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Editorial

Con la llegada del verano, nos complace presentaros el número 76 del Boletín del Grupo Español del Carbón.

Este número viene marcado por un relevo significativo en el equipo editorial. Tras varios años de dedicación, Covadonga Pevida deja su puesto como Editora Jefa del Boletín. Desde aquí queremos agradecerle profundamente su dedicación y su impulso constante para mantener este Boletín como un espacio de referencia para nuestra comunidad investigadora. En este mismo número, tenemos el placer de entrevistarla, repasando su trayectoria y su visión sobre los retos actuales a los que nos enfrentamos. Cova será sustituida por Juana María (Nani) Rosas (Profesora Titular de la Universidad de Málaga) como Editora Jefa, y se incorpora también al equipo editorial María Victoria García Rocha (Científica Titular del INCAR-CSIC). Gracias a ambas por aceptar este compromiso y por aportar su entusiasmo al boletín del Grupo Español del Carbón.

Continuamos con un artículo de nuestros colegas (y amigos) portugueses del Laboratory of Catalysis and Materials (LCM) de la Universidad de Oporto, en el que se ofrece una visión detallada sobre el desarrollo de materiales de carbono nanostructurados y sus aplicaciones en catálisis ambiental y tecnologías energéticas. El LCM, liderado por el Profesor Fernando Pereira, ha logrado avances significativos en la funcionalización de nanotubos de carbono y otros materiales grafénicos, mejorando sus propiedades catalíticas y su eficiencia en procesos de oxidación avanzada y reducción de contaminantes. Además, el artículo aborda su potencial en aplicaciones catalíticas en procesos de producción de energía, combustibles y productos químicos, demostrando la versatilidad y el impacto de la investigación en materiales de carbono.

Seguimos con una contribución de nuestros compañeros de la Universidad de Málaga sobre el uso de catalizadores basados en fibras de carbono para la obtención de metanol mediante la hidrogenación de CO_2.

En este número contamos con cinco reseñas de Tesis Doctorales: Óscar E. Medina (Universidad de Granada), Uziel Ortiz-Ramos (Universidad de Granada y Universidad Autónoma de San Luis Potosí), Cristian Daniel Jaimes-Paez (Universidad de Alicante), Gabriel Alemany Molina (Universidad de Alicante) y Mario García-Rodríguez (Universidad de Alicante).

También se incluye una reseña del proyecto europeo Bio-MeGaFuel, en el que participa el Instituto de Carboquímica (ICB-CSIC), centrado en la producción de biometanol mediante gasificación con transportadores sólidos de oxígeno y reactores de membrana.

Cerramos este número del Boletín con dos eventos organizados por miembros del GEC: el Curso Extraordinario de Verano de la Universidad de Zaragoza “Desafíos y Soluciones para la Transición Energética” organizado por el Instituto de Carboquímica (ICB-CSIC) que tendrá lugar del 30 de junio al 2 de julio en la localidad oscense de Jaca. Y la XVII Reunión del Grupo Español del Carbón, que se celebrará del 19 al 22 de octubre de 2025 en Zaragoza y en la que esperamos poder contar con vosotros. Será una excelente oportunidad para compartir avances, establecer nuevas colaboraciones y disfrutar de la hospitalidad maña. Toda la información está disponible en la web oficial del evento: www.gecarbon2025.org.

¡Nos vemos en Zaragoza!

José Luis Pinilla Ibarz
Juana María Rosas

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Entrevistamos a ...

En este número del Boletín tenemos el placer de entrevistar a Covadonga Pevida, quien ha ejercido como Editora Jefa de esta publicación hasta el pasado mes de enero. Cova es Investigadora Científica (pendiente de toma de posesión de su plaza como Profesora de Investigación) en el Instituto de Ciencia y Tecnología del Carbono (INCAR-CSIC), donde lidera el Grupo de Procesos Energéticos y Reducción de Emisiones (PrEM). Además, es Gestora del área científica de Energía y Transporte (EYT), subárea de Energía (ENE), en la Agencia Estatal de Investigación (AEI), y Vicepresidenta del Grupo Español del Carbón. Su investigación se centra en el desarrollo de tecnologías de utilización de biomasa, concretamente, la captura de CO_2 mediante adsorción y la producción de hidrógeno renovable.

Cova, recientemente has concluido tu etapa como editora jefa del Boletín del Grupo Español del Carbón. ¿Qué ha significado para ti esta labor? ¿Hay alguna acción que te hubiera gustado implementar y que se quedó en el tintero por falta de tiempo?

Ha sido una etapa muy enriquecedora, en gran medida gracias a la buena sintonía que hay entre los miembros del equipo editorial del Boletín. Hemos implementado nuevas secciones e incluso premios, siempre con la idea de adaptarnos a las necesidades de los distintos grupos de investigación del GEC y a que, en la medida de lo posible, el Boletín sea un canal de comunicación de interés para toda la comunidad “carbón”. En cuanto a acciones pendientes, quizás las redes sociales todavía las tenemos poco trabajadas y puede ser uno de los aspectos a reforzar. En cualquier caso, el equipo del Boletín va a seguir trabajando en este sentido y estoy segura que lograrán implementar muchas mejoras.

Tienes una carrera muy destacada en el ámbito de la energía y el medio ambiente. ¿Qué te motivó a especializarte en este campo?

Debo reconocer que durante mis estudios de Ingeniería Química no me había interesado demasiado por el ámbito de la Energía, algo más por el Medio Ambiente. Tampoco había desarrollado ninguna vocación investigadora aunque sí, mucha curiosidad e inquietud por seguir aprendiendo. Eso fue lo que me hizo interesarme por un anuncio de una beca de tesis doctoral para el departamento de Tecnología del INCAR. Y desde entonces, ha sido un camino marcado por trabajo y esfuerzo constantes con grandes satisfacciones y también, decepciones, para que nos vamos a engañar. En cualquier caso, el ámbito de la Energía y el Medio Ambiente siguen siendo temáticas de máxima actualidad donde todavía se requiere mucha investigación y desarrollo y donde espero poder seguir contribuyendo desde mi Grupo de investigación.

¿Cómo ha evolucionado tu trayectoria desde tus inicios hasta tu actual posición como responsable de un grupo de investigación? ¿Cuáles son actualmente las principales líneas de investigación del grupo?

Desde el punto de vista de la investigación, mis inicios en la investigación se desarrollaron en tecnologías asociadas a la conversión limpia de carbón, en concreto, en la reducción de NOx. Más tarde, me introduje en el mundo de la captura de CO_2 mediante adsorción y poco a poco fue comenzando a cobrar relevancia la utilización de biomasa. Esta última línea se ha ido imponiendo en el tiempo y, actualmente, constituye el eje central de mi Grupo de investigación, PrEM, de INCAR-CSIC. Desde el punto de vista personal, también ha habido una evolución, desde la investigadora puramente idealista y vehemente en los años de tesis doctoral a una investigadora más práctica y objetiva, o al menos, eso quiero creer.

En la actualidad mi Grupo está enfocado en la utilización de biomasa, tanto en aplicaciones energéticas como en la separación de gases mediante adsorción. Estamos desarrollando varios proyectos con el objetivo de poner en valor el potencial de la biomasa residual para la producción de hidrógeno renovable, la generación de calor/electricidad, o la purificación de corrientes gaseosas.

En los últimos años hemos visto un rápido crecimiento de la divulgación del conocimiento científico a través de diferentes medios y actividades, entre las que se encuentran las redes sociales. ¿Cuál es tu valoración al respecto?

Las redes sociales son una plataforma para hacer divulgación con un impacto extraordinario tanto por la inmediatez como por el alcance que pueden tener. Son muchos los estudios que así lo confirman y cada vez más Universidades y organismos de investigación incentivan a sus investigadores para que mantengan activos y actualizados sus perfiles en redes sociales.

Como Gestora del área de Energía en la AEI, ¿cuáles son los principales retos y oportunidades que identificas en la financiación de la investigación energética en España?

Desde que me incorporé como colaboradora en el área de Energía hemos visto un incremento exponencial tanto en el número de convocatorias, como de propuestas a evaluar. Esto ha estado motivado en gran parte por la financiación europea asociada a fondos del plan de recuperación y resiliencia. En cuanto a las temáticas, hemos visto una clara explosión de proyectos en el área de las energías renovables, con enfoques multidisciplinares y también en al ámbito de los biocombustibles y el almacenamiento de energía.

Y en relación con esto último, ¿cómo crees que se posicionan las líneas de investigación que desarrollan los miembros del Grupo Español del Carbón?

Los investigadores del GEC se han caracterizado por su buen posicionamiento en las distintas áreas de concurrencia dentro de la Agencia, tanto en convocatorias de proyectos como de recursos humanos. Las líneas de investigación que se están desarrollando en el seno del GEC son de máxima actualidad por lo que es previsible que esta posición destacada se mantenga en el tiempo. En general, creo que el GEC goza de una buena “salud” en cuanto a la oportunidad, calidad y novedad de las líneas de investigación que desarrollan sus miembros.

En los últimos años hemos observado una creciente dificultad para incorporar personal investigador en formación a los proyectos. Algunos investigadores lo atribuyen a los bajos salarios en comparación con la empresa privada y a la menor estabilidad laboral. Como IP de numerosos proyectos, ¿cuál es tu experiencia al respecto? ¿Qué medidas crees que podrían ayudar a revertir esta situación?

La incorporación de personal investigador en formación es, actualmente, una de las principales barreras a las que nos estamos enfrentando los grupos de investigación. En mi opinión, los contratos que ofertamos son, globalmente, remunerados justamente, máxime si se valoran en términos relativos a la responsabilidad o la disponibilidad, donde el sector industrial es indudablemente más exigente.

Por otro lado, se observa un salto generacional importante en cuanto a las inquietudes de los jóvenes recién graduados/máster y su percepción, en muchos casos negativa, respecto al compromiso de 3 o 4 años que supone una tesis doctoral.

Creo que necesitamos masa crítica para seguir manteniendo una estructura estable de la I+D en España. Revertir la situación actual no va a ser inmediato, pero desde luego aumentar la inversión es uno de los factores clave y, bajo mi punto de vista, desligar las ayudas predoctorales de una nota media de expediente académico como primer criterio de valoración sería otro aspecto a considerar.

¿Qué consejo darías a los jóvenes investigadores que se inician en el campo de la energía y el medio ambiente?

El campo de la Energía y el Medio Ambiente se posiciona como uno de los más prometedores y con más oportunidades laborales en los próximos veinte años. Mi consejo es simple: trabajo y esfuerzo constantes. La investigación es una carrera de fondo, no hay que precipitarse ni tampoco dormirse, pero sí estar concentrado en el objetivo que se persigue y no en buscar atajos que, después de muchos años en investigación lo que he visto es que suelen conducir al fracaso.

Laboratory of catalysis and materials

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LSRE-LCM, Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, is an R&D Unit leader in Chemical Engineering research, focusing on separation, reaction engineering, environmental technologies, catalysis, and materials science. LSRE-LCM's main headquarters is at the Department of Chemical Engineering of FEUP - Faculdade de Engenharia da Universidade do Porto, Porto - Portugal, with an external branch - the IPL branch at Instituto Politécnico de Leiria. The LSRE-LCM team consists of nearly,160 persons, including permanent professors and researchers, post-doctoral researchers, PhD students, project researchers, administrative staff, and visiting researchers.

The designation of LSRE-LCM R&D Unit was adopted in 2013 from the merger of the two research units: LSRE - Laboratory of Separation and Reaction Engineering, led by Professor Alírio Rodrigues; and the LCM - Laboratory of Catalysis and Materials, led by Professor José Luís Figueiredo, that started the partnership in 2002 and in 2004 awarded the status of Associated Laboratory LSRE-LCM.

More recently, in 2021, the LSRE-LCM R&D Unit in articulation with two more R&D Units based at the Department of Chemical Engineering at FEUP (LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy; and, CEFT - Centro de Estudos de de Fenómenos de Transporte, stands for Transport Phenomena Research Center in Portuguese) created the Associate Laboratory in Chemical Engineering – ALiCE, the largest Portuguese Associate Laboratory in the area of Chemical Engineering, with more than 450 researchers, 40 % of which with PhD, who over the past 20 years have contributed to consolidate a relevant international position in the Chemical Engineering field at the University of Porto (top-1, 20 and 100 at national, European and World level, respectively, according to well-known and different rankings).

LSRE-LCM R&D Unit is organised into five research groups (RG): RG1 - Cyclic Adsorption/Reaction Processes; RG2 - Product Engineering; RG3 - Environmental Engineering; RG4 - Carbon Materials, Catalysis and Environmental Assessment; RG5 - Photo-Electro-Chemistry and Nature-Inspired Systems. LCM includes mainly RG4 and RG5. Both groups work in the intersection of the fields of Catalysis and Carbon (as LCM – Laboratory of Catalysis and Materials in the past), extended to adjacent scientific domains that include three major research areas: Nanostructured Carbon Materials, Environmental Catalysis and Technologies, Energy, Fuels and Chemicals.

Nanostructured Carbon Materials

Nanostructured Carbon Materials is a transversal area of research in the LCM working on the development of carbon materials (nanotubes/nanofibers, graphene derivatives, graphitic carbon nitride, carbon dots, carbon gels, ordered mesoporous carbons, graphene derived, among others) with tuned textural and surface chemical properties. The tuning of textural properties and surface chemistry of carbon materials is a major research area of LCM, allowing these functionalized materials to be used as catalysts, adsorbents, material in membranes, supercapacitors, sensors, functional textiles, and biomedical devices.

The team has a lengthy background in the modification of textural properties and surface chemistry of carbon materials [1-3]. Functional groups containing O, N, S, B or P (Figure 1) can be incorporated on the surface of carbon materials [4] either by in-situ doping during synthesis [5, 6], or by post-doping in the presence of heteroatom-precursors [7-9]. Current developments focus on solvent-free methodologies using ball-milling mechanical treatments and thermal treatments to incorporate different heteroatoms (N, S, P, and B) [9-13]. The LCM is actively involved in synthesising biomass-derived carbon materials [13,14] and producing carbon nanotubes from simulated and solid plastic waste precursors [15].

José Luís Figueiredo (former LCM leader) and Fernando Pereira (LCM leader) co-authored the development of a reliable method for quantification and identification of oxygenated functionalities on carbons, providing a major asset to correlate the catalytic properties of the carbon materials with their surface chemistry. The technique was in the paper Modification of the surface chemistry of activated carbons [16], in Carbon journal in 1999. At the time, the article presented a novel method for quantitatively analysing the oxygenated groups on the surface of carbon materials released under heating during temperature-programmed desorption (TPD). The work has been used around the world by several researchers working on the subject (~2800 citations -Scopus, Feb.25) and, more recently, the basic principles required to perform an adequate analysis, allowing the correct assessment (qualitatively and quantitatively) of the oxygenated groups on the surface of carbon materials were revised and a set of “best practices” for the TPD analysis of carbon materials, in general, was established [17].

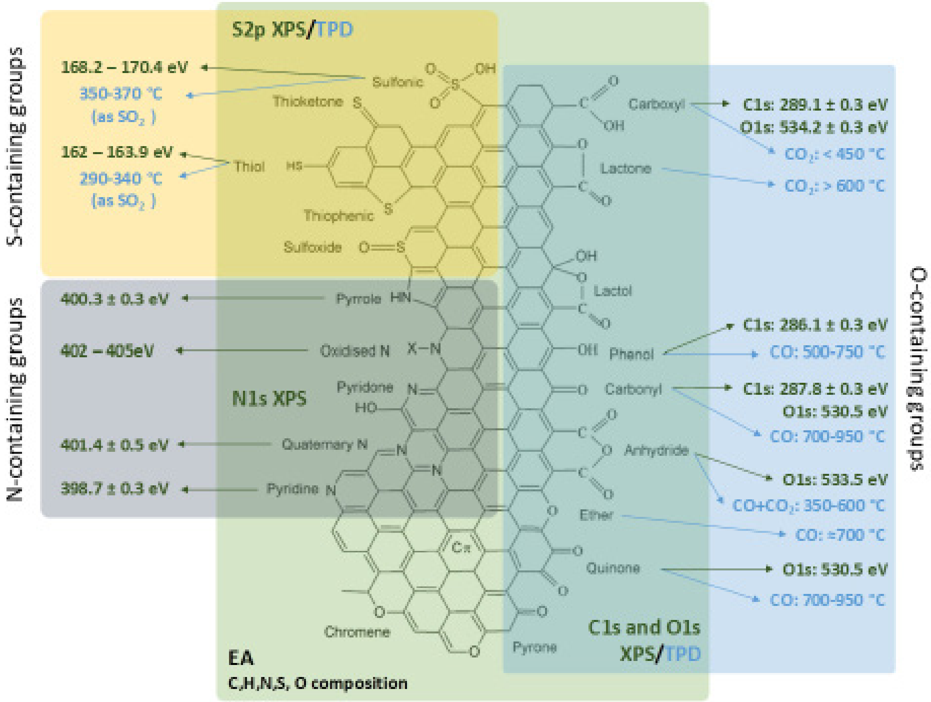


Figure 1. Oxygen, nitrogen and sulphur surface groups incorporated on carbon materials and techniques for their identification/quantification (reprinted from [33]).

Carbon materials can act as supports for several active and stable mono and bimetallic catalysts, incorporating different metal active centres on adequate carbon supports or hybrid materials [18, 19]. However, carbon materials can also function as catalysts on their own. Novel metal-free catalysts include acidic carbon xerogels/nanotubes for acid reactions like esterification of acetic acid [20], hydrolysis of cellulose and hemicelluloses, and the production of acetins via transesterification [21]. In addition, heteroatom-doped carbon nanotubes have been employed for the oxidation of organic compounds [12, 22].

Besides catalytic and adsorption applications, carbon materials have been investigated under the groups in the development of functional textiles. Photosensitive nanoparticles, led by titanium dioxide (TiO2) were investigated in cotton textile cleaning, replacing harsh industrial bleaching methods [23]. Graphitic carbon nitride, a metal-free photocatalyst, introduces eco-friendly self-cleaning and antimicrobial qualities through budget-friendly LED setups in textiles [24]. Innovative clothing designs achieving over 30 dB shielding effectiveness for electromagnetic interference were developed using carbon nanotubes, TiO_2, Fe_2O_3, and PEDOT:PSS [25]. Textiles coated with 70 wt.% Bi_2O_3 dispersed in a polymeric matrix surpassed heavy lead-based solutions in flexibility and efficacy for high-frequency radiation protection.

Environmental Catalysis and Technologies

The LCM has given special effort to design innovative solutions and methods for environmental protection technologies. Research is being carried out for water characterization, treatment, and desalination, as well as removing pollutants from gaseous and liquid effluents. The design of carbon-based catalysts for the oxidation of organic compounds in water by different advanced oxidation processes (AOPs) is a consolidated research area within the groups; materials are applied in catalytic ozonation [26-28], catalytic wet (air/peroxide) oxidation [22, 29, 30], persulphate activation [31], and photocatalysis [32-34].

For the reduction of inorganic compounds, the team has consolidated work on catalytic reduction of different oxyanions in water (such as NO_3-, BrO_3- and ClO_4-) [35-37], allowing them to be converted into less toxic species and avoiding the use of “trapping” technologies. Carbon materials [18, 38] and metal oxides [39] (such as TiO_2, Al_2O_3, ZrO_2, CeO, and ZnO, among others) were used as support for the active metal phase in an attempt to synthesize more stable and active catalysts for the reduction of inorganic ions. In this context, several combinations of noble/promoter metals, as well as their rearrangement on the surface of the catalyst (in alloy form or not), were studied to achieve efficient conversion and selectivity in the catalytic process. Different strategies were established to support mono [40] and bimetallic [18] catalysts in macrostructured monoliths, which were then applied for the continuous catalytic reduction of inorganic ions. Integrated technologies for oxidation and reduction of pollutants in water have been studied to improve the efficiency of water and wastewater treatment [41], resulting in a Provisional Patent Application PT 118885 (Figure 2). These methodologies were recently extended for the degradation of per- and polyfluoroalkyl substances (PFAS), also known as the Forever Chemicals [42].

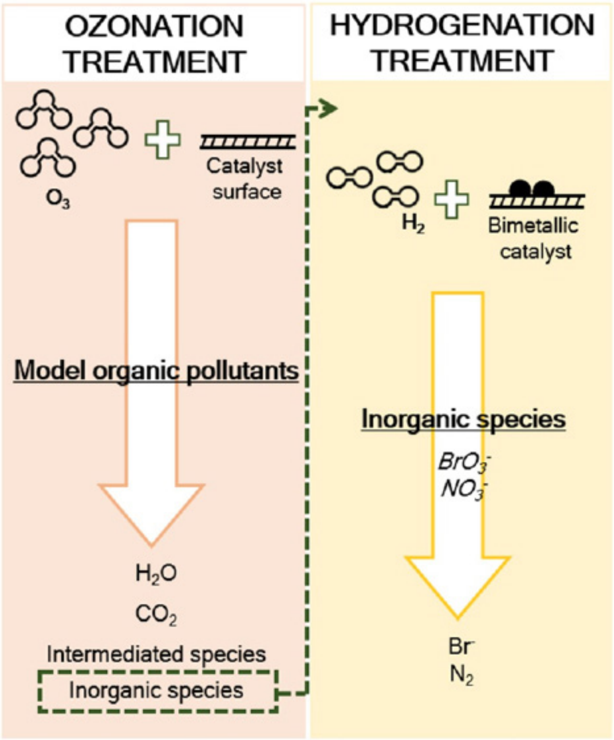


Figure 2

Concerning air pollution abatement, efficient metal oxide catalysts for the total oxidation of volatile organic compounds (VOCs) and carbon-based catalysts for NO reduction were developed. The team developed a cryptomelane-type manganese oxide synthesized by a novel solvent-free technique [22], and current research on VOCs abatement researcher is being made on the immobilization of powder catalysts on structured supports, like monoliths, to overcome the limitations of the use of powder catalysts [43]. In the selective catalytic reduction of NOx with carbon (SCR-C), different carbon materials (activated carbon, carbon nanotubes and carbon xerogel) functionalized with controlled physicochemical properties (texture and surface chemistry), as well as structured catalysts, have been investigated [44].

In the field of water characterization, relevant advances were made in the environmental monitoring and risk assessment with several solid-phase extraction and liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) methods being developed and optimized for the determination of more than 50 organic micropollutants in surface and wastewater matrices [45]. A new research topic on enantioselective analytical tools was started associated with an ERC granted to Ana Rita Ribeiro [46].

The increasing abundance and dispersion of microplastic particles (MPPs) in the environment and a better understanding of the resulting impacts have also been the focus of the LCM work, with some studies being carried out on the aging of MPPs under urban environment stressors and identifying the subsequent changes in their chemical structure [47]. Additionally, decontamination processes targeting microplastics and other water pollutants, such as adsorption, biocatalysis, and bioremediation, are being carried out [48].

The team employs comparative analysis of advanced wastewater treatment processes [49], identifying areas for improvement and assessing the environmental impacts associated with various oxidants used in decontamination procedures by the Life Cycle Assessment (LCA) methodology. Moreover, the LCA studies have been extended to the environmental performance of other technologies and products, such as packaging.

Energy, Fuels and Chemicals

This thematic area is focused on the development of new catalysts and technologies for the sustainable production of energy, fuels and chemicals, including photocatalysts for solar fuels and chemicals; electrocatalysts and carbon electrodes for energy conversion and storage; nanostructured catalysts for biomass conversion; and CO_2 utilization.

Photocatalytic technologies, including novel catalysts and innovative photoreactors, are being investigated: to produce renewable and sustainable hydrogen by visible-driven water splitting [50]; to the selective synthesis of aromatic aldehydes and imines [51]; to ammonia synthesis from water and nitrogen [52]; H_2O_2 production [53].

The team has been working on the continuous optimization of catalyst design, seeking effective yet less expensive electrochemical solutions for energy production and storage. From metal-free O-rich-carbon nanotubes [54, 55], to glucose-derived carbon materials [13], to their hybrids [56, 57], from cobalt and/or iron phthalocyanines [58-59] on CNTs, to the engineering of single atom Fe-N sites onto hollow carbon spheres [60] and carbon black [61], several materials have been deepen investigated in the oxygen reduction and evolution reactions with the support of the use of computational tools seeking for a better understanding of the processes/reactions involved.

Hierarchical carbons with different boron contents [62], glucose-derived carbons modified by introducing heteroatoms (O, P) and/or incorporating carbon nanotubes (CNTs) during the synthesis/ activation procedure demonstrated promising results as supercapacitors [9, 56, 63]. The use of low-cost biomass-based materials (such as cork-based activated carbons) from eco-sustainable supercapacitors has been investigated. Carbon-based materials for flexible supercapacitors and wearable electronic gadgets have appeared as an interesting application [64], with some work being conducted in the lab.

The catalytic valorisation of biomass wastes into valuable chemicals is a promising technology that can link traditional refineries and renewable sources. At LCM, various carbon-supported noble (Ru-W-CNTs [65]) and low-cost metal catalysts (Ni-W bimetallic catalysts supported on glucose/carbon nanotube hybrid carbons [66]) have been developed

The catalytic valorisation of biomass wastes into valuable chemicals is a promising technology that can link traditional refineries and renewable sources. At LCM, various carbon-supported noble (Ru-W-CNTs [65]) and low-cost metal catalysts (Ni-W bimetallic catalysts supported on glucose/carbon nanotube hybrid carbons [66]) have been developed that achieve notable yields of sorbitol and ethylene glycol from the direct catalytic valorization of agro-forestry and urban biomass residues (among the best obtained for the catalytic conversion of lignocellulosic biomass by an environmentally friendly process). The team is now unlocking the value of food waste (coffee grounds, orange and banana peels) as feedstock for sustainable production of ethylene glycol over low-cost Ni–W catalysts supported on glucose-derived carbons [67]. Still, in the field of biomass valorization, the team has worked in different tandem reactions using a green solvent (water) to obtain added-value products such as gluconic acid, sorbitol, xylitol, ethylene glycol, among others, using carbon-based catalysts obtained by hydrothermal carbonization of biomass-derived glucose [68]. The first steps towards the conversion of lignocellulosic biomass and bio-oils to aviation fuels and chemicals are already being taken [69]. Moreover, Co-Mo/CNT catalyst allowed to convert waste cooking oil into linear (and branched hydrocarbons in the aviation fuel range, while Ni-Mo/CNTox provided a higher selectivity in the green diesel hydrocarbons range [71].

The team has also been working on the development of technologies to transform excess CO_2 into valuable chemicals and fuels to protect the environment and reduce dependence on fossil fuels. Two front lines are under study: (i) utilization of CO_2 in the generation of C_1 products, and (ii) hydrogenation of CO_2 to C_2+ products (Figure 3). In the first, functionalized activated carbon (AC) and carbon nanotubes (CNTs) demonstrated to be high-performing supports for Ni-based CO_2 methanation catalysts, while the formation of a composite of AC and CeO_2 showed excellent performance in this application, with some property-performance relationships and reaction mechanisms being established by ex-situ and in-situ characterization [72]. For CO_2 hydrogenation to methanol and the reverse water-gas shift reaction, good performances were obtained using Cu-based catalysts supported on pristine CNTs and composites of pristine and functionalized CNTs : ZnO [73]. In the CO_2 hydrogenation to hydrocarbons through Fisher-Tropsch reactions, multimetallic catalysts (Fe, Co, K, Na) supported on carbon and aluminium oxide materials have been investigated, with the preliminary work showing that CNTs and Al_2O_3 are suitable catalytic supports for the reaction. Concerning the metallic phase, Na-containing catalysts promote the highest CO_2 conversion, whereas Fe catalysts have the highest selectivity in the C_2-C_4 products [74].

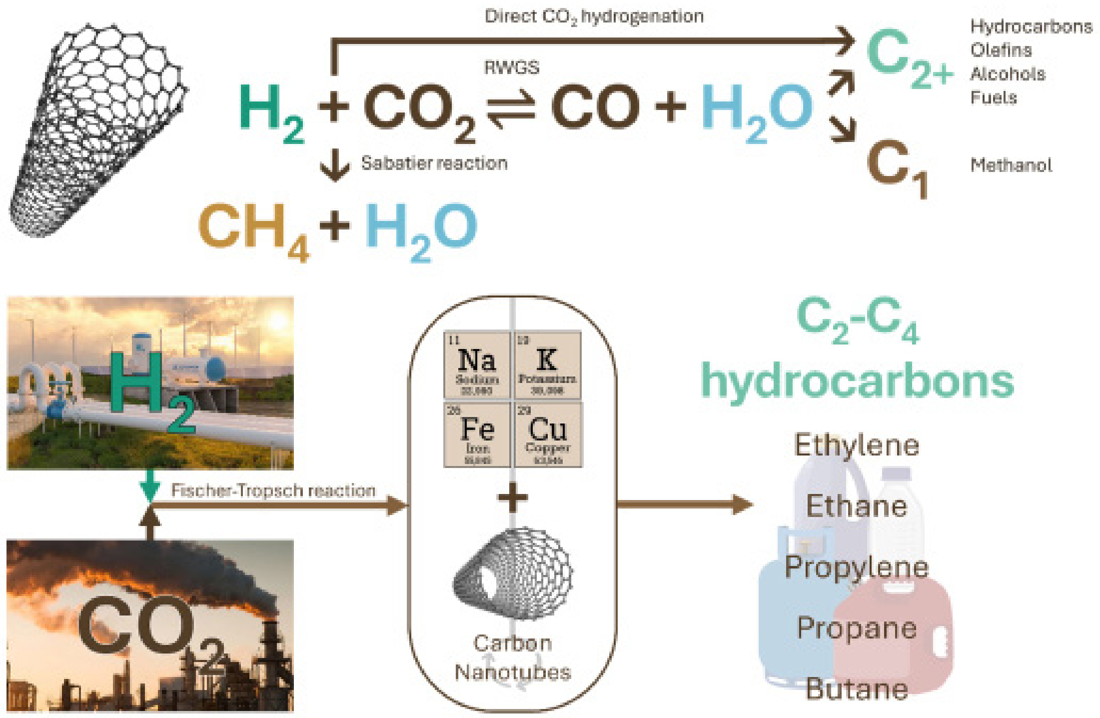
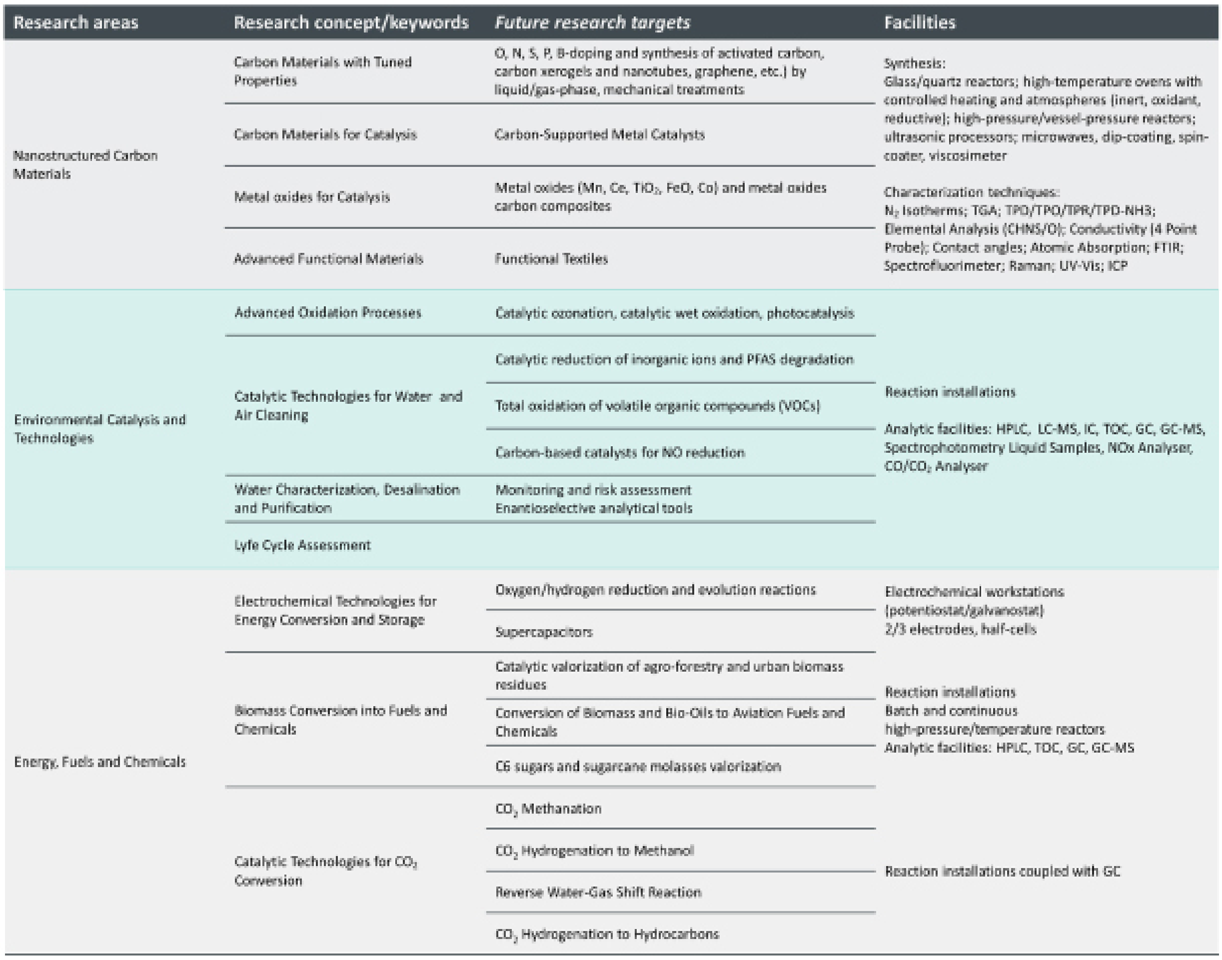


Figure 3

All these activities and discoveries are only possible due to the available facilities and collaborations of LCM (Figure 4). The lab is fully equipped to support advanced materials synthesis, modification, and characterizations. For synthesis, facilities include glass/quartz reactors; high-temperature ovens with controlled heating and atmospheres (inert, oxidant, reductive); high-pressure/vessel-pressure reactors; ultrasonic processors; microwaves, as well as several techniques for materials immobilization on macrostructured supports (dip-coating, spin-coater, viscosimeter). In-house, the materials characterisation can be assessed by N_2 adsorption-desorption isotherms; thermogravimetry analyses; temperature programmed desorption/oxidation/reduction (TPD/TPO/TPR), TPD of ammonia and CO_2, elemental analysis (CHNS/O); electrical conductivity (4-point-probe); contact angles; atomic absorption; and several spectroscopies: Fourier transform infrared spectroscopy (FTIR), spectrofluorimetry; Raman; UV-Vis spectroscopy; and inductively coupled plasma atomic emission spectroscopy (ICP).

To evaluate the material's performances under catalytic and other applications, versatile in-house made/adapted reactor installations are available, as well as some commercial options of batch and continuous high-pressure/temperature reactors, some with coupled analytical techniques. Analytic facilities are available for liquids and gases samples, including: high liquid chromatography – HPLC; liquid chromatography–mass spectrometry – LC-MS; gas chromatography - GC; gas chromatography-mass spectrometry – GC-MS; ion Chromatography – IC; total organic carbon – TOC; spectrophotometry of liquids; NOx Analyser; CO/CO_2 Analyser. Electrochemical workstations (potentiostat/galvanostat) are also available for the electrochemical assessment of materials with different cell configurations (two electrodes, three electrodes, half-cells).

Over the years, LCM accumulated collaborations with researchers from other R&I units around the world. It has participated in consortia for EU and transatlantic project funding, and it is part of collaborative laboratory networks, namely *BIOREF* - focused on R&I activities for advanced biorefineries. LCM is making a great effort to actively contribute to training high-level researchers and professionals through post-graduate and post-doctoral programs aligned with sustainable and scalable solutions for global energy and environmental challenges. For further information, we invite readers to visit our website at *lsre-lcm.fe.up.pt*.



Research areas	Research concept/keywords	*Future research targets*	Facilities
Nanostructured Carbon Materials	Carbon Materials with Tuned Properties	O, N, S, P, B-doping and synthesis of activated carbon, carbon xerogels and nanotubes, graphene, etc.) by liquid/gas-phase, mechanical treatments	Synthesis: Glass/quartz reactors; high-temperature ovens with controlled heating and atmospheres (inert, oxidant, reductive); high-pressure/vessel-pressure reactors; ultrasonic processors; microwaves, dip-coating, spin-coater, viscosimeter Characterization techniques: N_2 Isotherms; TGA; TPD/TPO/TPR/TPD-NH3; Elemental Analysis (CHNS/O); Conductivity (4 Point Probe); Contact angles; Atomic Absorption; FTIR; Spectrofluorimeter; Raman; UV-Vis; ICP
	Carbon Materials for Catalysis	Carbon-Supported Metal Catalysts	
	Metal oxides for Catalysis	Metal oxides (Mn, Ce, TiO_2, FeO, Co) and metal oxides carbon composites	
	Advanced Functional Materials	Functional Textiles	
Environmental Catalysis and Technologies	Advanced Oxidation Processes	Catalytic ozonation, catalytic wet oxidation, photocatalysis	Reaction installations Analytic facilities: HPLC, LC-MS, IC, TOC, GC, GC-MS, Spectrophotometry Liquid Samples, NOx Analyser, CO/CO_2 Analyser
	Catalytic Technologies for Water and Air Cleaning	Catalytic reduction of inorganic ions and PFAS degradation	
		Total oxidation of volatile organic compounds (VOCs)	
		Carbon-based catalysts for NO reduction	
	Water Characterization, Desalination and Purification	Monitoring and risk assessment Enantioselective analytical tools	
	Lyfe Cycle Assessment		
Energy, Fuels and Chemicals	Electrochemical Technologies for Energy Conversion and Storage	Oxygen/hydrogen reduction and evolution reactions	Electrochemical workstations (potentiostat/galvanostat) 2/3 electrodes, half-cells
		Supercapacitors	
	Biomass Conversion into Fuels and Chemicals	Catalytic valorization of agro-forestry and urban biomass residues	Reaction installations Batch and continuous high-pressure/temperature reactors Analytic facilities: HPLC, TOC, GC, GC-MS
		Conversion of Biomass and Bio-Oils to Aviation Fuels and Chemicals	
		C6 sugars and sugarcane molasses valorization	
	Catalytic Technologies for CO_2 Conversion	CO_2 Methanation	Reaction installations coupled with GC
		CO_2 Hydrogenation to Methanol	
		Reverse Water-Gas Shift Reaction	
		CO_2 Hydrogenation to Hydrocarbons	

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CO_2 hydrogenation to methanol using carbon fiber-based catalysts

Hidrogenación de CO_2 para obtener metanol usando catalizadores basados en fibras de carbono

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Abstract

CO_2 emissions are one of the main environmental problems in recent decades. The conversion of captured CO_2 into chemicals and fuels using renewable energy and materials is a promising option. Among them, thermocatalytic hydrogenation process to produce methanol stands out. This work reports the use of carbon fibres derived from lignin, a co-product of the paper industry, as catalyst/support to improve the sustainability of the process. The catalysts were prepared by two different techniques, electrospinning of the lignin solution, carbonization and active phase precursors wet impregnation of the carbon fibres and the direct electrospinning of lignin solution containing the active phase precursors followed by subsequent carbonization. In both cases, the active phase (Cu/Zn) precursors were added to obtain a final Cu/Zn mass ratio of 3/2. The catalysts were evaluated in the hydrogenation reaction of CO_2 at H_2/CO_2: 3/1, 220-340 ºC and 30 bar. The results show that the catalysts obtained by wet impregnation are the most active in the reaction, obtaining the highest methanol yield at 260 °C.

Resumen

Las emisiones de CO_2 siguen representado un problema ambiental de gran envergadura en las últimas décadas. La conversión de CO_2 en productos químicos y combustibles, mediante el uso de energía y materiales renovables, es una opción prometedora, donde destaca el proceso de hidrogenación termocatalítica para producir metanol. En este artículo se investiga el uso de fibras de carbono derivadas de lignina, un co-producto de la industria papelera, como soporte catalítico, con objeto de mejorar la sostenibilidad del proceso. Los catalizadores fueron preparados por dos técnicas distintas: electrohilado de una disolución de lignina, seguida de carbonización e impregnación húmeda de las fibras de carbono con los precursores de la fase activa; y electrohilado directo de la solución de lignina que contiene los precursores de la fase activa y su posterior carbonización. En ambos casos se adicionan las fases activas (Cu/Zn) en una relación másica de 3/2. Los catalizadores fueron evaluados en la reacción de hidrogenación de CO_2 a una relación H_2/CO_2: 3/1, entre 220-340 °C y 30 bar. Los resultados muestran que los catalizadores obtenidos por impregnación húmeda son más activos en la reacción y presentan un mayor rendimiento a metanol a 260 °C.

1. Introducción

A pesar de los avances en la diversificación de fuentes energéticas, las fuentes fósiles representan el 82 % del consumo total de energía primaria mundial. Su uso conlleva la generación de gran cantidad de gases de efectos invernadero, como el CO_2, uno de los principales impulsores del cambio climático. En este sentido, resulta de gran interés el aprovechamiento de este gas de efecto invernadero, para la producción de moléculas de elevado valor industrial, mediante su hidrogenación. Incluso tras completar la transición a una economía descarbonizada, la hidrogenación del CO_2, usando fuentes biogénicas o captura directa del aire, será necesaria para obtener los hidrocarburos demandados por la industria o el transporte pesado. La hidrogenación de CO_2 es un proceso con más de 100 años de antigüedad, apareciendo en la primera década del siglo XX en Alemania ante la necesidad de una fuente independiente de combustibles sintéticos y fertilizantes, que impulsó el desarrollo de procesos para la producción de metanol y amoniaco a partir del carbón [1]. En concreto, el metanol es una de las moléculas plataformas que puede obtenerse a través de estas reacciones. Actualmente, el metanol se emplea en la obtención de productos de interés industrial como plásticos, cosméticos, olefinas o dimetiléter entre otros, además de ser un vector energético usado en el sector marino como combustible. El tamaño del mercado mundial de metanol se valoró en 40670 millones de dólares en 2024, con un incremento del 4.6 % durante el periodo 2024-2031 [2].

La mayoría del metanol se obtiene a partir de gas de síntesis. Este se produce por reformado húmedo de gas natural o de los productos de gasificación del carbón, generando gases de efecto invernadero. La posibilidad de obtener metanol de carácter más renovable es esencial dentro de la transición a procesos de descarbonización, ya que permitiría reducir las emisiones de gases de efecto invernadero en aproximadamente 1.5 kg de CO_2 por cada kg de metanol obtenido [3- 4]. En base a esto, se ha establecido el concepto de Economía del Metanol, el cual engloba el uso de metanol como forma alternativa de almacenar, transportar y utilizar la energía. El proceso de producción renovable de metanol más prometedor se encuadra dentro de las Power-to-x, basadas en emplear electricidad renovable para producir hidrógeno por electrólisis, el cual se emplearía en la síntesis de moléculas (principalmente hidrocarburos, aunque también se postulan otras como el amoníaco), que servirían como almacén químico de energía o como materia prima de origen renovable. Dependiendo de la procedencia del metanol renovable, éste obtiene una diferente denominación, como e-metanol cuando procede de CO_2 capturado con hidrógeno verde (producido a partir de eléctrolisis del agua con energía renovable) u otra alternativa sería la producción de metanol a partir de gasificación de biomasa, dando lugar al biometanol. La alternativa que presenta una mayor evolución a lo largo de los últimos años es el e-metanol, alcanzando una capacidad de producción anual de 5 Mton [5].

1.1. Catalizadores basados en óxidos metálicos

La síntesis de metanol a partir del gas de síntesis ha sido un proceso comercial desde 1965 hasta la actualidad, empleando catalizadores de Cu/ZnO/Al_2O_3 (CZA) a 200-300 °C y 30-50 bar en un reactor de lecho fijo [6]. La mayoría de los catalizadores empleados, en la actualidad, son catalizadores heterogéneos formados por una mezcla de dos o más óxidos metálicos, de los cuales al menos uno de ellos no se puede reducir en presencia de hidrógeno y CO_2, de tal modo que se alcanza una estructura Metal/Óxido, que permite una doble funcionalidad. Mientras que el metal ofrece la capacidad para hidrogenar, el óxido aporta vacantes de oxígeno donde adsorber el CO_2, siendo estas vacantes útiles en el trancurso de la reacción por dar lugar a una movilidad electrónica mejorada, que aumenta el rendimiento catalítico al modular la selectividad. Entre las fases activas más usadas se encuentran metales de transición (Cu, In_2O_3, Fe_2O_3) y metales nobles (Rh, Pt, Pd), soportados sobre diferentes soportes inorgánicos, entre los que destacan el Al_2O_3 y el ZrO_2 [7].

En concreto, a escala comercial, el catalizador más empleado es el Cu/ZnO/Al_2O_3 con una relación másica de 60/30/10, donde cada uno de los componentes desempeñan una función específica. En este sistema, el cobre en estado metálico es la especie más activa en la reacción de hidrogenación de CO_2, la alúmina actúa como soporte, y el ZnO se introduce porque favorece la dispersión del Cu, así como su estabilidad, al evitar su lixiviado y sinterización. El ZnO también actúa como promotor, evitando que el cobre catalize la reacción de RWGS, lo que disminuiría la selectividad a metanol [8].

Este sistema catalítico presenta ciertos inconvenientes, como la desaluminización de la alumina en presencia de agua, que se obtiene como subproducto, la sinterización del cobre superficial y la deposición de coque. Para mejorar la eficiencia del catalizador se ha estudiado el empleo de ciertos promotores, como el bario, potasio y cerio, que favorecen la selectividad hacia metanol [9]. Por ejemplo, se ha visto que el uso del bario como promotor en un catalizador CZA aumentaba la selectividad a metanol desde un 46.6 % hasta un 62.2 %, gracias a que el bario modulaba la dispersión del cobre [10- 11]. Además de la adición de promotores, también se han realizado numerosos estudios centrados en el cambio del soporte para mejorar el rendimiento del proceso, sustituyendo la alúmina por SiO_2, TiO_2, ZrO2, ZnO y CeO_2 como soportes, con objeto de incrementar la movilidad electrónica a través de las vacantes de oxígeno [12-13]. Otro de los desafíos más importantes es la sustitución del soporte del catalizador de carácter inorgánico, por un soporte más sostenible y/o renovable, como pueden ser algunos materiales de carbono.

1.2. Catalizadores basados en materiales de carbono

Los catalizadores basados en materiales carbonosos pueden ser una alternativa muy interesante debido a su gran estabilidad en presencia de agua, comparado con la Al_2O_3 [12-13]. Además, su elevado desarrollo poroso permite una dispersión más efectiva de las fases activas. Por otro lado, se puede modificar su química superficial introduciendo grupos funcionales específicos o heteroátomos (N, P) que generen vacantes de oxígeno en la superficie del soporte para mejorar la activación del CO_2, al tiempo que es posible modificar las propiedades electrónicas de la superficie mejorando la interacción entre el soporte y las especies metálicas [14]. A pesar de todas estas ventajas, la más destacable en términos medioambientales, es la posibilidad de obtenerlos a partir de residuos biomásicos, lo que reduce el impacto ambiental y el coste de su obtención.

Sin embargo, su principal desventaja radica en que durante la reacción de hidrogenación de CO_2, el H_2 siempre está presente como reactivo, simultáneamente con el H_2O, que es el principal subproducto de la reacción. Tanto el CO_2 como el H_2O y el H_2 podrían gasificar los soportes carbonosos mediante:

$$C + 2H_2 \rightarrow CH_4 \qquad (5)$$

$$C + 2H_2O \rightarrow CO + H_2 \qquad (6)$$

$$C + CO_2 \rightarrow 2CO \qquad (7)$$

Las reacciones de gasificación (6, 7) están favorecidas a altas temperaturas (700-1000 oC), mientras que la reacción de metanación (5) se produce preferentemente a temperaturas menores. Sin embargo, en los rangos de temperatura y presión donde se lleva a cabo la síntesis de metanol, no cabe esperar una contribución significativa de estas reacciones.

Entre los principales tipos de materiales de carbono empleados en la reacción de hidrogenación del CO_2 se encuentran los nanomateriales altamente ordenados como nanotubos (CNT) y nanofibras de carbono (CNF). Se ha estudiado, por ejemplo, el efecto de la cantidad de ZnO en un catalizador Cu-ZrO_2/CNF. Algunos autores han encontrado que en ausencia de ZnO la conversión de CO_2 es más alta (14 %), pero la selectividad disminuye hasta el 78 %, a 240 °C y 20 bar. Estos autores han observado un óptimo de la selectividad a metanol de 92 % con la adición de un 3 % wt de ZnO, para una conversión de CO_2 del 9 % [15]. Otro sistema catalítico basado en metales nobles sería el Pd-Zn/CNT, que a 240 °C y presión de 50 bar presenta una conversión de CO_2 del 7.7 % y una selectividad a metanol entorno al 99 %. En este trabajo se analizó la influencia del tipo de material de carbono y se observó que la conversión de CO_2 de los sistemas catalíticos que usan CNT y CNF, como soportes, era superior a la de un catalizador que usa un carbón activado (AC), alcanzándose en este último caso un 6.4 % de conversión, con una selectividad a metanol entorno al 96 %. En ambos casos, el comportamiento catalítico fue superior al catalizador Pd-Zn/Al_2O_3, que presentó resultados inferiores de conversión (5 %) y selectividad a metanol (92.1 %) [16], bajo las condiciones estudiadas.

Entre los materiales grafénicos, la presencia de grupos oxigenados en el óxido de grafeno (GO), y la alta movilidad electrónica y accesibilidad superficial de los grafenos de bajo número de capas (FLG), convierte a ambos materiales carbonosos en soportes prometedores para esta reacción [11]. Yu Jua Fan et al., mostraron que el catalizador Cu/ZnO/ZrO_2/Al_2O_3/rGO (CZZA/rGO) permitía alcanzar una selectividad a metanol de 11.6 % en comparación con el CZZA que proporciona un 9.8 % con conversiones del 14.7 % y 13.2 % respectivamente. [12]. Liu Zhen-Juan et al., mostraron que el catalizador CZA permitía alcanzar una selectividad a metanol de 55.7 % y conversión del CO_2 del 8.5 %, mientras que adicionando nanoláminas de grafeno se obtendría una conversión y selectividad a metanol mayor. Se alcanzan un óptimo de conversión 14.6 % y selectividad de 62.3 % con el catalizador Cu/ZnO/Al_2O_3/ 10% nanoláminas de grafeno (CZA/10G) [17].

2. Objetivos

En este trabajo se estudia el aprovechamiento de un coproducto, como es la lignina, para la preparación de materiales carbonosos de morfología fibrilar, que se usan como soporte catalítico de fases activas de Cu y ZnO, estudiando su comportamiento como catalizadores de la hidrogenación de CO_2 a metanol.

3. Metodología experimental

En base a los resultados previamente mencionados, en este trabajo se estudia la preparación de fibras de carbono, mediante el electrohilado de disoluciones de lignina, que se usan como soporte catalítico de fases activas de Cu y ZnO, estudiando su comportamiento como catalizadores de la hidrogenación de CO_2 a metanol. Se han empleado dos ligninas de tipo organosolv, denominadas en este trabajo como AST (extraída con ácido acético) y FRA (extraída con etanol). Se ha estudiado el efecto del tipo de metodología empleada para incorporar las fases activas a la matriz carbonosa. Por un lado, se han preparado fibras de lignina con los precursores de las fases activas dispersas en su estructura, en un solo paso, mediante el electrohilado de disoluciones de lignina/precursores de fases activas, de modo que tras la estabilización y carbonización de estos materiales se obtengan fibras de carbono que contienen las fases activas. Por otro lado, se han preparado fibras de lignina, que han sido estabilizadas y carbonizadas, a las que se le han incorporado los precursores de las fases activas mediante impregnación húmeda, obteniéndose tras el proceso de carbonización fibras de carbono dopadas con las fases metálicas. Finalmente, se estudió su comportamiento catalítico en términos de conversión y distribución de productos bajo unas condiciones de reacción predefinidas (relación molar H_2/CO_2= 3/1, temperatura de reacción 220-340 oC, presión total= 30 bar y caudal total, FT =75 ml/min).

3.1. Preparación y morfología de fibras de carbono

La preparación de las fibras de carbono se ha realizado usando la técnica de electrohilado. Esta metodología permite controlar la morfología, porosidad y la química superficial de las fibras, mediante la combinación de condiciones de operación y características de la disolución [18]. Esta técnica requiere la preparación de una disolución polimérica de elevada concentración en un disolvente volátil, hasta obtener una viscosidad y conductividad eléctrica adecuadas.

Dado que la lignina AST es soluble en ácido acético y la lignina FRA en etanol, se emplarán estos disolventes para cada una de las ligninas, con una relación másica lignina/disolvente, 1/2.5 y 1/1, respectivamente. Además, la lignina AST presenta un menor peso molecular y una mayor polidispersidad en su estructura en comparación con FRA. Por ello, ha sido necesario emplear un 20 % de acetato de celulosa respecto a la lignina, como aglomerante, para mejorar las propiedades reológicas de la solución y permitir su electrohilado. En el proceso de electrohilado se ha empleado una configuración coaxial del equipo para evitar problemas asociados al secado de la solución, donde la disolución preparada se impulsa a través del capilar interno mientras que por la aguja externa se bombea disolvente. Un esquema de la instalación usada para la preparación de las fibras de lignina se muestra en la Figura 2A.

Una vez obtenidas las fibras de lignina, es necesario someterlas a un proceso previo de estabilización oxidativa en aire a baja velocidad de calentamiento y hasta 200 ºC, donde se generan enlaces éter que entrecruzan las cadenas poliméricas de la lignina, para aumentar la temperatura de transición vítrea de la lignina y evitar su fusión durante la carbonización posterior de las fibras [18]. Tras la estabilización, la carbonización se llevó a cabo a 900 °C para las fibras con lignina AST y a 500 ºC para las fibras con lignina FRA. En la Figura 2b se muestran diferentes fotografías de cada etapa del proceso de preparación de las fibras de carbono, así como una micrografía, obtenida por microscopía electrónica de barrido, de las fibras de carbono finales. Tras los tratamientos térmicos se observa que las fibras se van oscureciendo y se produce una reduccción de su tamaño. El diametro de las fibras de carbono obtenidas se encuentra entre 0.3 y 1 µm.

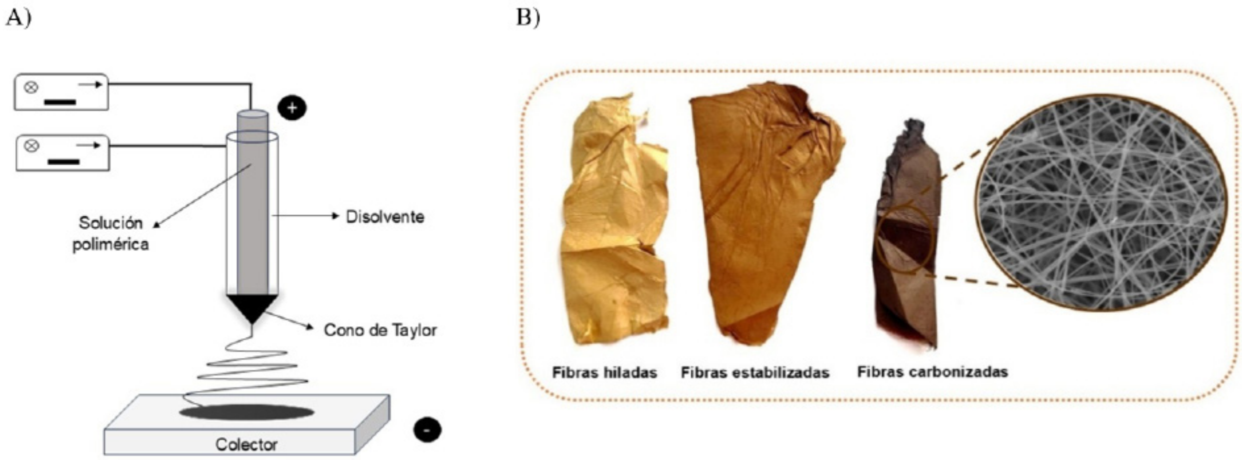

Figura 2. A) Esquema del equipo de electrohilado y B) Evolución de las fibras de lignina desde el proceso de electrohilado seguido de las distintas etapas de tratamiento térmico, estabilización termooxidativa y carbonización.

Figure 2. A) Configuration of the electrospinning process y B) Evolution of the lignin fibres from the electrospinning process followed by the different stages of heat treatment, thermo-oxidative stabilisation and carbonisation.

3.2. Preparación y propiedades superficiales de los catalizadores

Una vez optimizada la preparación de las fibras de carbono, se estudia la adición de los metales a través de distintos métodos. Se comenzó preparando fibras de carbono con las fases activas Cu/ZnO partiendo de disoluciones de lignina/precursores fases activas. Para ello, sobre las disoluciones previamente mencionadas, se añadieron sales de los metales correspondientes (Cu y Zn) con una relación másica de Cu/ZnO de 3:2, en cantidades calculadas para obtener cargas cercanas al 25% en el catalizador final. En el caso de la lignina AST, se emplearon las sales acetato de cobre y acetato de zinc mientras que para la lignina FRA se empleó nitrato de cobre y nitrato de zinc. Se emplearon voltajes de 16 kV y 26 kV y caudales de 1 y 1.8 mL/h para las ligninas FRA y AST y caudales de disolvente de 0.3 y 0.5 mL/h, respectivemente. Las fibras se estabilizan siguiendo el mismo protocolo descrito en la sección 5.1, para posteriormente carbonizarse a 400 °C.

Por otro lado, se produjeron catalizadores mediante impregnación húmeda sobre las fibras de carbono preparadas en la sección 5.1. Se preparó una disolución concentrada de nitrato de Cu y Zn, con relación másica Cu/ZnO de 3:2, para obtener una carga final teórica en la fibra de carbono del 25 % wt. El exceso de agua se elimina llevando las fibras húmedas a sequedad a 80 ºC. Una vez soportados los metales se les realiza un tratamiento térmico de carbonización a 400 °C. La nomenclatura usada para los catalizadores fibrilares preparados, será FCX_Z, donde FC hace referencia a que son fibras de carbono, X representa el precursor de lignina utilizado, A en caso de AST, F en caso de FRA y Z corresponde a la técnica por la que se han obtenido, donde IH hace referencia a la técnica de impregnación húmeda y E representa el proceso de electrohilado simultáneo de la disolución de lignina y precursores de las fases activas. Un ejemplo de esta nomenclatura sería FCA_E, es decir, fibras de carbono obtenidas a partir del electrohilado directo de la lignina AST junto con las fases activas.

4.Resultados y discusión

4.1. Estudio termodinámico

Diferentes autores han comprobado que el CO_2 puede sustituir parcialmente al CO como fuente de obtención de metanol, ya que la mezcla de gas de síntesis con CO_2 se traduce en mayores velocidades de reacción. Las reacciones implicadas teniendo en cuenta una alimentación que contenga ambos gases e hidrógeno son las siguientes:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H = -49.5\ \mathrm{kJ/mol} \qquad (1)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H = 41\ \mathrm{kJ/mol} \qquad (2)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -90.7\ \mathrm{kJ/mol} \qquad (3)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H = -165\ \mathrm{kJ/mol} \qquad (4)$$

Aunque es posible una reacción directa de conversión del CO_2 a metanol (1), existe una vía indirecta a través del desplazamiento inverso de la reacción de *water gas shift* (WGS, 2), seguida de la hidrogenación del CO (3). La presencia de la reacción de WGS implica que ningún catalizador sea 100 % selectivo a la producción de metanol, produciéndose CO como subproducto. Debido a que la conversión de CO_2 ronda el 25 %, es habitual operar a escala industrial con reactores con recirculación. La producción de metano también es termodinámicamente posible a partir de CO o CO_2, acorde con la reacción (4) [5].

En cuanto a la composición del gas de alimentación, el empleo de una mezcla de gases $CO/CO_2/H_2$ favorece mayores rendimientos a metanol en el equilibrio respecto a la mezcla CO_2/H_2 en el rango de temperaturas de 220 a 290 °C. Con el propósito de lograr un ciclo neutro en carbono, se ha llevado a cabo un estudio termodinámico realizado en Aspen Plus donde la alimentación de entrada será una mezcla de H2/CO2 debido a que dicho CO_2es considerado proveniente de la gasificación de biomasa. En este estudio se ha analizado el efecto de la temperatura (220-360 °C) y la presión (10-100 bar) de reacción, manteniendo constante la relación H_2/CO_2: 3/1. La Figura 1 muestra la conversión de CO_2 y el rendimiento a CH_3OH y CO a las diferentes condiciones de operación. Se puede observar como la producción de metanol frente a CO se ve favorecida a bajas temperaturas para una presión constante, debido a la exotermicidad de las reacciones (1) y (3). Además, cuanto mayor es la presión, mayor es la conversión de CO_2, ya que estas reacciones llevan asociadas una disminución del número de moles, mientras que la reacción RWGS no cambia el número de moles gaseosos en el reactor [6].

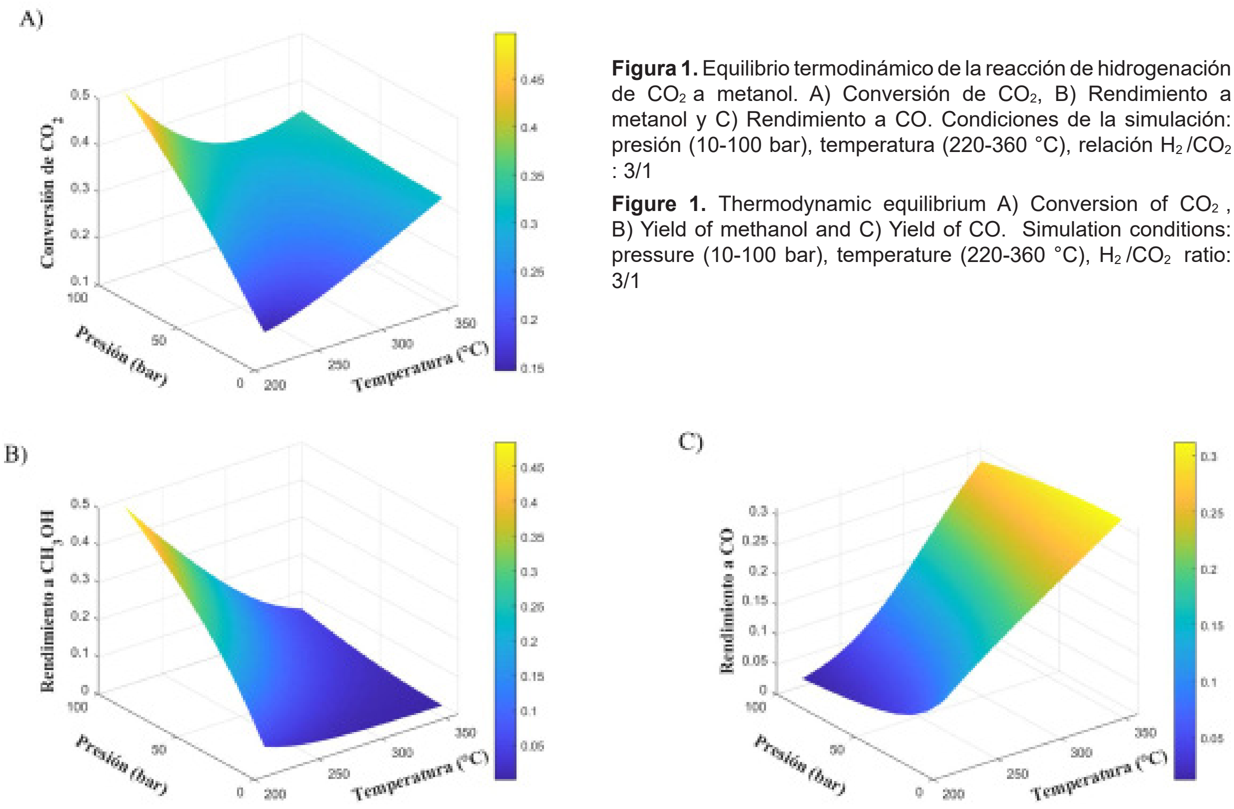

Figura 1. Equilibrio termodinámico de la reacción de hidrogenación de CO_2 a metanol. A) Conversión de CO_2, B) Rendimiento a metanol y C) Rendimiento a CO. Condiciones de la simulación: presión (10-100 bar), temperatura (220-360 °C), relación H_2/CO_2 : 3/1

Figure 1. Thermodynamic equilibrium A) Conversion of CO_2 , B) Yield of methanol and C) Yield of CO. Simulation conditions: pressure (10-100 bar), temperature (220-360 °C), H_2/CO_2 ratio: 3/1

4.2. Preparación y caracterización de los catalizadores

La Tabla 1 recoge las principales propiedades superficiales de los catalizadores. Se observa una clara diferencia en la porosidad dependiendo del método de preparación. Las fibras FCF presentan un mayor desarrollo poroso (497 m^2/g) que disminuye tras cargar la fase activa, sin embargo, la FCA presenta un menor desarrollo poroso (10 m^2/g) que tras la impregnación aumenta debido a la gasificación por las sales precursoras de las fases metálicas. Por el contrario, las fibras FCA_E y FCF_E muestran un menor desarrollo poroso debido a la presencia de los metales ocluidos dentro de la estructura carbonosa limitando la cantidad de fase activa superficial. Comparando las dos ligninas utilizadas, la lignina F muestra un mayor desarrollo poroso en sus catalizadores a la vez que una estructura más abierta que la lignina A ($V^{N2}_{microporo}/ V^{CO2}_{microporo}$). Por otro lado, aunque la cantidad teórica de metales incorporados es de aproximadamente 25 %wt, los valores obtenidos por XPS indican una cantidad notablemente menor. A pesar de esta reducción, se mantiene la relación 3:2 entre Cu y Zn, lo que sugiere que el resto de los metales no detectados se encuentran ocultos dentro de la estructura carbonosa, sin acceso directo en la superficie del material.

Tabla 1. Propiedades texturales y contenido en Cu y Zn superficial de los distintos catalizadores preparados
Table 1. Textural properties and surface Cu and Zn content of the different catalysts

	Adsorción-Desorción de N_2 (-196 °C) y Adsorción de CO_2 (0 °C)			XPS (% wt)	
Catalizador	**A_{BET}^{N2} (m^2/g)**	**V_{DR}^{N2} (cm^3/g)**	**V_{DR}^{CO2} (cm^3/g)**	**Cu**	**Zn**
FCA_E	6	< 0.01	0.09	4.1	3.1
FCF_E	9	< 0.01	0.14	22.0	12.0
FCA_IH	108	0.16	0.20	6.4	4.2
FCF_IH	279	0.10	0.16	4.7	2.9

4.3. Evaluación de los catalizadores en la reacción de hidrogenación de CO_2 a metanol

La reacción de hidrogenación de CO_2 ha sido estudiada en un reactor de lecho fijo a presión, donde se introducen 400 mg del catalizador. La composición volumétrica de los gases de alimentación $CO_2/H_2/N_2$ es de 1/3/1. Previo a la reaccion, se realiza la reducción in situ del catalizador a una temperatura de 300 °C durante 4 horas. La reacción se lleva a cabo a 30 bar, variando la temperatura de 220 °C hasta 340 °C, manteniendo cada temperatura hasta alcanzar estado estacionario.

En la Figura 3 se muestra la conversión de CO_2 y selectividad a metanol obtenida para cada catalizador. En términos generales, se observa que el catalizador FCA_E no es activo en la reacción. Esto puede ser debido a que la fase activa se encuentre en la parte más interna de las fibras de carbono, siendo inaccesible debido al bajo volumen de poros que presenta (0.09 m^3/g). Al usar la lignina FRA en la prepraración de fibras, muestra FCF_E, se aumenta el volumen de poros (0.14 m^3/g), estando más accesible la fase activa, lo que conlleva mayores conversiones de CO_2 y selectividades hacia metanol de hasta 80% a 220 °C. Para los catalizadores en los que la fase activa se ha incorporado por impregnación húmeda, FCF_IH y FCA_IH, se observa un aumento de la conversión. El aumento de la actividad de estos catalizadores está relacionado con la accesibilidad de las fases activas, al quedar estas en la parte más superficial del catalizador. En todos los catalizadores, la conversión de CO_2 aumenta con la temperatura, alcanzando el máximo para una temperatura de reacción de 340 °C. Sin embargo, la selectividad a metanol decae notablemente con la temperatura, desde un 80% a 220 °C hasta un 2% a los 340 °C para el catalizador FCF_E, como se observa en la Figura 3.B.

Por tanto, en resumen, se han preparado catalizadores fibrilares derivados de biomasa residual, que contienen cobre y zinc, siendo el catalizador FCF_E, el que presenta la mayor dispersión de la fase activa. Además, todos los catalizadores preparados son activos en la reacción de hidrogenación de CO_2 excepto el catalizador FCA_E que no muestra conversión de CO_2 debido a la baja porosidad que muestra, además de la baja cantidad de fases activa que tiene superficialmente. El catalizador más activo es el catalizador FCA_IH y también es el que presenta un mayor rendimiento a metanol (3.8 %), alcanzando su máximo a 260 °C en las condiciones estudiadas.

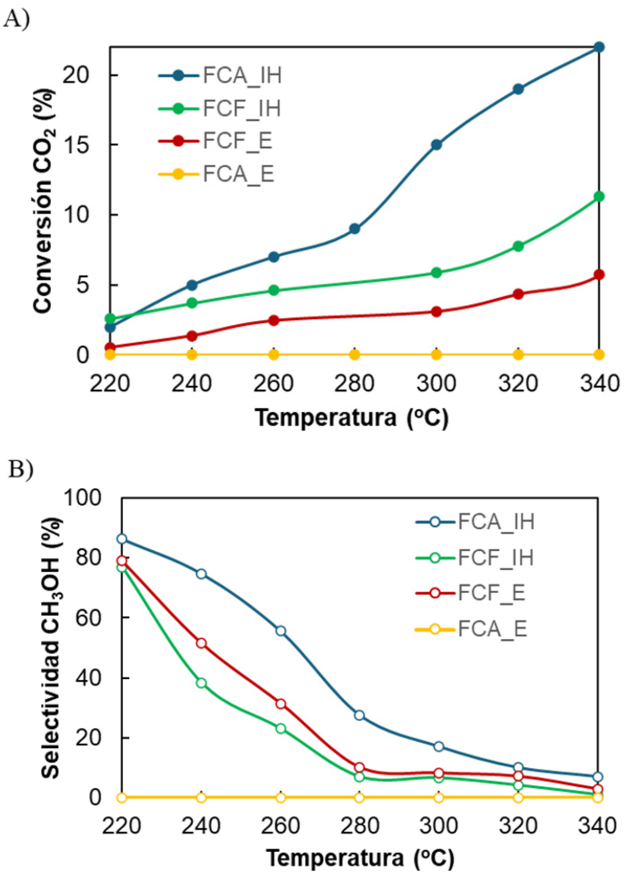

Figura 3. A) Conversión de CO_2 y B) Selectividad a metanol para los distintos tipos de catalizadores.

Figure 3. A) CO_2 conversion and B) Selectivity to methanol for the different types of catalysts.

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Development of multifunctional nanomaterials for the co-production of upgraded heavy crude oil and hydrogen at different pressures and temperatures

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Objective and Novelty

This thesis explores the development of multifunctional nanomaterials tailored to simultaneously improve the quality of heavy and extra-heavy crude oil and produce hydrogen at various pressures and temperatures. The novelty lies in the synthesis of advanced nanomaterials derived from lanthanide oxides, transition metal oxides, aluminosilicates, carbon-based materials, and composite structures, designed specifically for catalytic degradation of hydrocarbon macromolecules, heteroatoms, and crude oil under oxidation, gasification, and pyrolysis conditions. This dual-purpose approach not only addresses the need for more efficient crude oil upgrading but also supports the transition toward cleaner energy sources by enhancing hydrogen production as a complementary energy vector. These nanomaterials were designed to improve crude oil reactivity, reduce asphaltene aggregation, and increase hydrogen yield, all while operating at relatively low temperatures (<230 °C) and pressures up to 6.0 MPa. Additionally, the research investigates the integration of nanofluids into cyclic steam stimulation processes, demonstrating their potential to enhance oil recovery, improve crude quality, and increase hydrogen generation within the reservoir. This study highlights the successful scale-up and field implementation of synthesized nanoparticles into a cyclic steam stimulation process during field trials demonstrating their potential to enhance oil recovery, improve crude quality, and increase hydrogen generation within the reservoir. Additionally, the study confirmed that nanomaterials could capture and catalytically convert CO_2 into valuable gases, contributing to emission reduction and sustainable energy production.

Results

The results of this study encompass several key areas, including the thermal oxidation and reactivity of crude oil fractions, the catalytic performance of nanomaterials, hydrogen production, enhanced oil recovery, CO_2 capture and conversion, and sulfur removal. The catalytic performance of nanomaterials was evaluated using carbon xerogels and CeO_2 nanoparticles doped with Ni, Co, Fe, and Pd. Among the tested combinations, Ni-Pd-CeO_2 exhibited the highest catalytic efficiency, achieving 100% asphaltene conversion within 90 minutes at 220 °C while reducing activation energy by 80%. Morphological modifications further enhanced performance, with cubic Ni-Pd-CeO_2 demonstrating the best results due to its increased oxygen chemisorption capacity and lower decomposition temperatures. Hydrogen production was assessed during the catalytic steam gasification of asphaltenes and resins at low temperatures (<230 °C). The $CeNi_1Pd_1$ nanomaterial exhibited the highest hydrogen yield, achieving up to 55 vol% H_2 in the effluent gas, representing a 70% increase compared to non-catalytic systems. The integration of nanofluids into cyclic steam stimulation processes demonstrated significant improvements in oil recovery and crude quality. Injecting nanofluids dispersed in steam increased oil recovery by 25% during dynamic tests, with an additional 42% increase observed after a 12-hour soaking period compared to steam-only injection. Crude oil quality improved substantially, with API gravity increasing by 9.0° units (from 6.9° to 15.9°), representing a 130% increase. The study also demonstrated the potential of nanomaterials for CO_2 capture and catalytic conversion. Nanoparticles with adsorbed asphaltenes showed a higher tendency to capture CO_2, facilitating its catalytic conversion into valuable gases such as CO, CH_4, H_2, and light hydrocarbons. The most significant outcome of this study was the successful field application of the developed nanotechnology in a Colombian reservoir using cyclic steam stimulation (CSS). The field implementation of nanofluids in wells affected by steam injection demonstrated substantial improvements in oil production and quality. In Well A, treated between June and July 2022, the application of functionalized nanoparticles at a concentration of 500 $mg \cdot L^{-1}$ in a commercial carrier fluid resulted in an incremental production of 9,164 barrels of oil. Encouraged by these results, a second field trial was conducted in Well B between November and December 2022, leading to an additional production of 6,652 barrels. Both trials confirmed that nanofluids effectively enhanced oil mobility, reduced viscosity, and sustained improved oil quality over several months, validating the technology's scalability and broad applicability in enhanced oil recovery (EOR) operations. Hydrogen generation within the reservoir enhanced oil mobility, while CO_2 capture and conversion into CO, CH_4, and H_2 minimized emissions. The nanocatalysts maintained performance over multiple injection cycles, demonstrating their regenerative capacity, long-term efficiency, and industrial feasibility.

Conclusions

This study successfully advanced the nanofluid technology from TRL 3 to TRL 7, validating its effectiveness from laboratory experiments to field trials. The developed nanofluid significantly improved thermal enhanced oil recovery (TEOR) by enhancing oil production, asphaltene decomposition, in situ crude upgrading, hydrogen generation, and CO_2 capture and conversion. Field trials demonstrated increased oil recovery and API gravity, confirming improved crude quality and reservoir conditions. The nanofluid optimized hydrogen fugacity, promoting in situ upgrading while reducing hydrogen diffusion losses. Additionally, CO_2 capture and its catalytic conversion into valuable gases supported emission reduction and sustainable energy production. These findings confirm the scalability and industrial feasibility of nanofluid-assisted TEOR, positioning this technology as a promising solution for improving hydrocarbon recovery while supporting the transition to cleaner energy processes.

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Full thesis: *https://digibug.ugr.es/handle/10481/82586*

Adsorption of pharmaceutical compounds in aqueous solution on natural clays and carbon nanomaterials

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Supervisors: Francisco Carrasco-Marín (University of Granada, Spain) and Roberto Leyva Ramos (Autonomous University of San Luis Potosi, Mexico).

Objective and Novelty

The increasing presence of pharmaceutical contaminants in water requires innovative adsorption technologies beyond conventional fixed-bed systems, which often suffer from channeling, pressure drop, and inefficient mass transfer. This thesis presents, for the first time, the design and fabrication of 3D-printed carbon monoliths with precisely engineered porosity and complex channel geometries for liquid-phase adsorption. By integrating sol-gel polymerization with 3D printing, this approach overcomes the structural limitations of traditional monoliths, which often exhibit uncontrolled porosity and limited straight-channel configurations. The optimized textures and tailored channel architectures of these integral carbon monoliths improve fluid distribution, maximize contact between the fluid and adsorption sites, and improve mass transfer properties, resulting in higher adsorption capacities, lower pressure drops, and scalability in water treatment applications.

In addition, this study explores natural and hybrid clay-based materials as adsorbents. Their tunable surface chemistry, high surface area, and swelling properties make them promising candidates for pharmaceutical adsorption. While their direct integration into 3D-printed monoliths has not been implemented, they represent a strategic functionalization approach for future hybrid adsorption systems, enabling improved surface chemistry and selective contaminant interactions.

The main objectives of this thesis are i) to synthesize and characterize novel 3D-printed carbon monoliths with tailored porosity and complex channel geometries, ii) to evaluate their adsorption performance for pharmaceutical contaminants, iii) to analyze the effects of synthesis conditions, activation methods, and channel design on adsorption, and iv) to optimize performance through CFD modeling of fluid dynamics. In addition, v) synthesize and characterize natural and hybrid clay-based materials for pharmaceutical adsorption, and vi) assess the influence of their structural properties on the adsorption capacity and the mass transfer mechanisms governing the overall adsorption rate.

Results

Novel 3D-printed carbon monolith adsorbents with precisely tailored channel geometries and porous textures have been successfully fabricated for the removal of sulfamethoxazole (SMX), a hazardous antibiotic commonly found in water. The synthesis combined sol-gel polymerization of resorcinol (R) and formaldehyde (F), catalyzed by Cs_2CO_3 (Cs), with 3D printing of templates representing the desired channel geometries. Fig. 1a shows the meticulously designed 3D-printed template, which flawlessly replicates the original CAD model. After polymerization and curing processes, the organic monolith (Fig. 1b) exhibits seamless integration of the template within the organic gel-matrix, with no detectable interfacial gaps or detachment. This strong adhesion is indicative of the excellent compatibility between the template and the organic gel, ensuring precise structural control and optimal mechanical integrity in the final monoliths. Following carbonization, the template is then removed, and the final 3D-printed carbon monolith (Fig. 1c) shows a well-preserved, structurally intact channel morphology. In order to assess the influence of channel architecture on adsorption, three additional channel geometries: hexagonal (Fig. 1d), rhomboidal (Fig. 1e), and straight (Fig. 1f), were also designed and fabricated.

The R/Cs ratio was systematically varied at 100, 500, 1000, and 2000, significantly influencing the morphological, textural, chemical, and mechanical properties of the monoliths. These characteristics directly influence SMX adsorption [1]. It was observed that higher R/Cs ratios resulted in the presence of larger spherical primary particles, which in turn led to a modulating mean pore diameter in the macropore region (95.1-157.1 nm). This increased macroporosity, reduced flow resistance, and enhanced adsorption performance. The composition R/Cs = 1000 exhibited the best results, with longer breakthrough times and shorter mass transfer zone heights. The study found that adsorption was primarily driven by π-π stacking and electrostatic attractions.

The monoliths were further activated using steam and CO_2, significantly enhancing their porosity and adsorption capacity. Both methods effectively removed residual carbon deposits from the channel surfaces, remnants of the 3D template, preventing macropore blockage and increasing SBET values beyond 1000 m^2/g. CO_2 activation gradually enlarged micropores, increasing microporous surface area, while steam activation generated larger pores, shifting pore size distribution toward narrow mesopores. These structural modifications improved adsorption. Adsorption isotherms revealed a drastic increase in adsorption capacity with longer activation times. The highest adsorption capacities were 379.1 mg/g for the 8-hour CO_2-activated monolith and 488.6 mg/g for the 2-hour steam-activated monolith, surpassing most reported values. Breakthrough curves showed that extended activation prolonged breakthrough times due to a more open and accessible porous texture facilitating SMX adsorption.

Channel geometry significantly influenced breakthrough curves. The complex network of interconnected channels exhibited the longest breakthrough times across different flow rates (Fig. 1g). In contrast, hexagonal (Fig. 1h), rhomboidal (Fig. 1i), and straight (Fig. 1j) channels led to earlier breakthrough without reaching saturation, indicating partial adsorption. In these geometries, some SMX molecules exited unadsorbed, while mass transfer effects contributed to partial adsorption over time. The network of interconnected channels promoted intricate flow patterns and turbulence, enhancing fluid mixing and distribution (Fig. 1k). In contrast, the other geometries exhibited laminar flow, causing preferential pathways, channeling effects, and limited fluid-adsorbent interaction (Figs. 1l to 1n).

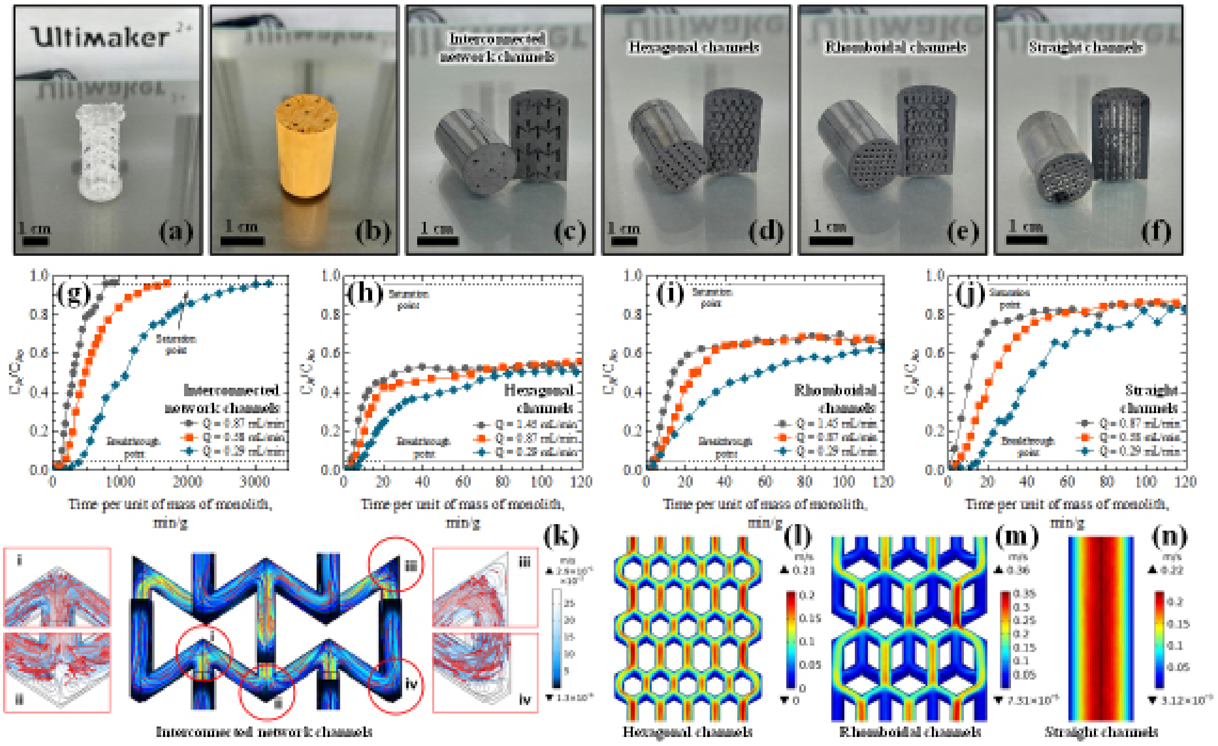

Figure 1. Schematic of 3D-printed carbon monolith synthesis (a-f), breakthrough curves for SMX adsorption on different channel geometries (g-j), and velocity profiles (k-n).

The adsorption capacity of raw clays for tetracycline (TC), trimethoprim (TMP), chlorphenamine (CPA), and SMX were strongly influenced by their structural arrangement, swelling capability, interlayer cations, and the molecular size of pharmaceuticals. Among the studied clays, bentonite showed the highest adsorption capacity for TC, TMP, and CPA, but lower for SMX [2]. Adsorption occurred on both the external surface and within interlayer spaces, primarily driven by cation exchange and electrostatic attractions. Diffusional model analysis indicated that TMP and TC adsorption was governed by both surface and pore volume diffusion, while CPA adsorption was controlled solely by pore volume diffusion [3].

To enhance SMX adsorption, hexadecyltrimethylammonium bromide-modified organobentonite was synthesized. The surfactant intercalated within the interlayer space, forming a double molecular layer. Adsorption isotherms demonstrated significantly higher SMX adsorption capacities than raw bentonite, as pharmaceutical ionic charge and adsorbent surface charge influenced adsorption. Electrostatic attractions and hydrophobic partitioning were the dominant mechanisms, with fast adsorption rates controlled by external mass transport [4]. These properties make organobentonite a promising functionalization agent for 3D-printed carbon monoliths.

Conclusions

This thesis presented a novel framework for the development of structured adsorbents, transforming fixed bed adsorbers into high performance, scalable 3D-printed carbon monolithic beds. By integrating computational design, 3D printing, and sol-gel polymerization, porosity and channel geometry were precisely tailored to optimize fluid dynamics and maximize adsorption of pharmaceutical contaminants. The results showed adsorption capacities surpassing those in the literature, demonstrating the superiority of 3D-printed monoliths over traditional adsorbents. Tailored channel architecture and activation methods enhanced adsorption, reduced pressure drops, mitigated flow channeling, and extended breakthrough times, offering a scalable and customizable alternative to conventional systems. Additionally, this work highlights hybrid clay-based materials as promising adsorbents. Organobentonite synthesis and characterization revealed improved hydrophobic interactions and adsorption capacity for SMX.

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Full Thesis can be downloaded from:
https://hdl.handle.net/10481/97437

Development of electrocatalysts based on colloidal graphene by electrochemical methods and other carbon materials for energy generation

Desarrollo de electrocatalizadores basados en grafeno coloidal por métodos electroquímicos y otros materiales carbonosos para la generación de energía

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Objectives and novelty

This Doctoral Thesis focuses on the development of carbon-based electrocatalysts to enhance efficiency and sustainability in energy production and storage, a field of global importance. The work involves the synthesis of electrocatalysts based on graphene, carbon fibers, activated carbons, and carbon black, using innovative techniques like electrochemical exfoliation, electrospinning, and microwave-assisted synthesis. The developed electrocatalysts are applied in key energy conversion reactions, such as the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER), with the aim of improving their performance.

The novelty of this work lies in the combination and optimization of advanced techniques to produce high-quality carbon-based materials, exploring the incorporation of metallic nanoparticles and modifying their structure with functional groups to enhance electrocatalytic activity. Additionally, the thesis develops bifunctional electrocatalysts, metal doped carbon fibers, and Pt-based materials with optimized characteristics, offering more efficient and sustainable alternatives for energy applications, such as in zinc-air batteries. The study includes a comprehensive characterization of the synthesized materials and a comparative analysis of their performance against commercial materials, significantly contributing to the advancement of electrocatalyst design for energy applications.

Results

This thesis achieved significant results in the development of carbon-based electrocatalysts. The synthesis of graphene materials through electrochemical exfoliation enabled the optimal incorporation of Pt nanoparticles, achieving excellent distribution and reduced particle size. This catalyst demonstrated superior performance in ORR and HER, with high stability and energy efficiency, outperforming the commercial Pt/C electrocatalyst while using less platinum (Figure 1).

Graphene-based materials enriched with nitrogen groups were also developed by integrating polyaniline and subsequent carbonization, which significantly enhanced their electrocatalytic properties towards ORR. Despite being metal-free, this material exhibited exceptional performance, opening the possibility of using metal-free catalysts for future applications. Additionally, a trifunctional composite material was created by combining poly(ionic liquids), graphene, and metal nanoparticles, achieving notable activity in ORR, HER, and oxygen evolution reaction (OER) with reduced platinum use.

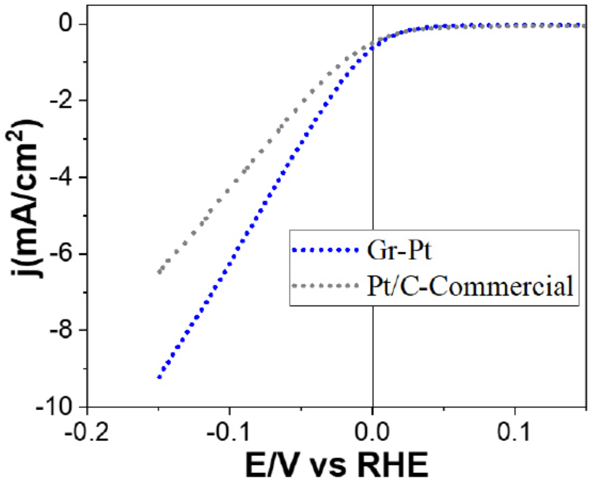

Figure 1. Linear sweep voltammograms for Gr-Pt and Pt/C-Commercial for HER, in 0.1M KOH saturated with N_2. Scan rate of 2 mV s^{-1} from 0.2 V to -0.15 v (vs RHE).

Furthermore, graphene-doped carbon fibers with metal nanoparticles were synthesized through electrospinning. These fibers demonstrated outstanding performance as electrodes in zinc-air batteries, showing improvements in charge-discharge voltage, durability, and stability, surpassing the commercial Pt/C material. Synergistic effects were observed between the carbon fibers and metal nanoparticles, particularly with palladium, resulting in high electrocatalytic activity with a lower metal loading.

Finally, Pt-based electrocatalysts on carbon supports were synthesized using a microwave-assisted method, achieving Pt nanoparticles smaller than one nanometer with high dispersion. These electrocatalysts showed high activity and selectivity for ORR and HER, as well as excellent stability and resistance to CO poisoning, demonstrating superior performance compared to the commercial catalyst with lower platinum loading, highlighting their improved energy efficiency (Figure 2).

Conclusions

This PhD thesis has successfully developed and evaluated a variety of carbon-based electrocatalysts, demonstrating their significant potential in energy conversion and storage applications. Through innovative synthesis techniques, such as electrochemical exfoliation and electrospinning, graphene materials and carbon fibers were created with enhanced properties, including optimal distribution of metal nanoparticles and improved electrochemical performance. These materials exhibited superior activity in key reactions like ORR and HER, often outperforming commercial catalysts while using less metal content. The results also highlighted the successful development of metal-free graphene composites and multifunctional materials that demonstrated outstanding catalytic behavior across various conditions.

The work also emphasized the importance of material composition and synthesis methods in achieving high-performance electrocatalysts. For instance, nitrogen-doped graphene materials, polymer-ionic liquid composites, and fibers doped with palladium or platinum showcased excellent stability, durability, and activity. These findings underscore the potential of carbon-based materials, not only for their intrinsic properties but also for their ability to serve as effective supports for metal nanoparticles, leading to efficient, cost-effective, and sustainable alternatives in electrochemical applications, such as in zinc-air batteries and other energy storage devices.

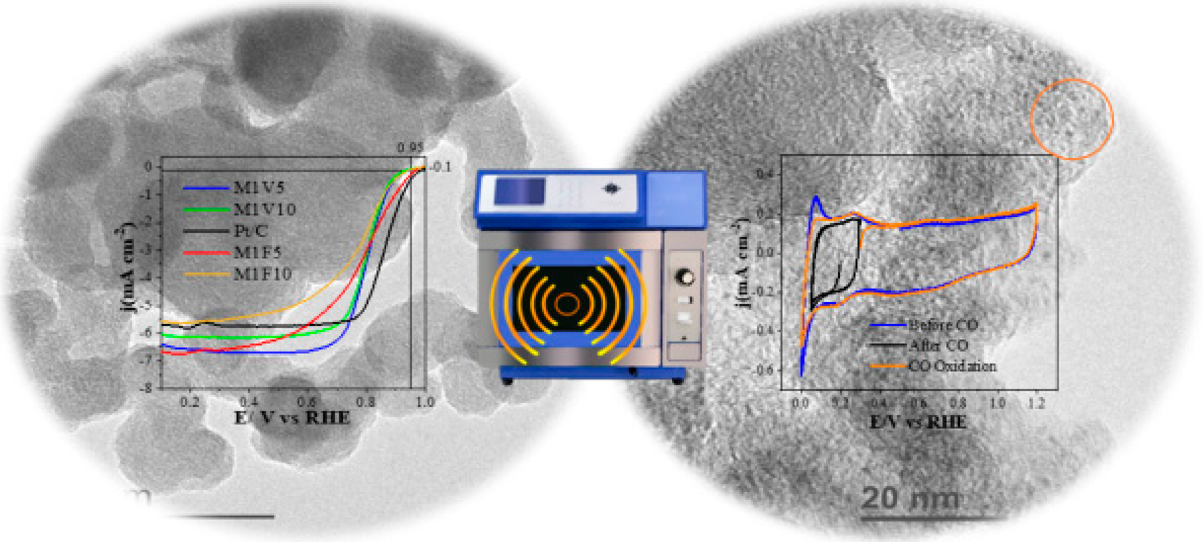

Figure 2. Linear sweep voltammograms for the electrocatalysts synthesized via microwave-assisted method, along with the evaluation of the CO poisoning resistance.

Acknowledgments

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Full Thesis can be downloaded from:
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Electrocatalysts based on carbon materials and transition metals for their application in hydrogen production and use

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Supervisors: Diego Cazorla Amorós and Emilia Morallón (University of Alicante, Spain).

Objectives and novelty

This Doctoral Thesis was dedicated to the development of novel materials based on highly dispersed metals supported over N-doped carbon materials for their use as electrocatalysts for energy applications including hydrogen production, fuel cells and zinc-air batteries. The preparation of carbon nitride and activated carbon composites, coordinating highly dispersed metals like Cu or Fe, was explored conducting both experimental and computational studies to understand the behavior towards the oxygen reduction reaction (ORR). The addition of low amounts of Pd was optimized to boost not only the electrocatalytic activity towards other reactions but also the durability. Additionally, alternative carbon supports with potential superior stability (different boron-doped diamond powder materials) were explored and a novel procedure for producing biomass-derived electrocatalysts reducing the cost and environmental impact of the available procedures in literature was developed. The feasibility of the use of the biomass-derived materials forming membrane electrodes assemblies (MEAs) was confirmed by different studies on a 5 cm^2 cell during a stay in the *Institute of Advanced Technologies for Energy of the Italian National Research Council* (CNR-ITAE).

The novelty of this Thesis lies in the combination of advanced synthesis strategies, computational calculations (Density Functional Theory (DFT)) and verification in real working conditions to study the viability of the production of more efficient and stable electrocatalysts decreasing the production cost and environmental impact. The preparation procedure of the biomass-derived electrocatalysts led to a patent application and the publications related to the Thesis are listed below following the order of the chapters. These contributions open new possibilities for more sustainable electrocatalysts production for different energy applications, especially for the ORR process in direct methanol fuel cells and hydrogen evolution reaction (HER) in electroreforming cells. Finally, in the last chapter, the electrosynthesis of hydrogen peroxide is addressed for the first time by a metal tellurate-based material.

Results

The characterization of carbon nitride (C_3N_4)/activated carbon composites revealed that the presence of Fe leads to the formation of larger C_3N_4 domains, whereas Cu-containing counterparts exhibited well-distributed nanodomains, more similar to metal-free composites. The samples with a moderate content of C_3N_4 demonstrated high electrocatalytic performance, as they provided an optimal balance of surface metal active sites and textural properties. DFT calculations suggested that Cu-C_3N_4 sites possess superior catalytic properties in terms of activity and selectivity (Fig. 1), aligning with experimental findings. The properties of Pd nanoparticles were found to be dependent on the composition of the C_3N_4/C support, with highly dispersed Fe and especially Cu leading to smaller and more uniform Pd particle size distributions. This observation correlated with the higher stabilization energy predicted by DFT for an 8-atom Pd cluster with the support in presence of a second metal. Among Pd-containing materials, the best HER performance was observed in Pd/Cu-C3N4 sites, whereas the Pd/Fe-C_3N_4 composite showed the highest ORR/OER bifunctionality. This material was tested in a Zn-air battery, where it demonstrated performance comparable to a Pt/C + RuO_2 reference at low current densities.

A method was successfully developed to synthesize ORR electrocatalysts from biomass residues (schemed in Fig. 2(a)). The use of conventional activation agents such as H_3PO_4 or KOH was avoided by optimizing the content of Fe precursor (FeC_2O_4) to obtain adequate textural properties and excellent electrocatalytic performance. Electron microscopy studies, performed at the University of Cadiz thanks to an Integrated Infrastructure for Electron Microscopy of Materials (ELECMI) project, confirmed that a significant fraction of Fe formed small clusters likely coordinated with N, with the best ORR activity observed in catalysts containing approximately 5 wt.% of Fe (Fig. 2 (b,c)). The reproducibility of this method was confirmed by studying different biomass residues, with oceanic posidonia yielding the best performance.

In an anion-exchange direct methanol fuel cell (ADMFC) device, one of the electrocatalyst prepared by the above-mentioned method achieved a power density similar to that of a 40 wt.% Pt/C in a membrane electrode assembly (MEA). While the power density did not surpass that of state-of-the-art metal-nitrogen-carbon catalysts, its potential was confirmed by the low resistance, high methanol tolerance, and excellent stability. The performance and durability of Fe-N_x-C based materials as cathode catalysts in ADMFCs was found to be enhanced by the presence of low amounts of Pt nanoparticles (~2 wt. %). Structural modifications in Pt, as observed through X-ray diffraction (XRD), were linked to an

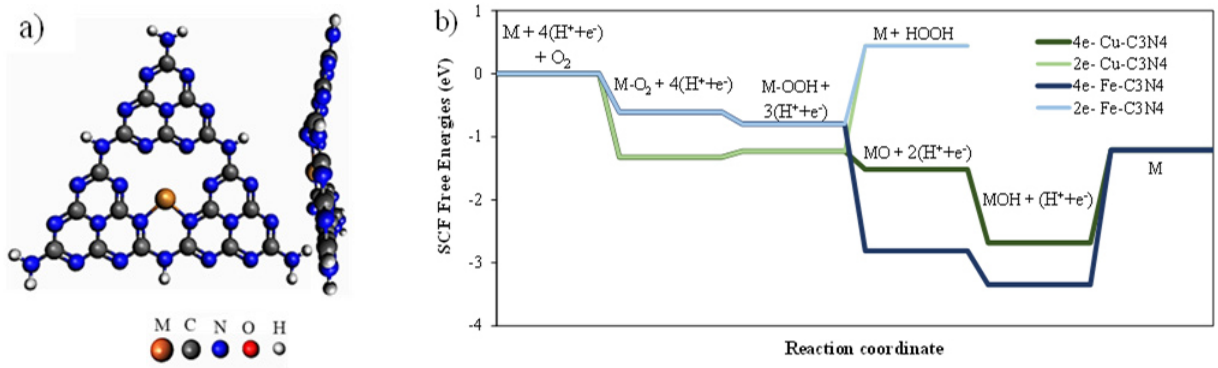

Figure 1. a) M-C3N4 optimized structure used and b) ORR free-energy diagrams (E = 0.8 V) showing 4- and 2-electrons pathways [1].

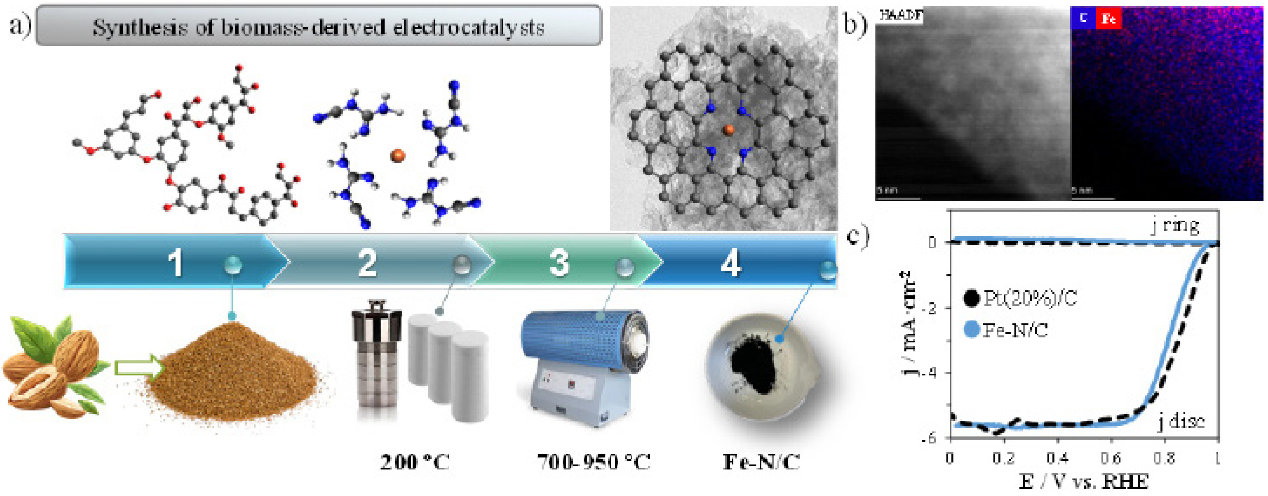

Figure 2. a) Scheme of the preparation procedure, b) characterization by scanning transmission electron microscopy with high-angle annular dark field imaging and energy dispersive X-ray spectroscopy, c) electrocatalytic activity towards ORR (1600 rpm, 0.1 M KOH solution) [5].

increased methanol tolerance. Pt-Fe based materials demonstrated superior durability compared to Pt-free materials, attributed to a synergistic effect preventing agglomeration and metal leaching. Additionally, a biomass-derived material with low Pt content was successfully applied as a cathode catalyst in an electroreforming cell, achieving a current at 60°C comparable to that of a Pt/C cathode containing 5-times higher Pt loading. A 30 h durability test at 125 mA cm^{-2} revealed significant degradation of the Pt/C catalyst mainly due to nanoparticle aggregation, whereas no significant modifications were detected for the biomass-derived catalyst. Finally, two metal tellurates were evaluated as ORR electrocatalysts for direct hydrogen peroxide electrosynthesis in alkaline media. Cu_3TeO_6 displayed instability at low potentials and mixed selectivity, whereas the Ni_3TeO_6-based composite exhibited excellent durability and selectivity. The addition of carbon black was necessary to enhance conductivity. However, excessive amounts negatively impacted selectivity, with the optimal Ni_2TeO_6:Vulcan ratio determined to be 2:1 by weight.

Conclusions

Carbon materials with different textural properties were prepared containing nitrogen heteroatoms such as nanodomains of C_3N_4 or N-functional groups on the carbon surface and several metallic phases including highly dispersed Cu and Fe, but also nanoparticles of Pd or Pt as second metallic phases. Some experimental studies were complemented with computational DFT modelling for a better understanding of the reactions and the nanoparticle-support interaction. ORR was the most studied electrochemical process during this Thesis, and some aspects like catalyst durability and methanol tolerance were especially addressed. Furthermore, the materials containing Pt and Pd were evaluated as HER electrocatalysts and Pd-based materials as bifunctional ORR/OER catalysts for a Zn-air battery air electrode. The feasibility of the biomass-derived materials production and application in an ADMFC device was confirmed by different studies in MEA conformation using real working conditions and long-term durability tests.

Acknowledgments

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High-performance and environmentally friendly electrocatalysts: perovskite, metal hexacyanoferrate, and carbon composites for Zn-batteries and beyond

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Objectives and novelty

The doctoral thesis investigates sustainable, low-cost, and safe alternatives for energy storage systems by developing advanced cathode materials for zinc-based batteries such as Zn-air (ZAB) and Zn-ion (ZIB) batteries, and electrocatalysts for the electrochemical reduction of nitrates (NO_3RR) to ammonia. The study focuses on synthesizing electrocatalysts based on perovskite-type metal oxides-carbon composites and metal hexacyanoferrates, optimizing green synthesis methodologies (including mechanochemical, hydrothermal, and sol-gel processes) to enhance electrochemical performance through improved particle size control, intimate phase interactions, and scalable, eco-friendly production routes.

A significant contribution of this work is its detailed examination of the role of the carbon material, which is pivotal in enhancing the electrocatalytic activity across all studied reactions yet often remain underemphasized in the literature, defined just as an "additive". By incorporating carbon materials, the results demonstrate improved electron transfer, increased exposure of active sites, and enhanced interfacial interactions with perovskite-type metal oxides, thereby enhancing the electrochemical performance in oxygen reduction (ORR) and oxygen evolution reactions (OER) for ZABs as well as the capacity in ZIBs. This comprehensive approach not only advances our understanding of electrocatalyst behavior but also paves the way for the development of more efficient and robust energy conversion systems based on materials mixed with carbon materials.

Results

The most significant outcomes of this doctoral work encompass the development and optimization of novel electrocatalysts that show enhanced performance in zinc-based energy storage systems and green ammonia synthesis. A major achievement is the successful synthesis of perovskite-type metal oxides-carbon composites and metal hexacyanoferrate-carbon materials-based electrocatalysts, which have been tailored for use as cathodes in ZABs and ZIBs, respectively. Through systematic studies using various synthesis methods, including mechanochemical processes (via a planetary ball mill), as well as hydrothermal and sol-gel treatments, this research demonstrated that optimizing key parameters in the mechanochemical approach (such as low rotation speeds, controlled atmospheres, and short milling times) produces electrocatalysts with smaller nanoparticles, more homogeneous phases, and stronger interactions between active metal oxides and the carbon material. These improvements directly translate into superior bifunctional for ORR and OER, key processes for the effective operation of these batteries.

Another remarkable result is the comprehensive investigation into the role of carbon materials in these electrocatalytic systems. The incorporation of carbon not only improves electrical conductivity but also enhances the dispersion of active sites, facilitates electron transfer, and increases the overall electrocatalytic efficiency. This synergistic effect was observed across multiple studies, including the *in-situ* synthesis of N-doped carbon encapsulated metal oxide nanostructures, followed by a CO_2 activation process, where the formation of porous carbon frameworks and active and well-distributed Co–N_x–C sites (Fig. 1A) significantly boosted electrocatalytic performance and ZAB durability. Additionally, by exploring the effect of Sr substitution in La-based perovskites, the work identified that lower levels of Sr doping (20 % molar ratio with respect La) preserve the perovskite structure while optimizing the oxidation states of Mn and Co, further enhancing the bifunctional electrocatalytic activity for ORR/OER in ZABs. Advanced characterization techniques, such as temperature-programmed desorption/reduction (TPD/TPR), X-ray photoelectron spectroscopy (XPS), and Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) tomography, provided deep insights into the structural and interfacial properties of the electrocatalysts. Specifically, the interaction between perovskite-type metal oxides and the carbon material was measured using the TPD technique, serving as a descriptor of the bifunctional electrocatalytic activity toward ORR/OER (Fig. 1B).

Additionally, the distribution of elements in the GDL was analyzed before and after a stability experiment in the ZAB to understand degradation processes, even though the sample was stable up to 120 h of charge-discharge ZAB cycling (Fig. 2). A different distribution of La within the carbon matrix of the GDL was observed, moving away from the region near the electrolyte, while the electroactive elements remained unchanged. Moreover, the study introduced a green mechanochemical synthesis approach that not only reduced the environmental impact of

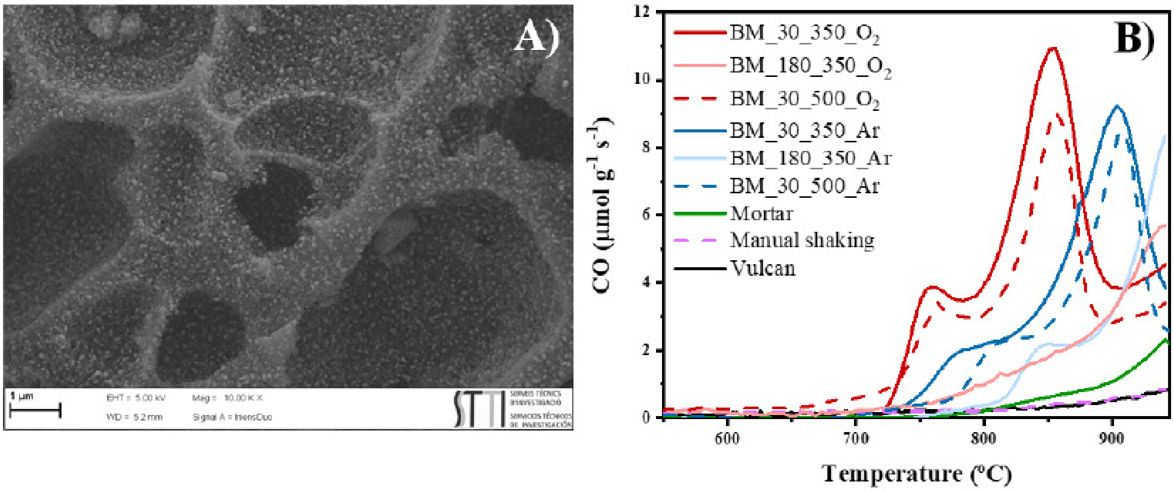

Figure 1. A) SEM image of the in-situ developed electrocatalyst. B) TPD technique results for the perovskite-type metal oxide-carbon composites.

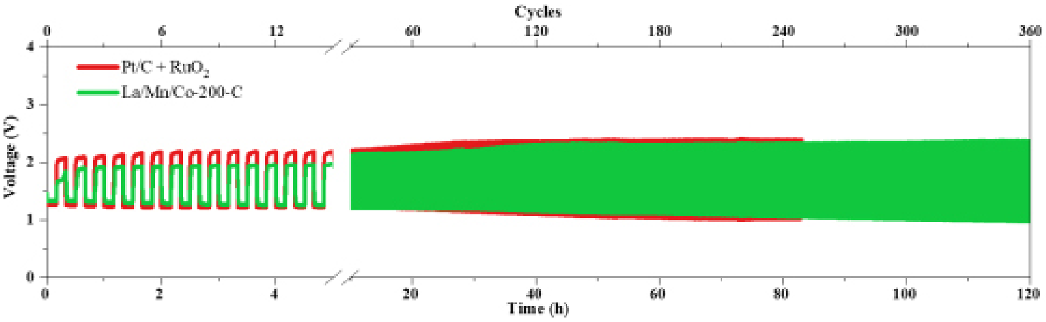

Figure 2. Long-term charge-discharge ZAB stability test. The La/Mn/Co-200-C sample is composed of a mixture of lanthanum, cobalt, and manganese (hydro-)oxides mixed with carbon black material (Vulcan XC72-R).

electrocatalyst production, measured by the E-factor, but also resulted in materials with outstanding electrochemical performance, thereby emphasizing the potential for scalable, eco-friendly manufacturing. Finally, the exploration of ZIBs cathodes through the structural modification of zinc hexacyanoferrate-carbon composites underscored the importance of phase transitions and [Fe(CN)$_6$] vacancy formation in enhancing electroactivity, enhancing the capacity values.

Conclusions

The conclusions of this doctoral research underscore the potential of innovative cathode materials based on metal oxide perovskite-carbon composites and metal hexacyanoferrates for advanced zinc-based batteries and green ammonia synthesis. The work demonstrates that optimized green synthesis strategies, such as mechanochemical, hydrothermal and sol-gel processes, can significantly enhance the electrocatalytic performance.

Advanced characterization techniques such as XPS, TPD/TPR, and FIB-SEM have provided valuable insights into the interfacial interactions between electrocatalyst components and the gas diffusion layer, revealing differentiated behavior of Mn, Co, and La during operation. The study also introduces innovative synthesis strategies, including a CO_2 activation process for in-situ formation of metal nanoparticles encapsulated in nitrogen-doped carbon and a solid-state synthesis method with a low environmental impact. In Zn-ion batteries, the ball-milling of zinc hexacyanoferrate in the presence of carbon materials has been shown to preserve structural integrity and enhance performance through the creation of [Fe(CN)$_6$] vacancies. Collectively, these findings not only advance the development of high-performance, sustainable energy conversion and storage systems but also underscore the crucial role of carbon materials in catalysis, a factor often underemphasized in the existing literature.

Acknowledgments

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Bio methanol production via chemical looping gasification coupled with membrane reactors

Producción de biometanol mediante gasificación con transportadores sólidos de oxígeno y reactores de membrana (Bio-MeGaFuel)

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Abstract

Bio-MeGaFuel is an European project focused on establishing a novel, efficient, and scalable process to convert low-value biogenic residues and organic waste into biomethanol at low cost. By developing chemical looping gasification coupled with membrane reactors, the project aims to achieve Technology Readiness Level 5 (TRL 5) by 2028. The project also aims to intensify the process, reduce the need for downstream treatments, and create synergies with renewable energy sources, such as renewable hydrogen integration. This breakthrough will pave the way for greater adoption of biomethanol in the chemical industry, marine transportation and notably as a feedstock to produce sustainable fuel alternative (SAF) for hard-to-abate sectors such as aviation. By reducing production costs and scaling up biomethanol output, Bio-MeGaFuel aims to offer a renewable, economically viable solution to the fuel challenges faced by sectors critical to the global economy.

Abstract (español)

El proyecto europeo Bio-MeGaFuel tiene por objetivo el desarrollo de un proceso innovador, eficiente y escalable para convertir residuos biogénicos de bajo valor y desechos orgánicos en biometanol a bajo coste. Mediante el desarrollo del proceso de gasificación con transportadores sólidos de oxígeno (Chemical Looping Gasification) acoplada con reactores de membrana, el proyecto tiene como objetivos alcanzar un Nivel de Madurez Tecnológica 5 (TRL 5) para 2028. El proyecto busca también intensificar el proceso, reducir los procesos de limpieza del gas de síntesis y generar sinergias con fuentes de energía renovables mediante la integración de hidrógeno renovable. La innovación propuesta abrirá el camino para un mayor uso del biometanol en la industria química, el transporte marítimo y, especialmente, como materia prima para la producción de combustible sostenible para sectores de difícil descarbonización, como la aviación. Al reducir los costes de producción y aumentar la producción de biometanol, el proyecto Bio-MeGaFuel tiene como objetivo ofrecer una solución renovable y económicamente viable a los desafíos energéticos que enfrentan sectores clave de la economía global.

Introduction

Biofuels play a vital role in decarbonizing the transport sector by providing a low-carbon solution for existing technologies [1]. Biofuel demand in 2022 reached a record high of 170 billion litres [2]. Furthermore, global demand for biofuels is expected to surge, primarily to aid in the decarbonization of sectors where emissions are challenging to mitigate, and alternative solutions are either unavailable or difficult to implement in the near future. These sectors include heavy industry, shipping, aviation, and heavy-duty transport.

Among the currently available types of biofuels, biomethanol, with its unique properties, stands out as one of the clearest alternatives for decarbonizing shipping, and heavy-duty transport. Methanol is a multipurpose fuel that can be used directly in internal combustion engines, blended with other fuels or for producing fuel additives, which improve engine performance. Besides its fuel properties, it is also an important chemical commodity [3]. Methanol is a stable chemical that is in liquid state at ambient temperature and pressure (no need for high pressure and cryogenic conditions), thus making transportation and storage more efficient compared to hydrogen.

However, two key issues may challenge the further uptake of methanol in energy systems: i) methanol is today produced from fossil resources, and ii) methanol is used mainly by chemical industries, leaving small room for the energy sector to count on it.

In fact, with a global production of about 100 million tons of methanol in 2020 (with expectations of increasing to 500 Mt/year by 2050), about 65% is produced by natural gas reforming and ~35% is produced by coal gasification [4]. Only less than 1% of global methanol production is renewable methanol. Therefore, to meet the net zero emission in the near future, the production of renewable methanol must increase significantly to maintain the production of several products we take for granted in modern society. The Bio-MeGaFuel project proposes a novel route that converts low value biomass to methanol via an intensified process with a minimum carbon footprint comparable to conventional methods.

The Bio-MeGaFuel Project

(https://www.biomegafuelproject.eu/)

The goal of Bio-MeGaFuel is to establish a novel efficient, and scalable process to convert low-value biogenic residues and organic waste to biomethanol through chemical looping gasification coupled with membrane reactors. Figure 1 schematically shows the novel proposed plant. The process is based on the novel chemical looping gasification (CLG) concept for producing syngas from biogenic residues and membrane reactors for methanol synthesis from syngas.

The main reactions involved in the biomethanol production process are the following:

$CO + 2\,H_2 \rightarrow CH_3OH$

$CO_2 + H_2 \leftrightarrow CO + H_2O$

$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$

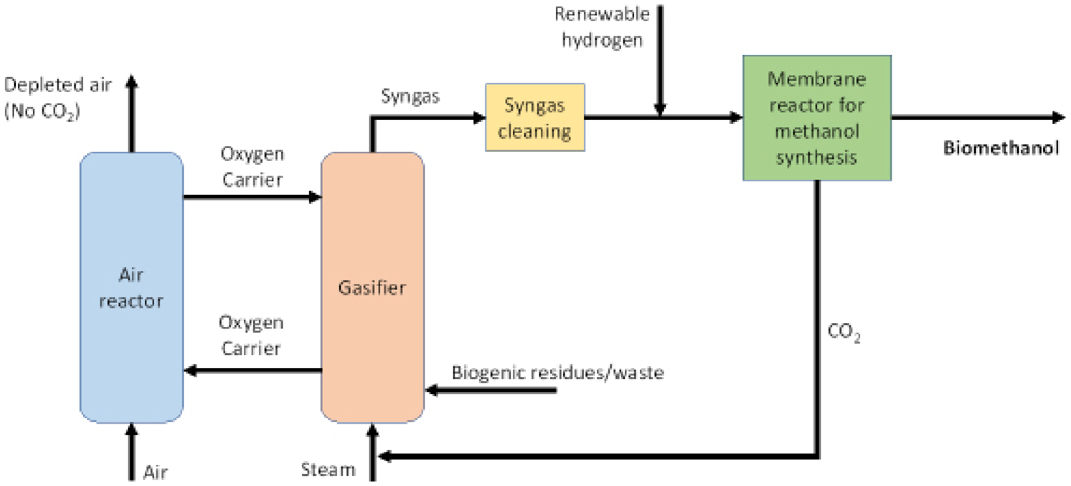


Figure 1. Biomethanol production from biogenic residues and wastes through chemical looping gasification coupled with membrane reactors.

Figura 1. Producción de biometanol a partir de residuos biogénicos mediante gasificación con transportadores sólidos de oxígeno acoplado con reactores de membrana.

Consortium

Bio-MeGaFuel is a collaborative effort between 9 partners from 5 European countries, namely: • RISE Research Institutes of Sweden (Sweden) • GIDARA Energy (Netherlands) • Technische Universität Darmstadt (TUDA) (Germany) • Eindhoven University of Technology (Netherlands) • Spanish National Research Council (CSIC) (Spain) • IVL Swedish Environmental Research Institute (Sweden) • Perpetual Next (Netherlands) • 1CUBE (Netherlands) • Blue World Technologies (Denmark)

The consortium consists of universities, research institutes, end-users and technology providers who individually will investigate and enhance a particular process-step. Many of the partners have been instrumental in the development of included processes and techniques, such as CLG (TUDA and CSIC), membrane reactors for methanol synthesis (TUE), and methanol synthesis through gasification. Dissemination will be also a relevant part of the project.

Figure 2. The Bio-MeGaFuel project value chain.

Figura 2. Cadena de valor del proyecto Bio-MeGaFuel

Bio-MeGaFuel

Funded by the European Union

The following key specific objectives are targeted:

1. Developing biogenic resides and wastes gasification with oxygen carriers to maximize the conversion of biogenic residues and wastes to syngas: Within Bio-MeGaFuel, it is intended to develop CLG of low-value biogenic residues and wastes in pilot units up to 1 MWth, thus establishing the technology at TRL 5-6. Here, 50-70 tons of biogenic residues will be gasified, and performance will be evaluated.

2. Developing of membrane reactors for methanol synthesis: TUE will develop novel thin carbon molecular sieve membranes based on the patented technologies developed by TUE (together with Tecnalia) in the past years. The aim is to significantly increase the yield of biomethanol production from syngas by two-fold.

3. Developing Single-step methanol synthesis with recirculation of CO_2 to maximize carbon and biomass conversion: One of the benefits of Bio-MeGaFuel is the application of membrane technology where unconverted biogenic CO_2 is separated and recirculated back to the gasifier to i) promote the gasification of biomass to reach a higher conversion, and ii) maximize the utilization of the carbon from biomass and its conversion to syngas to increase the syngas yield.

4. Exploitation and whole Value Chain analysis: Market analysis and product uptakes will be done considering the novel route proposed in Bio-MeGaFuel, that includes a lower cost and lower GHG emission. Therefore, several aspects of the new production route will be analyzed through production potential and market analysis, conceptual value chain, business models for the biomethanol, and the barriers and analysis of the end users.

Biomass Chemical Looping Gasification: Ongoing activities at ICB-CSIC

The Combustion and Gasification research group of the Instituto de Carboquímica (ICB-CSIC) is involved in developing biogenic resides and wastes gasification with oxygen carriers. In this sense, Biomass Chemical Looping Gasification (BCLG) represents an innovative process with the potential of reducing costs and emissions compared to other gasification technologies [5-7]. In BCLG, a solid oxygen carrier circulates between two interconnected fluidized bed reactors, fuel and air reactors, providing the oxygen needed for partial oxidation of the solid fuel and the heat necessary for the endothermic reactions taking place for syngas production. The main advantage of BCLG is the production of high-quality syngas with reduced tar content, non-diluted in nitrogen, without using costly pure oxygen and without CO_2 emissions to the atmosphere. In fact, BCLG process can operate at autothermal conditions with all the carbon compounds exiting the system in the fuel reactor stream. The separation and further storage of the CO_2 present in the syngas allows CLG operation without any emission.

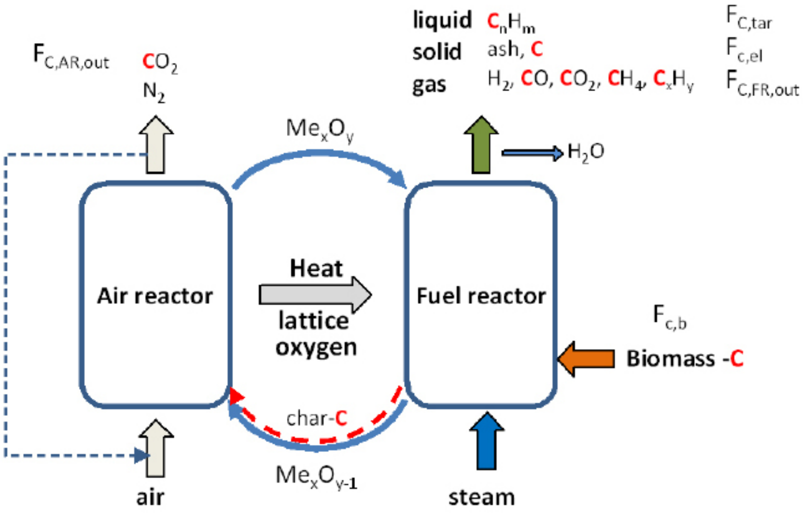


Figure 3. Scheme of the Chemical Looping Gasification process.

Figura 3. Esquema del proceso de gasificación con transportadores sólidos de oxígeno.

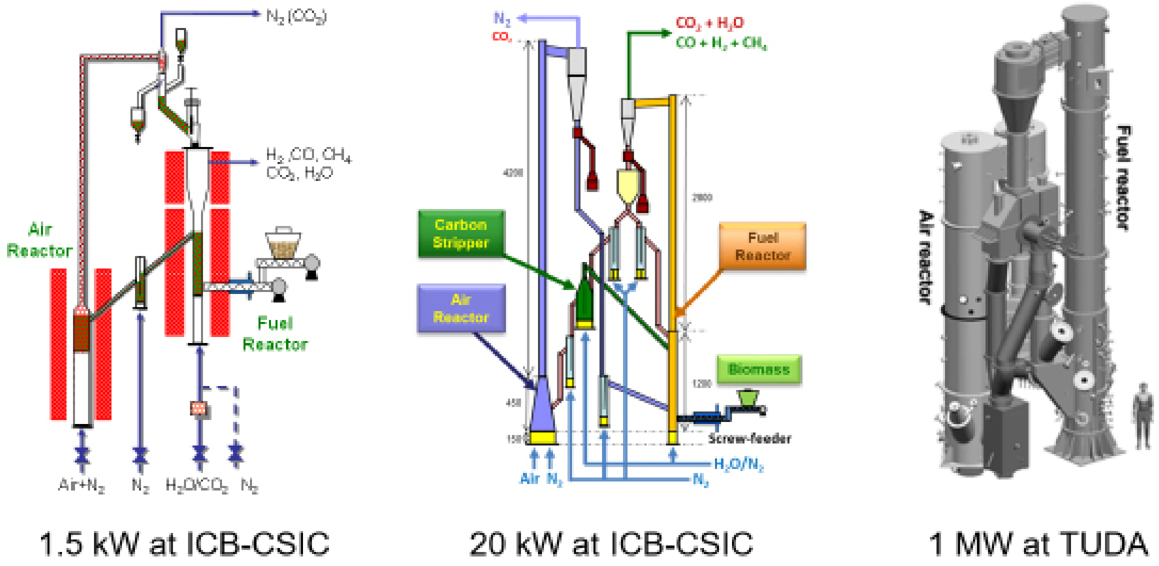
The schematic illustration of this process is shown in Figure 3. The biomass is converted into gaseous (pyrolysis gas), liquid (tar) and solid (char) products in the fuel reactor and then these products may be partially oxidized by the oxygen carrier and the gasifying agent. Thus, solid fuel is converted to synthesis gas and the oxygen carrier is reduced in parallel. The oxygen carrier is denoted by Me_xO_y and $Me_xO_{7\text{-}1}$, where MexOy is a metal oxide and $Me_xO_{7\text{-}1}$ its reduced compound. The reduced oxygen carrier goes to the air reactor where it is regenerated in air atmosphere to begin a new cycle. Moreover, the reactions that occur in the air reactor are exothermic, so the required heat for fuel gasification is provided by the oxygen carrier circulating from the air to the fuel reactor.

A relevant feature in the process operation is the method for controlling oxygen used for gasification. This oxygen can be perfectly controlled by feeding the required amount in the air reactor, that it is fully transferred to the oxygen carrier and then to the fuel for gasification. To allows operation, a part of the nitrogen obtained at the air reactor outlet is recirculated for fluidization. The main advantages of this method are that the oxygen transferred from the air reactor to the fuel reactor does not depend on the solid circulation flow, allowing high flows of oxygen carrier circulation, and the possibility of obtaining pure nitrogen in the outlet stream of the air reactor.

The oxygen carrier to be used in the project will be ilmenite. Ilmenite is a natural ore mainly composed by iron titanium oxide, $FeTiO_3$, that needs to be oxidised previously to be used in the process. The redox pair $FeTi_2O_5/FeTiO_3$ is system used in the process to transport oxygen from air to the fuel for gasification.

The potential feedstock includes abundantly available biogenic residues and wastes in five categories: biogenic waste (B-wood), waste streams (RDF), agricultural residue (olive pits, buckwheat husk, etc.), woody biomass and forestry residue, and microalgae. In fact, micro-algae can be an interesting precursor for third-generation biofuels and with no effect on the food change.

Several installations will be used in the project to produce pure syngas through BCLG. Figure 4 shows the schemes of the different CLG continuous units. Lab-scale gasification tests will be carried out in a 1.5 kWth CLG reactor at CSIC under continuous operation using ilmenite as the oxygen carrier and five biogenic fuels. Tests will be conducted at different temperatures and with two gasification agents (H_2O or CO_2 and their mix) to define viable gasification conditions. Thus, a comprehensive screening of fuels and operating conditions will be carried out based on the results obtained. Then, three types of biomasses (one of them being micro-algae) will be tested in a 20 kW CLG unit at CSIC using steam/CO_2 as gasifying agent. The results obtained will be considered for the selection of two types of feedstocks and the definition of operating conditions during pilot testing at 1 MWth scale at TUDA (Germany). Syngas composition obtained at 1 MWth scale will be used at TUE for the optimum design, production and testing of the membrane for biomethanol production.



1.5 kW at ICB-CSIC

20 kW at ICB-CSIC

1 MW at TUDA

Figure 3. Scheme of the CLG continuous units.

Figura 3. Esquema de las plantas de gasificación con transportadores sólidos de oxígeno.

Acknowledgements

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"Desafios y Soluciones para la Transición Energética"

Curso Extraordinario de Verano - Universidad de Zaragoza

Tomás García y José Luis Pinilla, directores del curso.

El Instituto de Carboquímica (ICB-CSIC) organiza el Curso Extraordinario de Verano de la Universidad de Zaragoza titulado "Desafíos y Soluciones para la Transición Energética".

Como en ocasiones anteriores, el curso tendrá lugar en Residencia Universitaria de Jaca. Las fechas elegidas para esta edición son del 30 de junio al 2 de julio de 2025.

Este curso ofrece una visión actualizada sobre los retos y avances tecnológicos clave en la transición hacia un modelo energético sostenible. Se abordarán soluciones innovadoras para la mitigación de emisiones y la descarbonización del sistema energético, con un enfoque multidisciplinar.

Está especialmente dirigido a estudiantes de últimos cursos de grado y máster, estudiantes de doctorado y profesionales interesados en el ámbito de la energía sostenible.

El programa se estructura en tres bloques temáticos, con ponencias a cargo de investigadores del ICB-CSIC, INCAR-CSIC, ICP-CSIC y la empresa MOEVE:

Bloque 1: Energía y Desarrollo Sostenible

- Bioenergía: la carrera hacia el balance cero de emisiones – Covadonga Pevida (INCAR-CSIC)
- Cambio climático: reducción de emisiones de CO_2 y más allá – Alberto Abad / María Teresa Izquierdo (ICB-CSIC)
- Amoníaco verde como vector energético – Christian Di Stasi (ICB-CSIC)
- Dinámica grupal: energía y cambio climático – Alberto Abad / María Teresa Izquierdo (ICB-CSIC)

Bloque 2: Economía Circular y Recursos Renovables

- Biorrefinerías: del petróleo a los residuos – Joana Frontela (MOEVE)
- Conversión de biomasa y residuos: Economía circular – Ramón Murillo (ICB-CSIC)
- Conversión de biomasa y residuos: Biocombustibles – Daniel Torres (ICB-CSIC)
- Conversión de CO_2 a combustibles renovables – José Enrique García-Bordejé (ICB-CSIC)
- Taller práctico: Aprovechamiento sostenible de recursos – Ramón Murillo / Daniel Torres (ICB-CSIC)

Bloque 3: Innovación en Almacenamiento y Nuevas Tecnologías Energéticas

- Hidrógeno: la energía del futuro – Miguel Antonio Peña (ICP-CSIC)
- Vectores energéticos sostenibles: Aprovechamiento solar – Alejandro Ansón (ICB-CSIC)
- Dispositivos electroquímicos de generación y almacenamiento de energía – Cinthia Alegre / David Sebastián (ICB-CSIC)
- Cómo hacer el almacenamiento de energía más circular – Cristina Pozo (ICB-CSIC)
- Quiz interactivo: retos de la energía hacia los ODS – José Luis Pinilla / Tomás García (ICB-CSIC)

Más información e inscripciones: ***https://cursosextraordinarios.unizar.es/index.php/node/2213***

El Grupo Español del Carbón tiene el placer de invitaros a su XVII Reunión que en esta edición tendrá su sede en Zaragoza. El evento, organizado por el Grupo Español del Carbón (GEC) con el apoyo de los socios del Instituto de Carboquímica (ICB-CSIC), se celebrará en el edificio Etopía, del 19 al 22 de octubre de 2025.

El Comité Organizador os invita a compartir vuestros últimos avances en el estudio de los materiales de carbono y sus aplicaciones y las tecnologías de generación limpia de energía, así como a establecer nuevas colaboraciones que permitirán la interacción con expertos y la creación de sinergias. Asimismo, animamos especialmente a los jóvenes investigadores a participar en este foro dónde encontrarán una inmejorable oportunidad para interactuar y exponer sus resultados.

Os animamos a enviar vuestras contribuciones en uno de los siguientes topics:

1. Materiales de carbono: Nanomateriales, materiales compuestos y materiales avanzados (1D, 2D, 3D).
2. Tecnologías de generación sostenible de energía.
3. Aplicaciones en almacenamiento de energía.
4. Aplicaciones catalíticas, medioambientales y en salud.

Además del programa científico, también se han preparado actividades socioculturales para que disfrutéis al máximo de vuestra estancia en Zaragoza, haciéndoos partícipes de la gastronomía y las tradiciones de la cultura aragonesa.

Podréis encontrar más información sobre la Reunión, el programa, la inscripción y el formato y envío de resúmenes en la página web ***www.gecarbon2025.org***

El Comité Organizador de la XVII Reunión del GEC

Socios protectores del Grupo Español del carbón

Química del Nalón

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