 21st century, being based on the conclusions of the pioneer studies of Hobert et al. in 1987, that is, proposing the stabilization of ethylene taking part of a metal lactone complex.⁶¹ These preliminary works were partial studies that analyze the process step by step. The first one analyzes the coupling step, proposing a theoretical mechanism for the ethylene carboxylation (Scheme 7).⁶² According to this mechanism, corroborated by DFT studies, the oxidative coupling step of the substrate to form metallactones is possible but the distance between the transition metal and β H is so large that the β H elimination (step required to the



Scheme 7. Reaction mechanism for the synthesis from ethylene and CO₂ (adapted from Ref. 59).

release of the acrylate and to regenerate the metal species) is not possible without the cleavage of metal-C bond. This drawback is a common problem identified in the first studies, despite proposing catalysts based on Ni,^{58,61,63} Mo or W.^{64–66} The stabilization of this bond has been the crucial point in most of the further studies, suggesting different ligands that could form stable intermediates. Thus, Walther and co-workers propose the use of bis(dicyclohexyl-phosphino)methane using Ni as transition metal.⁶⁷ This ligand produces a binuclear complex in which the methane acts as hydride acceptor, and the high flexibility of this complex (exhibiting monodentate, chelating or bidentate behavior) favors the βhydride transfer. Although the release of acrylic acid or an acrylate cannot be achieved, this study marked the starting point of further improvements in this issue.

In a specific work of 2007 about this release, Aresta *et al.* demonstrated that the acrylic acid liberation is possible if carboxylation is combined with the esterification of the carboxylic moiety (ethyl acrylate), using Pd complexes, preventing the formation of M-H and M-O stable bonds (see Scheme 8).⁶⁸ In the same direction, in 2010, Bruckmeier *et al.*, propose the use of methyl iodide to improve the βhydride elimination and the liberation of the acrylate, reaching maximum yields of 33% when the reaction was carried out at 40°C, using dichloromethane as solvent.⁶⁹ Based in all these previous studies, in 2012, Limbach and co-workers published the first complete catalytic synthesis of acrylate from CO₂ and ethylene, using a

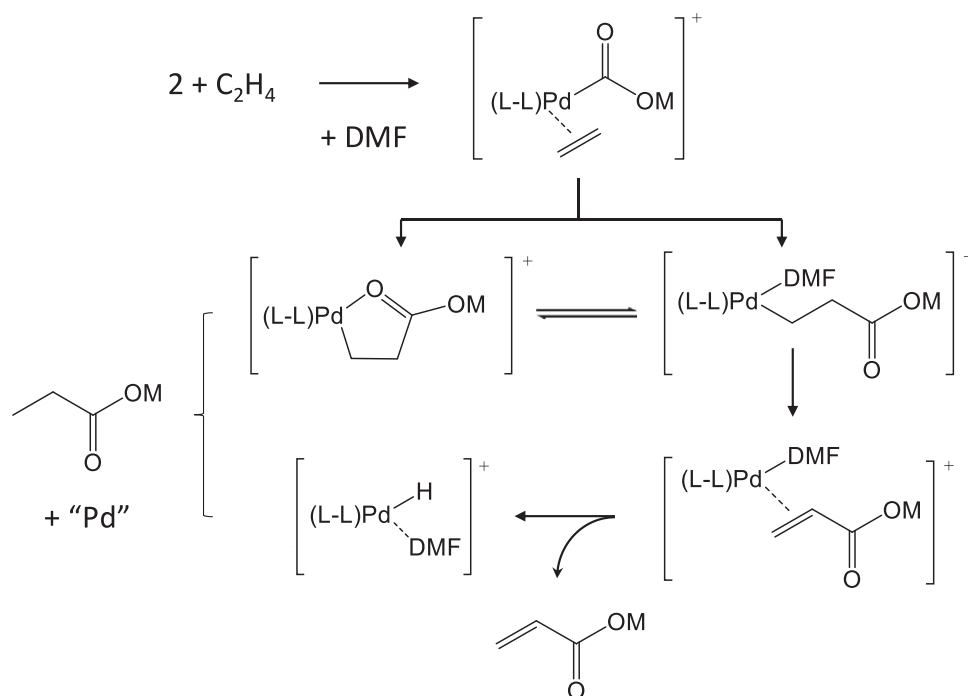
nickel complex as homogeneous catalyst, demonstrating a high dependence on the reaction conditions.⁷⁰ A temperature of 50°C allows the equilibrium that maximizes the kinetic of the process preventing the decomposition of any intermediate when using THF as solvent (54% yield after 6 h with 5 bar of ethylene and 40 bar of CO₂).

A significant increase in the reaction rate (91%) was observed by substituting the THF by PhCl, in this case at 60°C. Further studies deepen the influence of different reaction conditions, mainly analyzing the role of ligand, solvent and the reducing agent, typically working with high CO₂ pressure (20 bar) to guarantee the required solubility on the organic solvents used.^{71,72} In most of the cases, Ni is proposed as metal, but there are also relevant studies considering Mo, Ti, Pd, Pt, Fe and Ru complexes.⁷³ Mechanistic studies suggest similar pathways for all these materials, but with different limiting steps. The oxidative coupling of CO₂ and ethylene is easier with Group VI metals than with Ni systems, being possible at room temperature and pressures when using Mo/W complexes, requiring more severe conditions when using Ni. However, the strong oxophilicity of these metals is an impediment to the acrylate removal, requiring strong bases not needed when working with Ni complexes.

To sum up, the acrylic acid production by the direct carboxylation of ethylene with CO₂ has been successfully proposed as a synthesis route, using organometallic complexes. This approach has significant drawbacks hindering its scale-up, highlighting the low turnover numbers (<0.1 h⁻¹), the stoichiometric amount of reducing agent or base required and the use of solvents, which is contrary to the sustainability and the economy of the process.⁷⁴ These disadvantages justify the lack of references from an engineering point of view. A different approach, a gas-phase reaction using solid catalysts (following the model of Ziegler-Natta catalysts) could overcome these limitations but, so far, this route has not been proposed in the literature for the coupling between ethylene and CO₂.

From propylene to methacrylic acid

Methacrylic acid (MAA) is an important intermediate in the production of different polymers. The current industrial processes, such as acetone cyanohydrin or isobutylene oxidation and subsequent hydrolysis, the dehydrogenation of isobutyric acid, and the



Scheme 8. Reaction mechanism for methyl acrylate formation, according to Aresta *et al.*⁶⁸

decarboxylation of different organic acids, must be substituted by a renewable route that reduces the drawbacks in terms of environmental pollution, toxicity, low selectivity and high cost of the current ones.

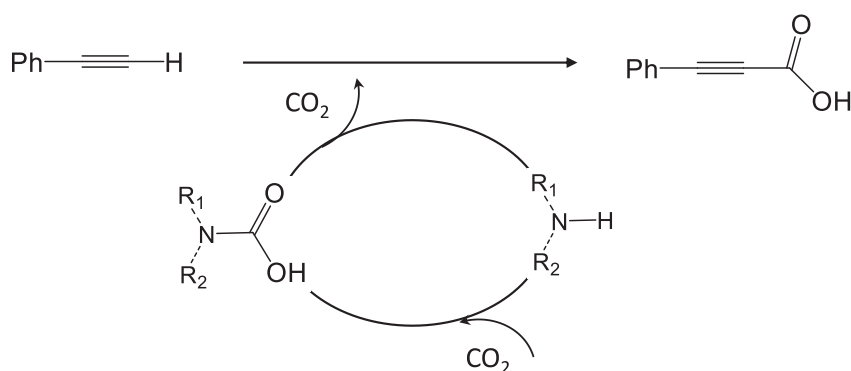
The propylene carboxylation using CO_2 was firstly proposed in 2003 by Zhong *et al.*, at $290^\circ C$ and 1 MPa using Ni, P, Mo and W heteropolyacids as catalysts.⁷⁵ According to promising results, the research interest in this route was focused on the development of heterogeneous catalysts that increase the sustainability of the process. Thus, these heteropolyacids were supported on TiO_2 . Despite the low propylene conversion obtained (4.2% at 1 MPa, $290^\circ C$), a high selectivity is reported (96%), demonstrating the relevance of Lewis base and acid sites to promote the chemisorption of both reactants.⁷⁵ These tentative results have been improved by modifying the polymetallic oxygen salts, the best results being obtained with $PW_{11}Ni/TiO_2$, with 12.6% of propene conversion and a MMA selectivity of 95%.⁷⁶ Unfortunately, the veracity of these results has been questioned, since Bentrup and co-workers tried to reproduce them without obtaining any conversion.⁷⁷ According to their study, the *in situ* FTIR spectroscopy reveals the chemisorption of CO_2 as carbonate species on the surface of supported POM catalysts. However,

these carbonates do not react with propene. Moreover, the strong oxidizing character of these catalysts promote the propylene oxidation, obtaining different CO_x . No further studies have been published on this topic, despite the undoubted interest of a heterogeneous catalytic carboxylic route to obtain methacrylic acid.

Other carboxylation of alkenes and alkynes with CO_2

Other olefins have been also studied in coupling with CO_2 since carbon dioxide is an extremely attractive C1 feedstock in organic synthesis. Several studies deal with the carboxylation of styrene derivatives to obtain aryl carboxylic acids, proposing organometallic systems similar to those indicated for ethylene valorization.^{78–85} In general, promising results were obtained but with homogeneous organometallic and configuration systems that make these configurations difficult to implement at an industrial scale. Moreover, the selectivity of the reaction decreases in presence of more than one $C=C$ unsaturation, such as in the case of butadiene^{86,87} or allene.^{88–90}

With the same strategy, different authors investigated the terminal carboxylation of alkynes as potential useful reactions to bear pyrones and, in the last years,



Scheme 9. Alkyne carboxylation using capture solutions (adapted from Yu *et al.*⁹⁷).

carboxylic acids or esters (see Scheme 9).^{91–96}

Experimental results demonstrate an easy reactivity of alkynes, obtaining molecules bearing the carboxylic functionality bonded to an olefin moiety.

As indicated before, these reactions are not relevant for the polymer industry, and they will not be explained in detail. However, there are some interesting works exploring these reactions in continuous configuration. These works have relevant information that could be the background of a future implementation of continuous carboxylation of more interesting platform molecules.

Liquid-phase carboxylation in continuous flow

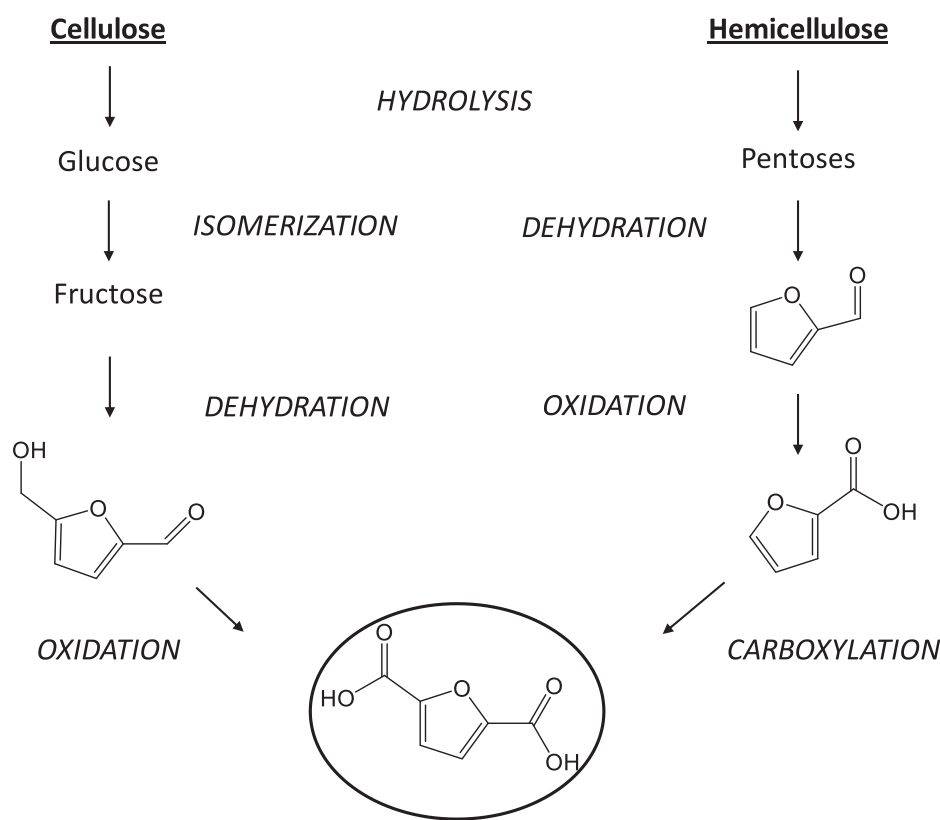
The first continuous flow carboxylation was carried out in 2011, obtaining promising results using a tube-in-tube gas–liquid biphasic reactor.⁹⁷ The Grignard reagents were pumped diluted in THF inside the inner tube. The space between the inner and the outer tubing was pressurized with 4 bar of CO₂, allowing the saturation of the liquid phase because the Teflon AF-2400 used for the inner tubing demonstrates a particularly effective gas permeability. Carboxylic acid was released after washing with a formic acid/THF solution the packed-bed columns used to trap the carboxylate intermediate. This procedure has been tested using aromatic, aliphatic, heteroatomic and alkynyl Grignard reagents with excellent yields (7 bar of CO₂, 1 mL·min^{−1}). In a further study, Broek and co-workers analyzed the influence of the mixing point, comparing the results obtained with a continuous CO₂ saturation of the THF and phenylmagnesium bromide solution with those reached when two THF streams (with CO₂ and the reactant) are independently

saturated. The first configuration demonstrates a higher conversion, but the second one presents a higher stability, being not significantly affected by differences in the temperature (up to 60°C, residence time (18–75 s) or CO₂ concentration (<2 M).⁹⁸ These studies were the basis or other works dealing with different aromatic alkenes,⁹⁹ and alkynes,¹⁰⁰ having a good background about reaction conditions as a function of the ligand used. Most of these studies are deeply analyzed in a review published in 2018.¹⁰¹

Though the development of catalytic systems for CO₂ carboxylation in continuous flow needs more studies to adapt these configurations to the sustainability requirements (heterogeneous catalysis, absence of solvents) and to make feasible the carboxylation of light alkenes (the most interesting ones from the industrial point of view), these works indicate relevant advantages of continuous flow to control this reaction.

Chemical carboxylation of aromatics and heterocyclic compounds

As mentioned in the introduction section, biomass has become the most effective substitute for petroleum to obtain polymers precursors. In this context, 2,5-furandicarboxylic acid (2,5-FDCA) is highlighted as one of the main pillars of the bioplastic industry. It is the ideal alternative to terephthalic acid (non-renewable monomer), allowing the substitution of polyethylene terephthalate (PET), one of the most used polymers, by a sustainable alternative, the polyethylene furoate (PEF), obtained by the 2,5FDCA polymerization with ethylene glycol. The chemical structures of both polymers are very comparable, which enables the almost direct substitution, obtaining a polymer with



Scheme 10. Routes to 2,5-FDCA synthesis from cellulose and hemicellulose.

45–55% lower greenhouse gas footprint, when calculated from cradle to grave,¹⁰² improved barriers and more attractive thermal properties with respect to its non-renewable predecessor (PEF's oxygen and CO₂ barriers are 10 and 6–10 times better, the glass transition temperature is 12°C higher, whereas the melting point decreases is 35°C).^{103,104} With a lower but also relevant market share, the production of 2,5FDCA is also relevant to obtain other polymers, as reviewed by Pandey *et al.* in 2021.¹⁰⁵

Currently, the production of 2,5-FDCA is studied from two different approaches (Scheme 10). The first one involves the oxidation of 5-hydroxymethylfurfural (5-HMF). This catalytic route allows obtaining high yields of 2,5FDCA with some problems in purity in the final mixtures.^{106–108} Moreover, most of the HMF is produced from edible biomass since its production from lignocellulose is characterized by its low purity and yield. To prevent conflicts with the food industry and to reduce the current cost of 2,5FDCA production, established in 2500 \$/kg,¹⁰⁹ the 2,5-FDCA production from lignocellulosic platform molecules that could be obtained from waste biomass, such as furfural,¹¹⁰ is essential.

The synthesis of 2,5-FDCA from furfural has been proposed in the literature by different catalytic routes, all of them considering furfural oxidation to obtain furoic acid (FA) as the first step. Once the carboxylic functional group is present, 2,5FDCA can be obtained by the disproportionation of FA (Henkel reaction), yielding furan as a co-product.^{111–116} By this route 2,4FDCA is also obtained, the 2,5FDCA is difficult to isolate due to the similar physical and chemical properties.^{111,117} Other alternative is the carbonylation pathway, include furoic acid bromination, esterification, carbonylation and hydrolysis steps.¹¹⁸ The restricted selectivity of the first approach, as well as the complexity and nonsustainable character of the second one, limit their future development, emphasizing the interest for the carboxylation routes.

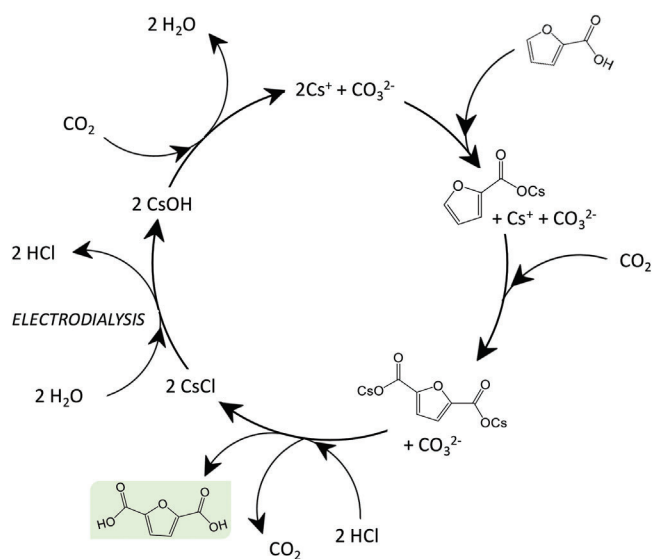
Furoic acid carboxylation in batch configuration

The carboxylation in acidic media requires a Lewis acid¹¹⁹ to activate via coordination of the CO₂, leading to a reaction with the furoic acid. Theoretically, this reaction occurs at relatively low temperatures but high

CO₂ pressure, making it impossible to take direct advantage of the CO₂ capture system (typically working at low pressure). Moreover, poor yield of the target product is reached due to the different parallel reactions yielding a large amount of undesired by-products. Due to these disadvantages, there are no further studies considering this approach.

The FA carboxylation using CO₂ and a base as reagent was proposed for the first time in 2016.¹²⁰ This reaction is a particular application of the Kolbe–Schmitt synthesis, possibly the oldest organic synthesis using CO₂, reported in 1860.¹²¹ The Kolbe–Schmitt reaction is a solidstate reaction usually carried out by contacting dry CO₂ with aromatic compounds activated by electron-donating substituents, such as alkaline cations. Although this reaction has been developed for hydrocarbon aromatics, its mechanism could be extended to other heterocyclic compounds with aromatic characteristics, such as pyridines or furans.¹²²

A pioneering work of Kanan and co-workers¹²⁰ establishes the pillars for future studies, obtaining very relevant conclusions about the mechanism and the reaction conditions. Previous researchers demonstrate that carbonates can deprotonate C–H bonds with pK_a values of up to 27 using organic solvents and high temperatures.^{123–125} Considering the high pK_a of the C–H at the five position of furan-2-carboxylate (≈35), the formation of 2,5-FDCA by carboxylation with CO₂ is thermodynamically unfavorable. This drawback is solved by the initial formation of metal furoate by the reaction of the furoic acid with an alkaline salt. Thus, the reaction involves two solids, and it is carried out in at solventless conditions. These solids must be melted to enable the ion mobility needed for the correct interaction of the different involved ions. Thus, the melting point of the carbonates is a critical aspect to prevent the decomposition of the organic compounds (furoic acid and reaction intermediates or side compounds). In this context, most of the alkaline salts are discarded (temperatures much higher than 200°C to melt), proposing Cs₂CO₃ as the best option. At working conditions, this carbonate deprotonates C–H bonds with pK_a > 40. This deprotonation leads to a strong nucleophilic carbon atom that could react with the weakly electrophilic CO₂. The reaction mechanisms proposed (Scheme 11) results in a net consumption of one equivalent of CO₂ per C–CO₂[–] produced. Working with high concentration of carbonates guarantees the stabilization of the



Scheme 11. Reaction mechanism to selectively obtain 2,5-FDCA by the base carboxylation of furoic acid and CO₂.

conjugated base of 2,5-FDCA by ion pairing. The 2,5-FDCA is obtained by protonation with HCl, whereas the carbonate is recovered by electrodialysis.

The best results proposed in this work correspond to 76% yield of 2,5-FDCA^{2–} after 12 h when heated at 260°C under a CO₂ flow of 40 mL·min^{–1}, using 10% of excess of Cs₂CO₃. Acetate and malonate, among others, are identified as the main decomposition products, their production being limited when working in a pressurized batch reactor (89% of 2,5-FDCA^{2–} yield after 7 h at 200°C with 8 bar of CO₂).¹²⁰ The limited role of Cs⁺ only to reduce the melting point of the salt is corroborated by substituting this alkaline by potassium salts (potassium carbonate and carboxylate as a co-salt). Yields higher than 60% were reached (so Cs⁺ has not any specific role in the mechanism), but the temperatures are so high (320°C) that decomposition reactions cannot be prevented. As expected by the semi-molten state of the reactant, the reaction occurs at the gas–solid interface. Preliminary scale-up studies (from 1–10 to 100 mmol) result in lower yields because of the lower surface area to volume ratio obtained.¹²⁰ These results are justified by the hindered transport of CO₂ into the salt and removal of H₂O.

In a different approach, Nocito *et al.*, compare the activity of different cheaper carbonates, trying to obtain more evidences of the reaction pathway and the intermediates involved, concluding that inorganic carbonates, especially those with monovalent cations,

are the active species, observing an increasing activity as the charge density on the cations decreases.¹²⁶ This study also demonstrates the correlation activity-melting (decomposition) point of the carbonates and proposes the use of copper-difuroate ($\text{Cu}(\text{FC})_2$) as an alternative esterification of the furoic acid, reducing the amount of Cs involved in the reaction. A complete comparison between the carboxylation of $\text{Cu}(\text{FC})_2$ and FA demonstrate a higher yield when using the copper complex (selectivity of 89% versus 70%, after 6 h at 493 K, 6 MPa of CO_2). Moreover, the reaction involving $\text{Cu}(\text{FC})_2$ produces more than 50% of 2,5FDCA using K_2CO_3 , whereas only 13% is obtained when using the FA. Based on these results, the optimum configuration considers the use of $\text{Cu}(\text{FC})_2$ with $\text{CsCO}_3/\text{MgCO}_3$ (0.1:1 Cs/Mg), yielding 94% of 2,5FDCA after 20 h of carboxylation at 493 K with 6 MPa of CO_2 .

Only few authors propose the carboxylation of furan derivatives using homogeneous catalysis, such as Cu and Pd salts. However, this approach is mainly focused on the 2,5FDCA synthesis through a multistep process involving cascade reactions: bromination, esterification, carboxylation, and hydrolysis. The main advances in this topic are summarized in a review of Drault *et al.*¹²⁷

Furoic acid carboxylation in continuous flow

Trying to improve these results and guarantee the scale-up of the process, Dick and co-workers investigate the furoate carboxylation in a fixed-bed flow reactor using carbonate with different mixtures of cations. Very promising results at mole-scale were obtained using a 2:1 K^+/Cs^+ blend, reaching 89% of 2,5FDCA after 24 h at 260–285°C with 8 bar of CO_2 .¹²⁸ These results are also relevant to improve the profitability of the process, comparing the prizes of Cs^+ and K^+ , despite the theoretical recovery proposed by electrodialysis. The similar reaction under static pressure was not efficient, producing a mixture enriched in decomposition products. It is concluded that the removal of H_2O suppresses decomposition and improves the yield of FDCA.

Based on these results, Zhou and coworkers proposed in 2019 the direct production of 2,5FDCA from HMF and furfural.¹²⁹ They developed a supported metal catalyst (Co/Zn-lignin complex to N-doped carbon supported Co single-atom catalyst, Co SAs/N@C) that,

in presence of Cs_2CO_3 produces the simultaneous oxidation of HMF and furfural, obtaining 2,5FDCA and furoic acid, respectively. Since the cesium carbonated acts as a base that facilitates the oxidative dehydrogenation of furfural (no reaction is observed in absence of this carbonate), the same system is used directly to transform the FA into 2,5FDCA, substituting the O_2 by CO_2 . After 36 h at 260°C, 71.1% of 2,5FDCA is obtained from furfural oxidation derived product with a selectivity close to 83%. These results demonstrate a high similarity with those optimized when using pure FA,¹²⁰ the longer times required being justified by the low CO_2 pressure (1 bar).

Wang *et al.* carried out a complete study about the reaction conditions in fixed-bed flow reactors, analyzing the effect of Cs_2CO_3 and FA-Cs ratio, the temperature, reaction time and CO_2 pressure on the 2,5FDCA yield,¹³⁰ obtaining interesting results in agreement with values reported by other authors. Even more, these results were theoretically explained based on DFT studies, being very helpful to establish the optimum conditions to maximize the production of 2,5FDCA. Thus, the positive effect of an excess of Cs_2CO_3 reaches a maximum with a molar ratio 3:5 (50.6% of yield at 270°C after 3 h), whereas higher excesses reduce the activity. It is suggested that this excess negatively affects the effective collision between reaction intermediates and CO_2 . A maximum yield of 2,5FDCA (54%) is also observed when analyzing the effect of the temperature since results over 270°C demonstrate a FA-Cs decomposition into acetate, malonate and other compounds. The reaction time is also relevant since prolonged times generate so much water in the reaction system that the dissociation of the reactants is affected at the same time as part of the CsCO_3 suffers solubilization. Both phenomena hinder the reaction, defining a well-marked maximum (3 h when the reaction takes place at 280°C with 8 bar of CO_2). As for the CO_2 pressure, an optimum value is defined for each reaction temperature since larger CO_2 pressures promotes the transformation of carbonates into bicarbonates, reducing their promoting activity.

To sum up, different studies demonstrate that the furoic acid heterogeneous carboxylation is feasible in absence of solvent. Furoic acid is readily synthesized from furfural, and inexpensive compound that can be produced from non-edible biomass.⁷⁴ In addition to the previously mentioned advantages, this solid-gas phase reaction is recommended over the liquidphase one since the use of alkali metal salts instead of

transition metal catalysts allows performing the reaction using relative low purity CO₂ (industrial grade) because the alkali metal salts are much more tolerant of impurities in the CO₂ stream than transition metals. However, according to the current state-of-art, the process must be improved before its scale-up, paying more attention to the substitution of Cs by a cheaper element, or to the complete regeneration of the carbon salt to guarantee its total reusability. Moreover, for larger industrial-scale production, the kinetics must be improved, as well as the control on some parameters, such as the mass transport effects.

Furoic acid enzymatic carboxylation

In parallel to these chemical approaches to carboxylation, biocatalytic routes have also gained relevance in recent years for 2,5FDCA production. Thus, the carboxylative activity of some enzymes of the family decarboxylases was identified as a side conclusion of biodegradation studies.^{131–133} These results were the starting point for the Payne and co-worker study, demonstrating the carboxylation ability of HmF enzymes to produce 2,5FDCA.¹³⁴ The results are not very high (0.3% of yield after 12 h) and the reaction requires a severe control on the reaction conditions since it is very sensitivity to temperature (50°C being the optimum one), pH (almost null activity out of the neutral range), and CO₂ pressure (32 bar required to observe results). However, the inherent sustainability of enzymatic reactions as well as the possibilities of DNA recombination and engineering define this biocatalytic route as a promising field for future studies.

Kawanabe *et al.* propose a biocatalytic route to produce 2,5FDCA directly from furfural using bicarbonate as the carbon source and recombinant *Escherichia coli* cells co-expressing different enzymes. The hydrogen peroxide obtained during the furfural oxidation is identified as an inhibitor of the carboxylation activity, proposing the reduction of H₂O₂ levels as the future work to improve this one-pot configuration.¹³⁵

Conclusion

In conclusion, carbon dioxide has a promising future as a renewable and environmentally friendly source of carbon to synthesize monomers, such as acrylic acid and 2,5-furandicarboxylic acid. This review has shortly analyzed the state of the art on the two main

carboxylation chemical routes, the direct solid-gas phase contact using a metal salt of the aromatic precursor, and the carboxylation using an organometallic intermediate as ligand to promote the reaction. Both routes are demonstrated to be feasible, but their industrial implementation still requires further studies to overcome the relevant current difficulties.

The ethylene carboxylation to produce acrylic acid using the current pathway is very difficult to scale-up. The difficult recovery of the organometallic ligands and the use of organic solvents hinder the sustainability of this route, the development of effective heterogeneous catalyst and the optimization of the reaction conditions are the biggest challenges in this topic.

In the case of the 2,5-furandicarboxylic acid, an effective solid-gas configuration is already proposed in the literature. However, the narrow range of reaction conditions to produce the salt melting without jeopardizing the thermal stability of the compounds requires the use of caesium salts. The high cost of this metal compromises the economic feasibility of this process. The recovery of this metal to guarantee the close cycle and the reutilization of this precursor is then compulsory to evaluate this approach at a bigger scale. The use of environmentally friendly solvents could be a good approach to obtain soluble salts without needing the use of caesium, increasing also the temperature range of the reaction, minimizing the undesired compounds.

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References

1. Ritchie H, Roser M, Rosado P. CO₂ and greenhouse gas emissions. <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions>. Accessed 11 May 2022.
2. Anwar MN, Fayyaz A, Sohail NF, Khokhar MF, Baqar M, Khan WD, *et al.* CO₂ capture and storage: a way forward for sustainable environment. *J Environ Manage.* 2018;226:131–44.
3. Zhang T, Zhang W, Yang R, Liu Y, Jafari M. CO₂ capture and storage monitoring based on remote sensing techniques: a review. *J Clean Prod.* 2021;281:124409.
4. Rubin ES. Understanding the pitfalls of CCS cost estimates. *Int J Greenh Gas Control.* 2012;10:181–90.

5. Li B, Duan Y, Luebke D, Morreale B. Advances in CO₂ capture technology: a patent review. *Appl Energy*. 2013;102:1439–47.
6. Steeneveldt R, Berger B, Torp T A. CO₂ Capture and storage: closing the knowing–doing gap. *Chem Eng Res Des*. 2006;84(9):739–63.
7. Dalton DM, Rovis T. C–H carboxylation takes gold. *Nat Chem*. 2010;2(9):710–1.
8. Shi F, Deng Y, SiMa T, Peng J, Gu Y, Qiao B. Alternatives to phosgene and carbon monoxide: synthesis of symmetric urea derivatives with carbon dioxide in ionic liquids. *Angew Chem-Int Edit*. 2003;42(28):3257–60.
9. Marković S, Marković Z, Begović N, Manojlović N. Mechanism of the Kolbe-Schmitt reaction with lithium and sodium phenoxides. *Russ J Phys Chem A*. 2007;81(9):1392–7.
10. Lu X-B, Darensbourg DJ. Cobalt catalysts for the coupling of CO₂ and epoxides to provide polycarbonates and cyclic carbonates. *Chem Soc Rev*. 2012;41(4):1462–84.
11. Sujith S, Min JK, Seong JE, Na SJ, Lee BY. A highly active and recyclable catalytic system for CO₂/propylene oxide copolymerization. *Angew Chem-Int Edit*. 2008;47(38):7306–9.
12. Darensbourg DJ. Making plastics from carbon dioxide: salen metal complexes as catalysts for the production of polycarbonates from epoxides and CO₂. *Chem Rev*. 2007;107(6):2388–410.
13. Nakano K, Kamada T, Nozaki K. Selective formation of polycarbonate over cyclic carbonate: copolymerization of epoxides with carbon dioxide catalyzed by a cobalt(III) complex with a piperidinium end-capping arm. *Angew Chem-Int Edit*. 2006;45(43):7274–7.
14. North M, Pasquale R, Young C. Synthesis of cyclic carbonates from epoxides and CO₂. *Green Chem*. 2010;12(9):1514–39.
15. Decortes A, Castilla AM, Kleij AW. Salen-complex-mediated formation of cyclic carbonates by cycloaddition of CO₂ to epoxides. *Angew Chem-Int Edit*. 2010;49(51):9822–37.
16. Luo J and Larrosa I. C–H carboxylation of aromatic compounds through CO₂ fixation. *ChemSusChem*. 2017;10(17):3317–32.
17. Kudo K, Shima M, Kume Y, Ikoma F, Mori S, Sugita N. Carboxylation of cesium 2-naphthoate in the alkali metal molten salts of carbonate and formate with CO₂ under high pressure. *J Jpn Pet Inst*. 1995;38(1):40–47.
18. Zhang Y, Cen J, Xiong W, Qi C, Jiang H. CO₂: C1 synthon in carboxylation reactions. *Prog Chem*. 2018;30(5):547–63.
19. Dabral S and Schaub T. The use of carbon dioxide (CO₂) as a building block in organic synthesis from an industrial perspective. *Adv Synth Catal*. 2019;361(2):223–46.
20. Ma J, Sun N, Zhang X, Zhao N, Xiao F, Wei W, et al. A short review of catalysis for CO₂ conversion. *Catal Today*. 2009;148(3):221–31.
21. Centi G, Perathoner S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal Today*. 2009;148(3):191–205.
22. Olah GA. Towards oil independence through renewable methanol chemistry. *Angew Chem-Int Edit*. 2013;52(1):104–7.
23. Behrens M, Studt F, Kasatkin I, Kühl S, Hävecker M, Abild-Pedersen F, et al. The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. *Science*. 2012;336(6083):893–7.
24. Kuld S, Thorhauge M, Falsig H, Elkjær Christian F, Helveg S, Chorkendorff I, et al. Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science*. 2016;352(6288):969–74.
25. Studt F, Behrens M, Kunkes EL, Thomas N, Zander S, Tarasov A, et al. The mechanism of CO and CO₂ hydrogenation to methanol over Cu-based catalysts. *ChemCatChem*. 2015;7(7):1105–11.
26. Rodriguez JA, Liu P, Stacchiola DJ, Senanayake SD, White MG, Chen JGG. Hydrogenation of CO₂ to methanol: importance of metal-oxide and metal-carbide interfaces in the activation of CO₂. *ACS Catal*. 2015;5(11):6696–706.
27. Behrens M, Studt F, Kasatkin I, Kühl S, Hävecker M, Abild-Pedersen F, et al. The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. *Science*. 2012;336(6083):893–7.
28. Kuld S, Thorhauge M, Falsig H, Elkjaer CF, Helveg S, Chorkendorff I, et al. Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science*. 2016;352(6288):969–74.
29. Duyar MS, Tsai C, Snider JL, Singh JA, Gallo A, Yoo JS, et al. Highly active molybdenum phosphide catalyst for methanol synthesis from CO and CO₂. *Angew Chem-Int Edit*. 2018;57(46):15045–50.
30. Lachowska M, Skrzypek J, Ga, Mn and Mg promoted copper/zinc/zirconia—catalysts for hydrogenation of carbon dioxide to methanol. *Stud Surf Sci Catal*. 2004;153:173–6.
31. Yang C, Ma Z, Zhao N, Wei W, Hu T, Sun Y. Methanol synthesis from CO₂-rich syngas over a ZrO₂ doped CuZnO catalyst. *Catal Today*. 2006;115(1-4):222–7.
32. Ghenciu AF. Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Curr Opin Solid State Mat Sci*. 2002;6(5):389–99.
33. Tanaka Y, Utaka T, Kikuchi R, Sasaki K, Eguchi K. CO removal from reformed fuel over Cu/ZnO/Al₂O₃ catalysts prepared by impregnation and coprecipitation methods. *Appl Catal A-Gen*. 2003;238(1):11–8.
34. Mignard D and Pritchard C. Processes for the synthesis of liquid fuels from CO₂ and marine energy. *Chem Eng Res Des*. 2006;84(9A):828–36.
35. Du C, Lu P, Tsubaki N. Efficient and new production methods of chemicals and liquid fuels by carbon monoxide hydrogenation. *ACS Omega*. 2020;5(1):49–56.
36. Stelmachowski M, Nowicki L. Fuel from the synthesis gas—the role of process engineering. *Appl Energy*. 2003;74(1):85–93.
37. Mohammadi M, Najafpour GD, Younesi H, Lahijani P, Uzir M H, Mohamed A R. Bioconversion of synthesis gas to second generation biofuels: A review. *Renew Sust Energ Rev*. 2011;15(9):4255–73.
38. van de Loosdrecht J, Niemantsverdriet J. In R. Schlogl editor. Synthesis gas to hydrogen, methanol, and synthetic fuels, Chemical energy storage. Walter de Gruyter, Duitsland; 2012. p. 443–58.
39. Fabien D, Snoussi Y, Itabaiana I, Wojcieszak R. The use of CO₂ in the production of bioplastics for an even greener chemistry. *Sustainability*. 2021;13(20). <https://doi.org/10.3390/su132011278>
40. Maity SK. Opportunities, recent trends and challenges of integrated biorefinery: part I. *Renew Sust Energ Rev*. 2015;43:1427–45.

41. Quesada J, Arreola-Sánchez R, Faba L, Díaz E, Rentería-Tapia VM, Ordóñez S. Effect of Au nanoparticles on the activity of TiO₂ for ethanol upgrading reactions. *Appl Catal A-Gen*. 2018;551:23–33.
42. Steinbach D, Kruse A, Sauer J. Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production—a review. *Biomass Convers Biorefinery*. 2017;7(2):247–74.
43. Wei W, Sun YH, Wen X, Sun NN. Opportunities and challenges of carbon dioxide utilization as a resource. *Chem Ind Eng Prog*. 2011;30(1):216–24.
44. Zhang Z, Zhou M, Sun J, Fang X. Carboxylative utilization of carbon dioxide. *Chem Ind Eng Prog*. 2019;38(1):236–50.
45. Correa A and Martín R. Metal-catalyzed carboxylation of organometallic reagents with carbon dioxide. *Angew Chem-Int Edit*. 2009;48(34):6201–4.
46. Cassar L, Chiusoli G, Guerrieri F. Synthesis of carboxylic acids and esters by carbonylation reactions at atmospheric pressure using transition metal catalysts. *Synthesis*. 1973;1973(09):509–23.
47. Souma Y, Tsumori N, Willner H, Xu Q, Mori H, Morisaki Y. Carbonylation of hydrocarbons and alcohols by cationic metal carbonyl catalysts. *J Mol Catal A-Chem*. 2002;189(1):67–77.
48. Yan S-S, Fu Q, Liao L-L, Sun G-Q, Ye J-H, Gong L, *et al*. Transition metal-catalyzed carboxylation of unsaturated substrates with CO₂. *Coord Chem Rev*. 2018;374:439–63.
49. Zhang Land Hou Z. Transition metal promoted carboxylation of unsaturated substrates with carbon dioxide. *Curr Opin Green Sustain Chem*. 2017;3:17–21.
50. Saini S, Prajapati PK, Jain SL. Transition metal-catalyzed carboxylation of olefins with carbon dioxide: a comprehensive review. *Catal Rev-Sci Eng*. 2020;64(3):631–637. <https://doi.org/10.1080/01614940.2020.1831757>.
51. Ohishi T, Nishiura M, Hou Z. Carboxylation of organoboron esters catalyzed by N-heterocyclic carbene copper(I) complexes. *Angew Chem Int Edit*. 2008;47(31):5792–5.
52. Saito S, Nakagawa S, Koizumi T, Hirayama K, Yamamoto Y. Nickel-mediated regio- and chemoselective carboxylation of alkynes in the presence of carbon dioxide. *J Org Chem*. 1999;64(11):3975–8.
53. Aoki M, Kaneko M, Izumi S, Ukai K, Iwasawa N. Bidentate amidine ligands for nickel(0)-mediated coupling of carbon dioxide with unsaturated hydrocarbons. *Chem Commun*. 2004;(22):2568–9. <https://doi.org/10.1039/B411802B>
54. Zhang X, Zhang WZ, Shi LL, Guo CX, Zhang LL, Lu XB. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem Commun*. 2012;48(50):6292–4.
55. Kuge K, Luo Y, Fujita Y, Mori Y, Onodera G, Kimura M. Copper-catalyzed stereodefined construction of acrylic acid derivatives from terminal alkynes via CO₂ insertion. *Org Lett*. 2017;19(4):854–7.
56. Kolbe H. Ueber synthese der salicylsäure. *Ann Chem Pharm*. 1860;113(1):125–7.
57. Schmitt R. Beitrag zur kenntniss der kolbe'schen salicylsäure synthese. *J für Praktische Chemie*. 1885;31(1):397–411.
58. Hoberg H, Schaefer D. Nickel(0)-induzierte c-c-verknüpfung zwischen alkenen und kohlendioxid. *J Organomet Chem*. 1982;236(1):C28–30.
59. Yu B, Diao Z-F, Guo C-X, He L-N. Carboxylation of olefins/alkynes with CO₂ to industrially relevant acrylic acid derivatives. *J CO₂ Util*. 2013;1:60–68.
60. Lari GM, Pastore G, Haus M, Ding Y, Papadokonstantakis S, Mondelli C, *et al*. Environmental and economical perspectives of a glycerol biorefinery. *Energy Environ Sci*. 2018;11(5):1012–29.
61. Hoberg H, Jenni K, Angermund K, Krüger C. CC-Linkages of ethene with CO₂ on an iron(0) complex—synthesis and crystal structure analysis of [(PET₃)₂Fe(C₂H₄)₂]. *Angew Chem-Int Edit*. 1987;26(2):153–5.
62. Graham DC, Mitchell C, Bruce MI, Metha GF, Bowie JH, Buntine M A. Production of acrylic acid through nickel-mediated coupling of ethylene and carbon dioxide—a DFT study. *Organometallics*. 2007;26(27):6784–92.
63. Hoberg H, Schaefer D. Sorbinsäure aus piperylen und CO₂ durch cC-Verknüpfung an nickel(0). *J Organomet Chem*. 1983;255(1):C15–7.
64. Alvarez R, Carmona E, Cole-Hamilton DJ, Galindo A, Gutierrez-Puebla E, Monge A, *et al*. Formation of acrylic acid derivatives from the reaction of carbon dioxide with ethylene complexes of molybdenum and tungsten. *J Am Chem Soc*. 1985;107(19):5529–31.
65. Alvarez R, Carmona E, Galindo A, Gutierrez E, Marin JM, Monge A, *et al*. Formation of carboxylate complexes from the reactions of carbon dioxide with ethylene complexes of molybdenum and tungsten. X-ray and neutron diffraction studies. *Organometallics*. 1989;8(10):2430–9.
66. Galindo A, Pastor A, Perez PJ, Carmona E. Bis (ethylene) complexes of molybdenum and tungsten and their reactivity toward carbon dioxide. New examples of acrylate formation by coupling of ethylene and carbon dioxide. *Organometallics*. 1993;12(11):4443–51.
67. Fischer R, Langer J, Malassa A, Walther D, Görls H, Vaughan G. A key step in the formation of acrylic acid from CO₂ and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex. *Chem Commun*. 2006;23:2510–2. <https://doi.org/10.1039/B603540J>
68. Aresta M, Pastore C, Giannoccaro P, Kovács G, Dibeneditto A, Pápai I. Evidence for spontaneous release of acrylates from a transition-metal complex upon coupling ethene or propene with a carboxylic moiety or CO₂. *Chem-Eur J*. 2007;13(32):9028–34.
69. Bruckmeier C, Lehenmeier M W, Reichardt R, Vagin S, Rieger B. Formation of methyl acrylate from CO₂ and ethylene via methylation of nickelalactones. *Organometallics*. 2010;29(10):2199–202.
70. Lejkowski ML, Lindner R, Kageyama T, Bódizs GÉ, Plessow PN, Müller IB, *et al*. The first catalytic synthesis of an acrylate from CO₂ and an alkene—a rational approach. *Chem-Eur J*. 2012;18(44):14017–25.
71. Huguet N, Jevtovikj I, Gordillo A, Lejkowski ML, Lindner R, Bru M, *et al*. Nickel-catalyzed direct carboxylation of olefins with CO₂: one-pot synthesis of α,β -unsaturated carboxylic acid salts. *Chem-Eur J*. 2014;20(51):16858–62.
72. Hendriksen C, Pidko EA, Yang G, Schäffner B, Vogt D. Catalytic formation of acrylate from carbon dioxide and ethene. *Chem-Eur J*. 2014;20(38):12037–40.
73. Hollering M, Dutta B, Kühn FE. Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates. *Coord Chem Rev*. 2016;309:51–67.

74. Burkart MD, Hazari N, Tway CL, Zeitler EL. Opportunities and challenges for catalysis in carbon dioxide utilization. *ACS Catal.* 2019;9(9):7937–56.
75. Wang D, Zhong S. Study on CuPMo/TiO₂ catalyst for direct synthesis of methacrylic acid from propylene and carbon dioxide. *Chin J Catal.* 2003;24(9):705–10.
76. Wang R, Yang F. A catalytic and application for carbon dioxide into methacrylic acid. China patent 200910255801. 2009.
77. Rajagopalan P, Kühnle M, Polyakov M, Müller K, Arlt W, Kruse D, et al. Methacrylic acid by carboxylation of propene with CO₂ over POM catalysts — reality or wishful thinking? *Catal Commun.* 2014;48:19–23.
78. Ren Q, Wu N, Cai Y, Fang J. DFT study of the mechanisms of iron-catalyzed regioselective synthesis of α -aryl carboxylic acids from styrene derivatives and CO₂. *Organometallics.* 2016;35(23):3932–8.
79. Shao P, Wang S, Chen C, Xi C. Cp₂TiCl₂-Catalyzed regioselective hydrocarboxylation of alkenes with CO₂. *Org Lett.* 2016;18(9):2050–3.
80. Correa A, Martín R. Palladium-catalyzed direct carboxylation of aryl bromides with carbon dioxide. *J Am Chem Soc.* 2009;131(44):15974–5.
81. Tran-Vu H, Daugulis O. Copper-catalyzed carboxylation of aryl iodides with carbon dioxide. *ACS Catal.* 2013;3(10):2417–20.
82. Fujihara T, Nogi K, Xu T, Terao J, Tsuji Y. Nickel-catalyzed carboxylation of aryl and vinyl chlorides employing carbon dioxide. *J Am Chem Soc.* 2012;134(22):9106–9.
83. Tanaka S, Watanabe K, Tanaka Y, Hattori T. EtAlCl₂/2,6-disubstituted pyridine-mediated carboxylation of alkenes with carbon dioxide. *Org Lett.* 2016;18(11):2576–9.
84. Engel RV, Alsaiahi R, Nowicka E, Pattisson S, Miedziak PJ, Kondrat SA, et al. Oxidative carboxylation of 1-decene to 1,2-decylene carbonate. *Top Catal.* 2018;61(5):509–18.
85. Williams CM, Johnson JB, Rovis T. Nickel-catalyzed reductive carboxylation of styrenes using CO₂. *J Am Chem Soc.* 2008;130(45):14936–7.
86. Aresta M, Quaranta E, Tommasi I. The role of metal centres in reduction and carboxylation reactions utilizing carbon dioxide. *New J Chem.* 1994;18(1):133–142.
87. Mason MG. A study of the interaction of carbon dioxide and carbon disulfide with low valent transition metal complexes. Northwestern University; 1982.
88. Takaya J, Iwasawa N. Hydrocarboxylation of allenes with CO₂ catalyzed by silyl pincer-type palladium complex. *J Am Chem Soc.* 2008;130(46):15254–5.
89. Albano P, Aresta M. Some catalytic properties of Rh(diphos)(η -BPh₄). *J Organomet Chem.* 1980;190(3):243–6.
90. Döhring A, Jolly PW. The palladium catalyzed reaction of carbon dioxide with allene. *Tetrahedron Lett.* 1980;21(32):3021–4.
91. Tsuda T, Morikawa S, Sumiya R, Saegusa T. Nickel(0)-catalyzed cycloaddition of diynes and carbon dioxide to give bicyclic α -pyrones. *J Org Chem.* 1988;53(14):3140–5.
92. Hoberg H. Carbon dioxide as a source of carbon. NATO ASI Series C. 1987;206:275.
93. Hoberg H, Schaefer D, Burkhart G, Krüger C, Romão MJ. Nickel(0)-induzierte C-C-verknüpfung zwischen kohlendioxid und alkenen sowie alkenen. *J Organomet Chem.* 1984;266(2):203–24.
94. Burkhart G, Hoberg H. Oxanickelacyclopentene derivatives from nickel(0), carbon dioxide, and alkynes. *Angew Chem-Int Edit.* 1982;21(1):76–76.
95. Hoberg H, Schaefer D. Modellkomplexe des nickels für die [2+2+2]-cycloaddition von alkenen mit kohlendioxid. *J Organomet Chem.* 1982;238(4):383–7.
96. Albano P, Aresta M. Some catalytic properties of Rh(diphos)(η -BPh₄). *J Organomet Chem.* 1980;190:243–6.
97. Polyzos A, O'Brien M, Petersen TP, Baxendale IR, Ley S V. The continuous-flow synthesis of carboxylic acids using CO₂ in a tube-in-tube gas permeable membrane reactor. *Angew Chem-Int Edit.* 2011;50(5):1190–3.
98. van Gool J J F, van den Broek S A M W, Ripken RM, Nieuwland PJ, Koch K, Rutjes FPJT. Highly controlled gas/liquid processes in a continuous lab-scale device. *Chem Eng Technol.* 2013;36(6):1042–6.
99. Nagaki A, Takahashi Y, Yoshida J-i. Extremely fast gas/liquid reactions in flow microreactors: carboxylation of short-lived organolithiums. *Chem-Eur J.* 2014;20(26):7931–4.
100. Pieber B, Glasnov T, Kappe CO. Flash carboxylation: fast lithiation-carboxylation sequence at room temperature in continuous flow. *RSC Adv.* 2014;4(26):13430–3.
101. Seo H, Nguyen LV, Jamison TF. Using carbon dioxide as a building block in continuous flow synthesis. *Adv Synth Catal.* 2019;361(2):247–64.
102. Eerhart AJJE, Faaij APC, Patel MK. Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy Environ Sci.* 2012;5(4):6407–22.
103. Araujo CF, Nolasco MM, Ribeiro-Claro PJA, Rudić S, Silvestre AJD, Vaz PD, et al. Inside PEF: chain conformation and dynamics in crystalline and amorphous domains. *Macromolecules.* 2018;51(9):3515–26.
104. Avantium, Avantium annual report. <https://www.avantium.com>. Accessed 23 May 2022.
105. Pandey S, Dumont M-J, Orsat V, Rodrigue D. Biobased 2,5-furandicarboxylic acid (FDCA) and its emerging copolyesters' properties for packaging applications. *Eur Polym J.* 2021;160:110778.
106. Casanova O, Iborra S, Corma A. Biomass into chemicals: aerobic oxidation of 5-hydroxymethyl-2-furfural into 2,5-furandicarboxylic acid with gold nanoparticle catalysts. *ChemSusChem.* 2009;2(12):1138–44.
107. Miao Z, Zhang Y, Pan X, Wu T, Zhang B, Li J, et al. Superior catalytic performance of Ce1-xBixO2- δ solid solution and Au/Ce1-xBixO2- δ for 5-hydroxymethylfurfural conversion in alkaline aqueous solution. *Catal Sci Technol.* 2015;5(2):1314–22.
108. Davis SE, Houk LR, Tamargo EC, Datsy AK, Davis RJ. Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts. *Catal Today.* 2011;160(1):55–60.
109. Wojcieszak R, Itabaiana I. Engineering the future: perspectives in the 2,5-furandicarboxylic acid synthesis. *Catal Today.* 2020;354:211–7.
110. Faba L, Díaz E, Ordóñez S. From biomass to second generation biofuels. *Madera Bosques.* 2014;20(3):11–24.
111. Pan T, Deng J, Xu Q, Zuo Y, Guo Q-X, Fu Y. Catalytic conversion of furfural into a 2,5-furandicarboxylic acid-based polyester with total carbon utilization. *ChemSusChem.* 2013;6(1):47–50.

112. Patton J W, Son M O. The synthesis of naphthalene-2, 3-dicarboxylic acid by the henkel process. *J Org Chem* 1965;30(8):2869–70.
113. Furuyama S. An investigation of the mechanism of the henkel reaction by deuterium and carbon-14 isotope techniques. *Bull Chem Soc Jpn.* 1967;40(5):1212–7.
114. Ogata Y, Nakajima K. Kinetics and mechanism of the rearrangement of potassium phthalate. *Tetrahedron.* 1965;21(9):2393–400.
115. Ratusky J. Transcarboxylation reactions of salts of organic acids .14. Reactions of salts of deuterated benzene-carboxylic acids. *J Label Compd Radiopharm.* 1970;6(2):124.
116. Fujishiro K, Mitamura S. The zinc(II)-catalyzed henkel reaction of dipotassium 1,8-naphthalenedicarboxylate in a dispersion medium. *Bull Chem Soc Jpn.* 1989;62(3):786–90.
117. Thiyagarajan S, Pukin A, Van Haveren J, Lutz M, Van Es D S. Concurrent formation of furan-2,5- and furan-2,4-dicarboxylic acid: unexpected aspects of the Henkel reaction. *RSC Adv.* 2013;3(36):15678–86.
118. Zhang S, Lan J, Chen Z, Yin G, Li G. Catalytic synthesis of 2,5-furandicarboxylic acid from furoic acid: transformation from C5 Platform to C6 derivatives in biomass utilizations. *ACS Sustain Chem Eng.* 2017;5(10):9360–9.
119. Olah GA, Török B, Joschek JP, Bucsi I, Esteves PM, Rasul G, *et al.* Efficient chemoselective carboxylation of aromatics to arylcarboxylic acids with a superelectrophilically activated carbon dioxide–Al₂Cl₆/Al system. *J Am Chem Soc.* 2002;124(38):11379–91.
120. Banerjee A, Dick GR, Yoshino T, Kanan MW. Carbon dioxide utilization via carbonate-promoted C–H carboxylation. *Nature.* 2016;531(7593):215–9.
121. Kolbe H, Lautemann E. Ueber die constitution und basicität der salicylsäure. *Ann Chem Pharm.* 1860;115(2):157–206.
122. Gibson JA, Kynaston W, Lindsey AS. The infrared spectra of some pyridones and quinolones and their behaviour in the Kolbe–Schmitt reaction. *J Chem Soc.* 1955;(0):4340–4. <https://doi.org/10.1039/JR9550004340>
123. Dingyi Y, Yugen Z. The direct carboxylation of terminal alkynes with carbon dioxide. *Green Chem.* 2011;13(5):1275–9.
124. Kudo K, Ikoma F, Mori S, Sugita N. Synthesis of glutaconic acid salt from cesium 3-butenate with carbon dioxide. *J Jpn Pet Inst.* 1995;38(1):48–51.
125. Vechorkin O, Hirt N, Hu X. Carbon dioxide as the C1 source for direct C–H functionalization of aromatic heterocycles. *Org Lett.* 2010;12(15):3567–9.
126. Nocito F, Ditaranto N, Dibenedetto A. Valorization of C5 polyols by direct carboxylation to FDCA: synthesis and characterization of a key intermediate and role of carbon dioxide. *J CO₂ Util.* 2019;32:170–7.
127. Drault F, Snoussi Y, Paul S, Itabaiana I Jr, Wojcieszak R. Recent advances in carboxylation of furoic acid into 2,5-furandicarboxylic acid: pathways towards bio-based polymers. *ChemSusChem.* 2020;13(19): 5164–72.
128. Dick GR, Frankhouser AD, Banerjee A, Kanan MW. A scalable carboxylation route to furan-2,5-dicarboxylic acid. *Green Chem.* 2017;19(13):2966–72.
129. Zhou H, Xu H, Wang X, Liu Y. Convergent production of 2,5-furandicarboxylic acid from biomass and CO₂. *Green Chem.* 2019;21(11):2923–7.
130. Wang Y-G, Guo C-Y, Shen J, Sun Y-Q, Niu Y-X, Li P, *et al.* A sustainable and green route to furan-2,5-dicarboxylic acid by direct carboxylation of 2-furoic acid and CO₂. *J CO₂ Util.* 2021;48:101524.
131. Cajnko MM, Novak U, Grilc M, Likozar B. Enzymatic conversion reactions of 5-hydroxymethylfurfural (HMF) to bio-based 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA) with air: mechanisms, pathways and synthesis selectivity. *Biotechnol Biofuels.* 2020;13(1):66.
132. Lupa B, Lyon D, Gibbs MD, Reeves RA, Wiegel J. Distribution of genes encoding the microbial non-oxidative reversible hydroxyarylic acid decarboxylases/phenol carboxylases. *Genomics.* 2005;86(3):342–51.
133. Wierckx N, Koopman F, Bandounas L, De Winde JH, Ruijsenaars HJ. Isolation and characterization of *Cupriavidus basilensis* HMF14 for biological removal of inhibitors from lignocellulosic hydrolysate. *Microb Biotechnol.* 2010;3(3):336–43.
134. Payne KAP, Marshall SA, Fisher K, Cliff MJ, Cannas DM, Yan C, *et al.* Enzymatic carboxylation of 2-furoic acid yields 2,5-furandicarboxylic acid (FDCA). *ACS Catal.* 2019;9(4):2854–65.
135. Kawanabe K, Aono R, Kino K. 2,5-Furandicarboxylic acid production from furfural by sequential biocatalytic reactions. *J Biosci Bioeng.* 2021;132(1):18–24.

