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Editores Jefe:

Covadonga Pevida García
Instituto de Ciencia y Tecnología del Carbono (CSIC)

José Luis Pinilla Ibarz
Instituto de Carboquímica (CSIC)

Editores:

Víctor Karim Abdelkader Fernández
Universidad de Granada

Noelia Alonso Morales
Universidad Autónoma de Madrid

Raúl Berenguer Betrián
Universidad de Alicante

Francisco Heras Muñoz
Universidad Autónoma de Madrid

Juana María Rosas Martínez
Universidad de Málaga

Fabián Suárez García
Instituto de Ciencia y Tecnología del Carbono (CSIC)

Editorial

Abrimos este número 73 del Boletín del Grupo Español del Carbón con una entrevista a Semih Eser, Profesor de Ingeniería Energética y Geoambiental en la Universidad de Penn State (Estados Unidos). El profesor Eser mantiene una larga relación con el GEC, fruto de su colaboración con destacados miembros de nuestro grupo. En la entrevista, nos habla sobre estas colaboraciones y comparte su visión sobre la investigación en materiales de carbono.

Continuamos con una reseña de la cuarta edición del curso de verano "Nanomateriales de carbono y sistemas relacionados: Síntesis, caracterización, propiedades y aplicaciones en Energía", dirigido por el Dr. Raúl Arenal (INMA, CSIC-Universidad de Zaragoza) y por el Prof. Wolfgang Maser (Instituto de Carboquímica, ICB-CSIC, Zaragoza) que tuvo lugar en Jaca el pasado Julio.

En este número contamos también con dos reseñas de proyectos de la Universidad de Alicante. El proyecto EVACAR, desarrollado por el Grupo de Investigación en Materiales Carbonosos y Medio Ambiente (MCMA) y financiado por la Agencia Valenciana de la Innovación. Este proyecto tiene como objetivo la investigación y desarrollo de recubrimientos y rellenos basados en carbón activado procedentes de residuos de biomasa, que sean capaces de mejorar el almacenamiento y uso del hidrógeno. Por otra parte, el proyecto BioEnH₂, que es una colaboración entre el grupo MCMA y el grupo de Electrocatalisis y Electroquímica de Polímeros. Este proyecto se centra en el estudio de obtención, almacenamiento y distribución de energía e hidrógeno renovables a partir de biomasa como vector para una transición energética sostenible, y está financiado por el Centro para el Desarrollo Tecnológico Industrial (CDTI) y la Agencia Estatal de Investigación (AEI) a través del programa Líneas Estratégicas TransMisiones.

Cerramos este número con tres

reseñas de Tesis Doctorales: Iván Samprón Alonso (Instituto de Carboquímica-CSIC), Miguel Ángel Rodríguez-Cano (Universidad de Málaga) y Jéssica Justicia González (Universidad Autónoma de Madrid).

Aprovechamos para recordaros los diferentes premios que se otorgan anualmente a los mejores trabajos publicados en el Boletín en varias categorías: artículo científico, artículo de divulgación y/o investigación docente, y la contribución de un artículo científico en la sección "Nuevos Grupos". ¡Os animamos a todos a participar!

Covadonga Pevida García
José Luis Pinilla Ibarz

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Entrevistamos a ...

Hoy tenemos el placer de entrevistar al profesor Semih Eser. Muchos de vosotros lo conoceréis, además de por su trayectoria científica y su carácter bondadoso y colaborativo, porque es un “fan” del GEC.

Semih Eser is a Professor of Energy and Geo-Environmental Engineering at Penn State. He obtained his Ph.D. (1986) in Fuel Science from this University. After a brief period at the Department of Chemical Engineering at Auburn University, he returned to Penn State (1988) and he has been there since then. Over his career, he has held several key positions, such as Acting Head of Department of Energy and Geo-Environmental Engineering and Director of the Laboratory for Hydrocarbon Process Chemistry at the EMS Energy Institute. He currently teaches at the John and Willie Leone Family Department of Energy and Mineral Engineering and direct the Carbon Materials Program at the EMS Energy Institute.

Professor Eser is also actively involved in academic publishing, serving on the editorial boards of the Journal of Oil, Gas and Coal Technology, Journal of New Carbon Materials, and as section editor of Energy Sustainability in the Journal Sustainability. Eser's research interests include the reactivity and microscopic characterization of cokes and carbons, coke/carbon formation and deposition mechanisms, inhibition of undesired carbon deposition, molecular analysis and processing of petroleum feedstocks.

Muchas gracias Professor Eser por aceptar nuestra invitación.

Nos consta que su relación con científicos españoles comenzó hace muchos años y que se ha mantenido durante su trayectoria profesional. Remember your first interaction with a Spanish scientist? What stands out from your professional collaboration with Spanish researchers? Any interesting anecdotes?

Thank you for your kind invitation. It is an honor to be invited, as I consider GEC the premier organization of carbon scientists and researchers in recent decades.

As you mentioned, I have had the pleasure of meeting and collaborating with several Spanish scientists. My first interaction was with Juan Jose Rodriguez at a carbon conference in Granada. Our initial conversation led to a wonderful friendship and collaboration in research. Quite a few years later, I had a great sabbatical year with Juan at UAM, where I met a remarkable group of faculty members and students. I must also mention my collaboration with Ana Garcia at INCAR and my visit with Pepe and Tomas in Malaga, all in the same year.

I also had the pleasure of hosting several Spanish researchers at Penn State over the years, exchanging ideas and sharing experimental facilities. In this context, I would like to mention the terrific work Noelia did during her stay here.

What stands out in all my collaborations with Spanish researchers is their friendliness and modesty, along with their command of their area of research. An elegant sense of humor and great camaraderie also struck me as common traits of the Spanish researchers I have met. At international meetings, you will always find me with the Spanish group, the liveliest group in every meeting. Outsiders often think that I am from Spain.

I don't have a good memory for recalling anecdotes, but there are many happenings that I will never forget. For example, sitting on a hill with Juan and conversing while gazing at the lights of Alhambra, and joyful interactions with Pepe and Tomas along with their students at Chiringuitos in Malaga.

Professor Eser, you have participated in several GEC Meetings, what was your experience at these conferences?

While my Spanish comprehension is not yet at the level to fully understand the presentations and discussions, I enjoy observing the lively interactions among the colleagues. Such immersion in Spanish language and culture at these meetings and their venues gives me great pleasure.

I should note that these meetings are very well organized and provide excellent opportunities for all participants to engage in focused learning and networking.

Tell us a little about your career in carbon science. How did you start doing research in carbon and how has it evolved over the years? What are your main topics of expertise? Do you anticipate a bright future for carbon research?

My research journey started at the Middle East Technical University, where I conducted a master's thesis study on the pyrolysis of coals and related materials. The primary objective of that work was to develop liquid products rather than solid carbons, because at the time the world was seeking alternatives to petroleum following the 1973 and 1979 petroleum supply crises.

In 1981, I received a scholarship to pursue a PhD degree at Penn State University to study making solid carbons by carbonization of petroleum feedstocks. While my lab colleagues explored liquefaction or gasification of coal, the purpose my research was to identify suitable feedstocks and carbonization conditions for producing high-quality sponge coke. Sponge coke is used to manufacture carbon anodes for aluminum smelting. This research provided insight into the formation of shot coke, a troublesome byproduct, formed during the delayed coking process. Developing the means of preventing shot coke formation has been of significant interest for some petroleum companies.

I also need to mention another product of delayed

coking, needle coke, which has played a central role in my research career. My research on needle coke focused on understanding the relationships between the chemical constitution of petroleum feedstocks and the development of an intermediate carbonaceous mesophase, a crucial liquid crystalline phase that hardens into graphitizable needle coke. Needle coke is used in manufacturing graphite electrodes in electric-arc furnaces. The research challenge in this area involved unraveling the exceedingly complex chemistry of carbonaceous mesophase formation. The procedures developed in our laboratory associated the chemical constitution of feeds with needle coke quality. These procedures have been adopted by three major petroleum/coke companies, enabling them to manufacture better needle cokes for graphite electrodes to afford more efficient recycling of iron and steel, resulting in significant energy and materials savings.

In the area of amorphous carbons, Katia Gergova and I adapted one-step pyrolysis activation techniques to produce activated carbons from anthracite and agricultural byproducts, such as fruit stones. The conventional activated carbon preparation technique involves separate carbonization and activation (with steam) steps. Carrying out pyrolysis in the presence of water vapor (one-step pyrolysis/activation) has proved to be a useful method for tailor-making activated carbon materials. These carbons have unique properties with respect to porosity and surface functional groups. Achieving this conversion with lower energy inputs helps optimize the activated carbon manufacturing processes for the desired end uses. I must note that Spanish researchers have been very successful in the development of activated carbons from different sources, including agricultural byproducts.

As well known, solid carbons possess impressively diverse structures and properties. Consequently, they find many diverse applications in the materials industry. One weakness of carbon materials in some applications is their low resistance to oxidation. Understanding oxidation reactivity of carbon materials in different environments is, therefore, critical. My research in this area has focused on studying the relationships between microstructure and reactivity of carbon materials using in-situ techniques. These techniques include environmental SEM, and in-situ x-ray diffraction (in collaboration with Isabel Fonseca from NOVA in Portugal) coupled with the use of microscopic characterization and Temperature-Program Oxidation. The applications from this research program have ranged from understanding the failure of C-C composite aircraft breaks in the presence of de-icing fluids on airport runways, to clarifying the mechanism of carbon deposit formation on metal surfaces, and quantifying the extent of graphitization in carbon materials.

Not all carbons are good! I have also done research on undesirable formation of solid carbon deposits that accumulate on metal surfaces from decomposition of jet fuel, diesel fuel, and gasoline, as well as lubricating

oils. This problem has become more pressing since combustion engines are being operated at higher temperatures and pressures for increased performance and efficiency. A particular concern with solid deposition relates to the operation of advanced aircraft. Our research program has identified different mechanisms of solid carbon deposition on metal surfaces that led to the development of strategies for inhibiting the deposit formation. This can be accomplished through judicious selection of metal alloys for manufacturing the fuel system components and by pre-oxidation or by coating of metal surfaces to produce protective thin films.

The future of carbon materials looks very promising, considering the unique diversity in allotropy with 0-, 1-, 2-, and 3-dimensional geometry spanning a wide range of materials, including fullerenes, nanotubes, graphenes, graphite, and diamond, and all with just one element of wonder. I believe that innovative applications of carbon materials will bring forth new revolutions, in corollary to charcoal and metallurgical coke that ushered in the 2nd Industrial Revolution. A summer school organized by Raul Arenal and Wolfgang Maser of the University of Zaragoza this year has helped me envision the new frontiers of carbon nanomaterials in energy conversion and storage, environmental remediation, biomedical engineering, and functional material applications. Graphite has the distinction of being the only material that gets stronger with increasing temperature; new architectures of carbon nanomaterials, possibly their hybrids, will continue to surprise us, as Professor Philip L. Walker, Jr. had foreseen half a century ago in “Carbon: An Old But New Material.”

During your extensive career in carbon science and application, you have frequently collaborated with companies and industry partners. Can you offer advice to young scientists on fostering scientific collaboration?

I can share some insights that I have gained throughout my career.

It is important to remember that industry primarily focuses on the R&D question of know-how to gain a competitive advantage. As a scientist, your focus must also encompass scientific inquiry (know-what) and the social and environmental relevance of your research (know-why). Establishing a good balance between these interests, which usually should not clash, can play a crucial role in securing and maintaining support for your research program.

You have been honored with multiple awards from the American Chemical Society, most recently from the Division of Energy and Fuels in 2023. How have these accolades impacted your career?

It is undoubtedly gratifying to be recognized by one's peers. Moreover, receiving an award increases your chances of being considered for subsequent recognition. I believe, for example, that having

received a Fulbright Scholarship had a positive impact on my selection as an ACS Fellow. Further, the nomination process for an award gives an opportunity for self-reflection and self-evaluation. Correspondence with your referees and peers during a nomination process also affords means of closer acquaintances that can be mutually beneficial.

We believe there are significant differences in conducting research in Spain and the USA. Could you outline the main contrasts?

My response to this question is based solely on my personal observations and is not supported by formal inquiry. The main contrasts I have noticed lie in two areas: How research is funded, and how it is conducted.

In Spain, there is a stronger public funding structure from both central and local governments compared to the United States. These funding opportunities are distributed more equitably, with fewer instances of unfair practices interfering with the process. In contrast, private enterprises in the United States play a larger role in funding research than governmental organizations. This leads to research programs that are more biased toward the agendas of the funding companies rather than focusing on pressing social, environmental, and public health issues.

Regarding university research, the main contrast lies in how individuals are involved in the research organization. In the United States, tenure-line assistant professors are given a start-up fund that may include support for graduate students. They are expected to establish their own laboratories and generate data for publications to meet the tenure review requirements typically within six years. Often, they need to establish internal or external collaborations themselves.

In Spain, young researchers are incorporated into multi-faculty research groups mentored by senior faculty members. This provides a built-in mentoring structure and a natural environment for research collaboration within the group. I perceive this as a less stressful entry into academic research and advancement into higher ranks than the lone wolf approach that prevails in US universities.

One must note that both systems have their advantages and disadvantages, and different approaches have serious implications for teaching, research, and service tasks of faculty members, as well as the quality of graduate and undergraduate education in academia.

What are your thoughts on the increasing number of manuscripts being submitted to scientific journals? Do you think this has impacted the quality of publications? Additionally, what is your take on the growing number of scientific journals?

I have not given much thought to these trends, although they clearly relate to the classic dichotomy

of quality versus quantity in terms of the number of publications. Scientific review of submitted publications is a voluntary activity. Hence, increasing numbers of submitted manuscripts put pressure on journal editors to find qualified reviewers. This, in turn, increases the pressure on reviewers for timely completion. Further, the limited number of papers that can be accommodated in a journal issue leads to a higher rejection rate from journals with high impact factors.

In the publications market, the increasing demand to publish has led to a growing number of scientific journals. One factor contributing to this demand may be the requirement by academic departments for students to publish in peer-reviewed journals as a condition for earning their PhD degrees. I am confident that journal editors and journal owners are working on addressing these issues, but the challenge lies in bringing all the involved parties (academic departments and journal editors) together to find a solution.

4th International Summer School on "Carbon and related nanomaterials: Synthesis, characterization, properties and applications in energy"

Del 15 al 19 de Julio de 2024 tuvo lugar en Jaca (Huesca), en el marco de los Cursos Extraordinarios de la Universidad de Zaragoza, la “Cuarta Escuela de verano sobre “Nanomateriales de carbono y sistemas relacionados: Síntesis, caracterización, propiedades y aplicaciones en Energía”, dirigido por el Dr. Raúl Arenal (INMA, CSIC-Universidad de Zaragoza) y por el Dr. Wolfgang Maser (Instituto de Carboquímica, ICB, CSIC, Zaragoza).

Esta nueva edición de la Escuela internacional ofreció una introducción multidisciplinaria al campo de los nanomateriales de carbono (Fullerenos, nanotubos de carbono, grafeno y derivados, carbon dots, etc.) y sistemas relacionados (sistemas 2D, TMDs, MOFs, perovskitas entre otros). En la Escuela, un curso reconocido con 1 crédito ECTS por la Universidad de Zaragoza, participaron 16 alumnos procedentes de España, Reino Unido, EEUU, Brasil, e Irán, con un amplio abanico de diversas especialidades en áreas de física, química, ingeniería, materiales y energías renovables, entre otros. Gracias al patrocinio del curso por parte de La Fundación Agencia Aragonesa para la Investigación y el Desarrollo (ARAID), La Real Sociedad Española De Química (RSEQ) y su grupo especializado de Nanociencia y Materiales Moleculares (GENAM) y La Universidad Pública de Navarra (UPNA) el curso pudo ofrecer este año varias becas de inscripción para estudiantes y jóvenes investigadores en su primera etapa de carrera.

Las clases, impartidas en 25 horas por 12 docentes procedentes de España (tanto del CSIC (ICB-CSIC, ICN2-CSIC) como de Universidades (Zaragoza, Valencia, Murcia, Cartagena), Francia (Univ. Montpellier II) y Reino Unido (Univ. Sussex) cubrieron temáticas de diferentes bloques: Introducción a los diferentes tipos de nanomateriales enfocándose en la particularidad y relevancia de los diversos nanomateriales en el contexto de aplicaciones ya abordando aspectos de su síntesis, funcionalización y procesado; Técnicas de caracterización y de acercamientos teóricos ofreciendo una sólida base a las diferentes técnicas y describiendo su importancia para determinar las propiedades de los nanomateriales a diferentes escalas; Aplicaciones en energía abordando los fundamentos de dispositivos relacionados como la relevancia especial de los nanomateriales como componente en aplicaciones fotovoltaicas, baterías y para la generación de hidrógeno verde. Los detalles del programa se encuentran en la página web:

<https://cursosextraordinarios.unizar.es/curso/2024/4th-international-summer-school-carbon-and-related-nanomaterials-synthesis>.

Además del programa oficial, se organizó una mesa redonda a mitad de curso debatiendo retos y oportunidades relacionados con los nanomateriales (Prof. Wolfgang Maser), la caracterización (Dr. Raúl Arenal) y aspectos en aplicaciones fotovoltaicas (Prof. Antonio Urbina). Fue una sesión con mucha interacción directa entre alumnado y profesorado proporcionando un valor añadido a la escuela. La Escuela finalizó con resumen general en la que se debatió aspectos de relevancia de los tres diferentes bloques abordados en la escuela subrayando el progreso científico-tecnológico, asimismo su importancia para afrontar los actuales retos de la sociedad en la temática de energía y sostenibilidad. Se consensuó que el desarrollo de soluciones requiere el esfuerzo de colaboración inter- y multidisciplinario entre científicos y tecnólogos.

El desarrollo de la Escuela en el ambiente “único” de la residencia de Jaca contribuyó a establecer interacciones fructíferas entre docentes y alumnos. Asimismo, cabe destacar el apoyo recibido por parte del equipo de los Cursos Extraordinarios de la Universidad de Zaragoza en todo momento. Con todo ello, la vista ya está puesta en la quinta edición de esta Escuela para julio de 2026.

Los organizadores

Raúl Arenal (LMA, INMA, CSIC-Universidad de Zaragoza) y Wolfgang Maser* (ICB-CSIC)



Foto con los docentes y participantes del curso en frente de la residencia universitaria de Jaca.

Desarrollo de recubrimientos basados en eva-carbón activado con propiedades aislantes para el almacenamiento de hidrógeno (EVACAR)

Jessica Chaparro Garnica, Cristian Jaimes Paez y Diego Cazorla Amorós

Departamento de Química Inorgánica e Instituto de Materiales. Universidad de Alicante. Apartado 99. 03080 Alicante

El grupo de investigación Materiales Carbonoso y Medio Ambiente (MCMA) de la Universidad de Alicante a través del proyecto EVACAR, aprovecha residuos para la preparación de carbones activados con excelentes propiedades para el almacenamiento de hidrógeno. Con el proyecto EVACAR, se pretende la construcción de un novedoso prototipo de tanque ligero y con unas propiedades aislantes mejoradas que permitan un buen almacenamiento de hidrógeno a largo plazo en condiciones criogénicas, así como la realización de un modelado de tanque de almacenamiento para su escalabilidad industrial. El equipo de EVACAR, proyecto financiado por la Agencia Valenciana de la Innovación en el programa valorización y transferencia de resultados de investigación a las empresas (INNEST/2023/7), lo forman Diego Cazorla Amorós, Emilia Morallón, María Ángeles Lillo Rodenas, Ángel Berenguer Murcia, Jessica Chaparro Garnica y Cristian Jaimes Paez. Asimismo, esta investigación se realiza en cooperación con sectores empresariales y entidades de I+D+i, como el Instituto Tecnológico del Plástico (AIMPLAS), Evatalking, GreenE, GreeneE W_2H_2 , en donde cada una de ellas juega un papel esencial para la consecución del proyecto.

El objetivo principal de EVACAR es la investigación y desarrollo de recubrimientos y rellenos basados en carbón activado procedentes de residuos de biomasa, que sean capaces de mejorar el almacenamiento y uso del hidrógeno. Se llevará a cabo la investigación de recubrimientos basados en materiales con gran capacidad de aislamiento térmico empleando polímeros como poli(etilen-vinil acetato) (EVA) y alcohol polivinílico (PVOH) que se combinarán con materiales de alto rendimiento como el carbón activado procedente de la gasificación de residuos biomásicos para conseguir un sistema de almacenamiento de hidrógeno de alta capacidad en condiciones criogénicas. Las principales características de dichos recubrimientos y rellenos serían:

- Aumentar la capacidad de almacenamiento de hidrógeno.
- Mejorar las propiedades de aislamiento térmico de los depósitos.

La investigación que se realizará durante el proyecto permitirá desarrollar tecnologías que mejoren el almacenamiento de hidrógeno como vector energético, con el propósito de facilitar su despliegue en España y posicionar al país como un referente tecnológico en el futuro. Se espera que el hidrógeno

juegue un papel importante en la descarbonización de varios sectores de la economía española, por lo que la investigación realizada en este proyecto es clave para el avance hacia un futuro más sostenible. El proyecto EVACAR surge ante la necesidad de reducir el consumo energético generado durante el almacenamiento del hidrógeno y aumentar la densidad volumétrica del tanque mediante el uso de espumas aislantes basadas en polímeros con cantidades controladas de material carbonoso como material aislante dentro del tanque de hidrógeno y con la incorporación de carbón activado en forma de grano o monolito de forma que se puedan conseguir cantidades de hidrógeno almacenadas del orden de unas 2-3 veces superior a la cantidad de hidrógeno almacenada por compresión. Este sistema de almacenamiento consistirá en el almacenamiento criogénico de hidrógeno a una presión de trabajo de unos 40 bar y a una temperatura de 77 K.

En España, se está desarrollando el almacenamiento de hidrógeno a través de gas comprimido y líquido criogénico, principalmente para abastecer estaciones de servicio de hidrógeno con vehículos con pilas de combustible. Además, el almacenamiento subterráneo de hidrógeno se está considerando como una opción a largo plazo para el almacenamiento a gran escala de hidrógeno renovable. Sin embargo, el principal desafío es la falta de infraestructura de almacenamiento y distribución de hidrógeno en todo el país, lo que dificulta su suministro y distribución a gran escala. El costo y la eficiencia del almacenamiento de hidrógeno también son problemas importantes a resolver. Por lo tanto, la aplicación de tecnologías más avanzadas como el almacenamiento por adsorción en sólidos porosos puede contribuir a la solución de estos problemas. En este caso, la adsorción trabaja a temperaturas y presiones moderadas (a temperatura ambiente se pueden emplear 200 atm y a 77 K se puede trabajar a 40 atm) y se pueden llegar a conseguir valores de almacenamiento gravimétrico y volumétrico cercanos a los requeridos por el DOE para aplicaciones móviles en 2025 (40 kg H_2/m^3).

El almacenamiento en sólidos porosos requiere materiales con adecuada porosidad y forma física (polvo, partícula o monolito). En el almacenamiento criogénico a 77 K, la capacidad de adsorción está determinada por la textura porosa, y existe una correlación entre la superficie específica, capacidad de adsorción y capacidad de almacenamiento. Para la máxima capacidad de almacenamiento volumétrico, es necesario maximizar el contenido en material adsorbente en el tanque reduciendo al máximo su volumen entre partículas, lo que se logra

de polvo compactado o monolitos. La opción de monolitos de carbón activado facilita la manipulación del material y mejora la conductividad térmica del sistema.

La investigación del proyecto se enfoca en desarrollar un material que permita conseguir la porosidad óptima y la densidad máxima para conseguir altas capacidades volumétricas de almacenamiento de hidrógeno. Se busca diseñar materiales aislantes para recubrir los tanques de almacenamiento y el carbón activado en polvo o como monolito será utilizado como relleno en los tanques de almacenamiento de hidrógeno para aumentar la capacidad volumétrica del tanque.

En definitiva, EVACAR se enfoca en adoptar tecnologías que mejoren el almacenamiento y uso del hidrógeno para cumplir con los retos de descarbonización establecidos por el CEIE. Además, dado que los objetivos nacionales van dirigidos no sólo a la producción de hidrógeno renovable sino también al estudio y la minimización de los costes asociados al transporte y almacenamiento del hidrógeno, este proyecto centrado en el almacenamiento es de gran interés y actualidad.

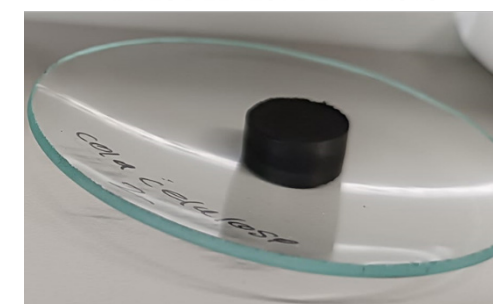
Durante la ejecución del proyecto, se está llevando a cabo la síntesis con éxito de los carbones activados a partir de los residuos de biomasa y la preparación de monolitos utilizando carbón activado comercial y diferentes aglomerantes. En lo que respecta a la preparación de los monolitos, se siguen los siguientes pasos y criterios. Es fundamental homogenizar correctamente la mezcla inicial de carbón activado con los aglomerantes. Posteriormente, se debe monitorear y controlar la cantidad de agua añadida a la mezcla, ya que esta es crucial para la plasticidad y la unión de los componentes. Encontrar un porcentaje óptimo de humedad es esencial en el proceso. Se debe realizar un secado en horno para eliminar la mayor parte de la humedad superficial sin deshidratar completamente la mezcla, lo que facilita el manejo y la posterior compactación. Durante el prensado con prensa hidráulica, es clave mantener los émbolos alineados para asegurar una distribución uniforme de la presión. Finalmente, el curado, tanto a baja como a alta temperatura, es crucial para mejorar la integridad estructural del monolito antes de someterlo a la prueba de impacto.

Tras la preparación de los monolitos, se miden sus propiedades mecánicas y la textura porosa. Hasta el momento, se han evaluado las propiedades mecánicas de los monolitos mediante pruebas

de impacto sobre una placa de acero, siguiendo estándares similares a los establecidos en las normas ASTM-D4169-23 y ASTM-D5276-19. Se ha determinado que los monolitos deben superar al menos 25 caídas libres desde una altura de 45.7 cm sobre la placa de acero sin romperse.

La Figura 1 muestra uno de los monolitos preparados usando el carbón activado comercial y un aglomerante basado en celulosa, antes y después de la prueba de impacto. No se observó presencia de grietas en la superficie externa del monolito. Además, el monolito soportó las 25 caídas libres teniendo solo una pequeña pérdida de masa. Por tanto, se está consiguiendo con éxito la fabricación de los monolitos con buenas propiedades mecánicas y con una reducción de la porosidad inferior al 20% de la del material inicial.

ANTES DEL TEST DE IMPACTO



DESPUÉS DEL TEST DE IMPACTO



Figure 1. Monolito antes y después del test de impacto.

El equipo de investigadores de EVACAR se encuentra en fase de caracterización de los monolitos obtenidos. En la caracterización se están llevando a cabo medidas de la textura porosa mediante adsorción de gases y medidas de la densidad de los monolitos. Una vez caracterizados los monolitos, se llevará a cabo la medida de almacenamiento de hidrógeno mediante experimentos de adsorción de hidrógeno a 77K y hasta 40 atm.

Estudio de obtención, almacenamiento y distribución de energía e hidrógeno renovables a partir de biomasa como vector para una transición energética sostenible (BioEnH₂)

Jessica Chaparro Garnica y Diego Cazorla Amorós

Instituto de Materiales. Universidad de Alicante. Apartado 99. 03080 Alicante

Los grupos de investigación Materiales Carbonosos y Medio Ambiente (MCMA) y Electrocatálisis y Electroquímica de Polímeros (GEPE) de la Universidad de Alicante participan en el proyecto **BioEnH₂**, que se centra en el estudio de obtención, almacenamiento y distribución de energía e hidrógeno renovables a partir de biomasa como vector para una transición energética sostenible. **BioEnH₂** plantea una actuación en cooperación que une a varios sectores empresariales y entidades de I+D+i como el grupo de investigación MCMA de la Universidad de Alicante, Greene, Greene W₂H₂, CIEMAT, CSIC-ITQ, U. Loyola, ACTECO, Hydrogen Onsite, y Protio en donde cada una de ellas juega un papel esencial para la consecución del proyecto. El proyecto es financiado por el Centro para el Desarrollo Tecnológico Industrial (CDTI) y la Agencia Estatal de Investigación (AEI) en el programa Líneas Estratégicas TransMisiones (PLEC2023-010216), el presupuesto por parte del CDTI es 4.181.388,00 € y por parte de la AEI es 2.079.726,43 €. El presupuesto del grupo de la UA para los cuatro años del proyecto es 438.227,78 €. El equipo de **BioEnH₂** lo forman Diego Cazorla Amorós, Emilia Morallón, Ángel Berenguer Murcia, Miriam Navlani García, Jessica Chaparro Garnica y una nueva contratación como Investigador predoctoral.

El objetivo principal del proyecto **BioEnH₂** es el aprovechamiento de residuos de biomasa para la generación de hidrógeno renovable mediante procesos termoquímicos y catalíticos siguiendo dos vías alternativas: i) una ruta catalítica que contempla la limpieza y depuración de los gases, ii) una ruta electrocatalítica en la que se utiliza un reformador electroquímico alimentado con la corriente de

gases sin depurar. De forma simultánea durante los procesos termoquímicos sobre el mismo residuo de biomasa se genera una fracción sólida como subproducto que el proyecto buscará aprovechar con el fin de favorecer un proceso *zero waste*; así buscará obtener carbones activados de alto valor añadido, aplicables en el almacenamiento de energía como electrodos en supercondensadores.

Este proyecto nace para dar respuesta a la necesidad de cambio en el modelo energético que se plantea tanto a nivel nacional como europeo. Nuestras necesidades de consumo y por ende las necesidades energéticas han sufrido un aumento desproporcionado en los últimos años, lo que ha puesto en evidencia aún más la insostenibilidad de nuestro modelo energético, basado en recursos finitos (combustibles fósiles). En este contexto, el proyecto **BioEnH₂** plantea el uso de la biomasa como vehículo hacia la transición energética menos dependiente de los combustibles fósiles y capaz de generar energía verde.

El proyecto aborda uno de los principales desafíos asociados al hidrógeno, que es su almacenamiento. Además de enfocarse en la producción eficiente y sostenible de hidrógeno a partir de biomasa, también busca soluciones innovadoras para el almacenamiento seguro y eficiente de este valioso recurso energético. Al abordar tanto la producción como el almacenamiento, **BioEnH₂** tiene el potencial de ofrecer una solución integral y completa para la transición hacia un modelo energético más limpio y sostenible, impulsando así la producción masiva del hidrógeno como vector energético en el futuro.

En la Figura 1 se presentan las actividades previstas a lo largo del proyecto.

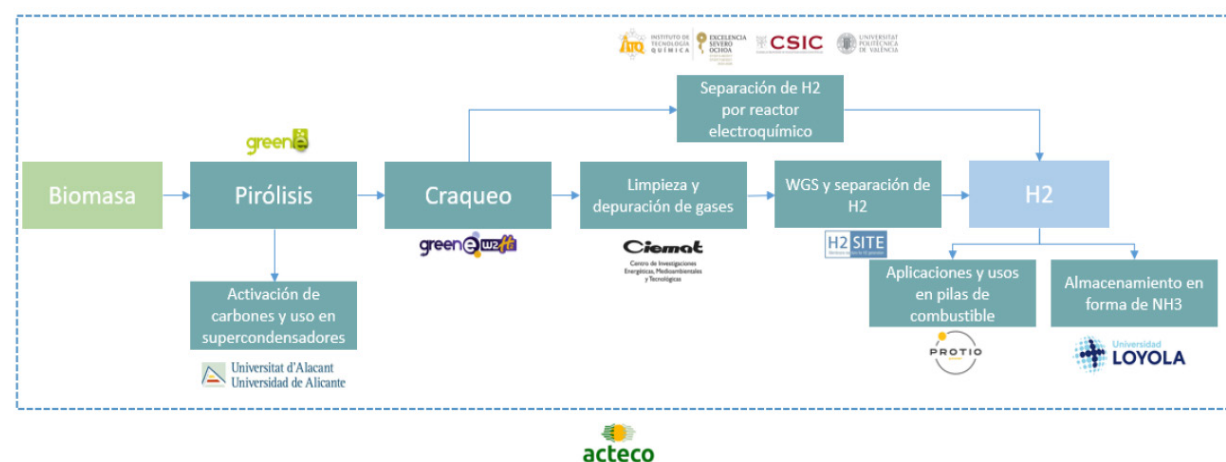


Figura 1. Diagrama general del proyecto BioEnH₂

Se estima que España tiene una disponibilidad anual de más de 20 millones de toneladas de biomasa, la mayoría de origen forestal y agrícola, pero también procedente de parques y jardines. La gran mayoría de esta biomasa no sufre una gestión real en la actualidad, acumulándose en los montes (con el potencial riesgo de incendios que esto supone), o quemándose intencionadamente en otros casos para reducir precisamente este riesgo de incendios, lo que supone el desaprovechamiento del potencial energético contenido en esa biomasa.

El primer campo en materia de valorización que contempla el proyecto es la pirólisis, un método termoquímico que en los últimos años se ha convertido en un proceso atractivo y prometedor por su potencial carácter transformador del modelo energético actual. Este proceso de transformación, que partirá en este caso de biomasa, permite convertir la materia orgánica en combustible útil, mediante la aplicación de energía en forma de calor a temperatura moderada alta (350-650 °C) y, en ausencia de oxígeno, permitirá obtener del producto de partida una serie de gases de pirólisis (pirogás) y una fracción sólida carbonosa (*biochar*). Por su capacidad de tratamiento, es el método más eficaz para competir con las fuentes de combustibles no renovables. Desde un punto de vista químico, la pirólisis es un proceso complejo. Generalmente, se lleva a cabo a través de una serie de reacciones en las que influyen muchos factores: la estructura y composición de la materia prima, la tecnología utilizada, la velocidad de calentamiento, el tiempo de residencia y la temperatura del proceso. Es importante destacar que la fracción sólida que se obtiene tras el proceso de pirólisis se empleará para obtener carbones activados.

La preparación de carbones activados por activación física incluye una gasificación controlada del material carbonoso previamente carbonizado, aunque en ocasiones, la activación del precursor se puede realizar directamente. Así, las muestras se tratan a 800-1000 °C con un gas reactivo (CO₂ o vapor de agua), de manera que los átomos de carbono se van eliminando de forma selectiva. El carbón activado se utiliza comúnmente como material de electrodo en supercondensadores debido a sus propiedades únicas, que incluyen una gran área superficial, porosidad, relativa conductividad eléctrica y estabilidad química.

Los condensadores electroquímicos o supercondensadores son dispositivos de almacenamiento de energía que utilizan la adsorción de iones en la interfase electrodo-electrolito para almacenar energía. A diferencia de las baterías convencionales, que almacenan energía mediante reacciones químicas, los supercondensadores almacenan energía de manera electrostática, lo que les permite cargar y descargar rápidamente y tener una vida útil mucho más larga que las baterías. Sin embargo, la energía almacenada es menor. Estos dispositivos tienen un gran potencial para su aplicación en áreas como vehículos eléctricos, almacenamiento de energía renovable, electrónica portátil y sistemas de respaldo de energía.

La estructura porosa de los carbones activados con una alta área superficial y una distribución de tamaños de poro adecuada son idóneos para la adsorción de iones en la interfase electrodo-electrolito. Además, es fundamental adaptar la química superficial para conseguir la menor reactividad electroquímica posible con el fin de asegurar el máximo tiempo de vida útil.

Actualmente, para la mejora de las propiedades de los supercondensadores se trabaja en el diseño de los materiales que se utilizan en los electrodos. Se están investigando nuevas técnicas para sintetizar carbones activados de bajo coste con propiedades mejoradas, como una mayor área superficial, mayor porosidad, baja reactividad electroquímica y una estructura más ordenada y, en este sentido, el proyecto **BioEnH₂** podría suponer un avance importante en la selección de estos materiales, pues la transformación de biomasa por pirólisis siempre va a producir un porcentaje de esta fracción carbonosa que puede llegar a aprovecharse en supercondensadores, estando alineado este proceso de síntesis de carbón activado con la transición verde a la que se compromete ayudar el presente proyecto.

En concreto, los grupos de investigación de la Universidad de Alicante desarrollarán un proceso eficiente para valorizar los residuos de biomasa y preparar carbones activados con propiedades adecuadas para su uso en supercondensadores y estudiará las condiciones óptimas del pretratamiento de la biomasa de entrada.



Biomass Chemical Looping Gasification for syngas/H₂ production without CO₂ emissions

Iván Samprón Alonso

Presented in 2024, Instituto de Carboquímica (ICB-CSIC), 50018 Zaragoza, Spain

Supervisors: F. García-Labiano (Instituto de Carboquímica, ICB-CSIC, Spain) and L. F. de Diego (Instituto de Carboquímica, ICB-CSIC, Spain).

Objectives and novelty

Fuels and chemicals produced from renewable sources are expected to play a key role on the decarbonization of industry and transport. Through the gasification of lignocellulosic biomass, a wide range of bioproducts such as diesel, gasoline, methanol or even ammonia can be synthesized. Although there are several gasification processes already developed, Biomass Chemical Looping Gasification (BCLG) has emerged recently due to its advantages over conventional gasification. In the BCLG process, a solid oxygen carrier is used to transfer oxygen and heat from an oxidation reactor to a reduction reactor, avoiding the direct contact between air and fuel (Figure 1).

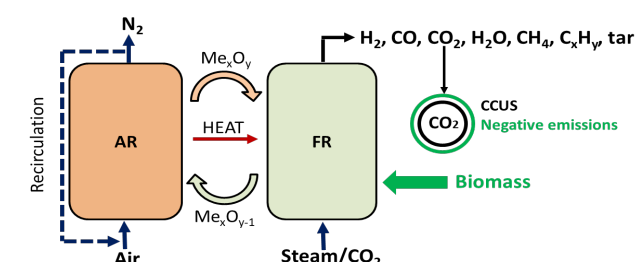


Figure 1. Main scheme of the BCLG process.

The oxygen carrier can also reduce tar generation, improving the syngas quality. Thus, BCLG enables the production of high purity and N₂-free syngas at autothermal conditions whereas pure oxygen needing is avoided. In addition, CO₂ generated is concentrated in a single reactor, permitting its capture for further use or storage. Therefore, it allows not only the production of high interest products, such as fuels, but also the removal of carbon from the atmosphere. In literature it can be found several works investigating different parameters of the BCLG process, but most of these studies have been carried out in discontinuous reactors, where unrealistic conditions take place. In spite of the high research about oxygen carriers, the increase of its lifetime still being a goal, and the obtention of an oxygen carrier suitable to resist a large number of redox cycles while preserving its chemical properties is required.

Present work investigates the BCLG process in a 1.5 kW_{th} continuous unit using four synthetic solids. It was investigated the whole process; from the selection and preparation of the oxygen carriers, to the testing the different variables affecting the operation. Also, a study to improve the quantity and quality of syngas was carried out. Finally, the process was optimized, determining the conditions that permit the operation of the system under autothermal state. An innovative method for better controlling of the oxygen

transference between reactors was also proposed.

Results

Three synthetic oxygen carriers with different Fe₂O₃ contents (10, 20 and 25%) over Al₂O₃ were tested in the 1.5 kW_{th} unit during more than 150 h. The oxygen transferred between reactors was controlled by limiting the air fed in the oxidation reactor. The Fe-solids showed similar trends on the molar flows of gases generated and on the gasification parameters when oxygen-to-fuel ratio and temperature were varied. A high CH₄ generation was also found for the three solids (Figure 2a). A syngas yield about 0.9 Nm³/Kg was obtained for a typical oxygen-to-fuel ratio about 0.3. The increase of temperature improved the gasification rate, enhancing the CO₂ capture, which reached values >95 % and reduced tar formation as can be seen in Figure 2b.

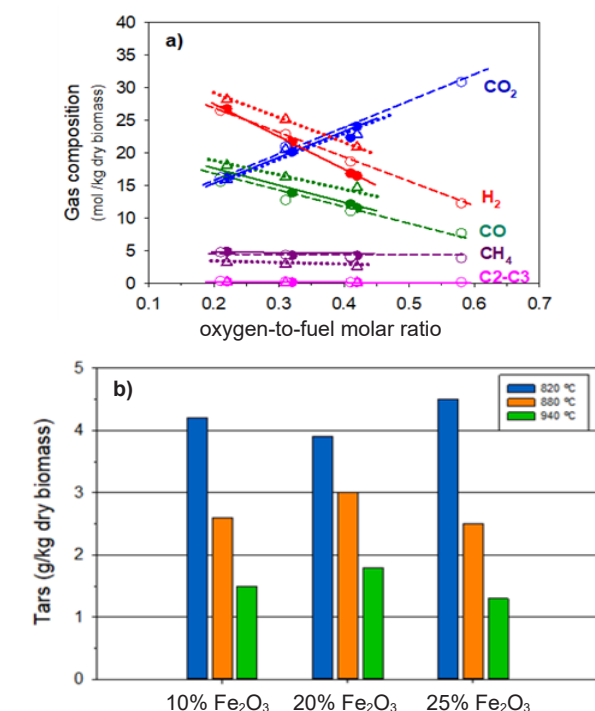


Figure 2. Syngas compositions (a) and tar generation (b) using Fe-based oxygen carriers.

The characterization of the Fe solids showed that lifetime increased from 100 to 900 h as Fe₂O₃ content in the oxygen carriers decreased from 25 to 10 %. This behaviour was studied in detail carrying out redox cycles in TGA. It was observed that a reducing atmosphere, the increase in temperature and high Fe₂O₃ contents promoted the weakening of oxygen carrier particles. In this sense, it was revealed that the oxygen carrier consisting in a 10 % of Fe₂O₃ over Al₂O₃ was suitable for the BCLG process since

over Al₂O₃ was suitable for the BCLG process since it performed a high lifetime and kept its chemical properties.

In order to improve the syngas quantity, the catalytic activity of eight oxygen carriers over CH₄ reforming was studied in batch fluidized bed reactor. It was found that a new oxygen carrier based on a 14 % of CuO over Al₂O₃ was able to convert the 85 % of CH₄ fed at a temperature of 940 °C. In another work conducted to increase the syngas quality by the elimination of tars, this oxygen carrier removed >95 % of the ethylene fed whereas complete benzene conversion was achieved at 940 °C. Thus, the Cu-based solid was selected for its evaluation in the 1.5 kW_{th} unit.

	Syngas Yield (Nm ³ /kg)	Tar (g/kg bio)	Lifetime (h)
Ilmenite	0.6	1.3	630
Mn-ore	0.8	5.1	130
Fe-ore	0.6	11.5	300
10 % Fe ₂ O ₃	0.8	1.5	900
20 % Fe ₂ O ₃	0.8	1.8	350
25 % Fe ₂ O ₃	0.9	1.3	100
14 % CuO	1.14	0.3	8000

Table 1. Comparison of results obtained in BCLG continuous operation at similar conditions.

Finally, the BCLG process was optimized by solving mass and energy balances in order to determine the conditions that permit the autothermal operation. The oxygen controlling method consisting in limiting the oxygen fed in the oxidation reactor (proposed in this work) allows to obtain a higher amount of syngas and to operate in a wide range of oxygen carrier circulation flows. Using this method, a cold gas efficiency about 86% can be obtained operation under autothermal conditions. Also, it was found that it enables the generation of a nearly pure stream of N₂ in the outlet of air reactor, which can be considered a valuable product.

Conclusions

BCLG continuous operation was demonstrated during 200 h of operation in a 1.5 kW_{th} unit using Fe- and Cu-based oxygen carriers.

The Fe oxygen carriers showed almost similar values in gas compositions and gasification parameters, being its main difference on lifetime, which increased as Fe₂O₃ content decreased.

The oxygen carrier composed by a 14 % of CuO over Al₂O₃ is the optimal candidate for the BCLG process. This solid performed the highest lifetime found in literature, and the lowest tar concentration. A syngas yield about 1.14 Nm³/kg was obtained.

An oxygen to fuel ratio about 0.3-0.35 is required to operate without external energy supply. The oxygen controlling method proposed permits to operate under autothermal conditions obtaining a higher syngas yield and producing a nearly pure stream of N₂.

Related Publications

[1] Samprón I, de Diego LF, García-Labiano F, Izquierdo MT, Abad A, Adánez J. Biomass Chemical Looping Gasification

About 45 h of continuous operation were done in the 1.5 kW_{th} unit using the Cu-based oxygen carrier. It was revealed that this solid reduced the CH₄ concentration in the produced gas whereas the syngas generation increased. A carbon capture >90 % and syngas yield reached about 1.14 Nm³/kg at a typical oxygen-to-fuel ratio about 0.3 and 940 °C. Furthermore, tar generation was reduced until 0.3 g/kg bio, which is the lowest tar concentration found in literature. It was revealed an excellent behaviour of the solid particles, which showed an estimated lifetime about 8000 h. This is the highest lifetime found under gasification conditions as can be seen in Table 1.

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[4] Samprón I, de Diego LF, García-Labiano F, Izquierdo MT, Adánez J. Influence of an Oxygen Carrier on the CH₄ Reforming Reaction Linked to the Biomass Chemical Looping Gasification Process. Energy Fuels 2022; 36(17): 9460-9469. Published JCR(FI) 2022: 5.3; (Chemical Engineering): 28/142 - Q1

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Full thesis can be downloaded from <https://digital.csic.es/handle/10261/355908>

Treatment and Valorization to hydrogen of the aqueous fraction of bio-oil from lignocellulosic biomass pyrolysis by aqueous phase reforming

Jéssica Justicia González

Presented in 2024, Departamento de Ingeniería Química (Facultad de Ciencias). Universidad Autónoma de Madrid, 28049 Madrid, Spain

Supervisors: Francisco Heras Muñoz and Miguel Ángel Gilarranz Redondo (Universidad Autónoma de Madrid, Spain).

jessica.justicia@estudiante.uam.es

Objectives and novelty

The aqueous fractions of pyrolysis bio-oils (AFBs) have a high water content (75-90 wt%) and include a wide variety of polar organic compounds, which makes difficult their valorization or management as a waste stream by conventional processes. Promising technologies, such as aqueous phase reforming (APR), are currently being developed to valorize this type of streams. APR is a catalytic process in aqueous solution whereby an organic substrate reacts with water to produce a gas phase (mainly composed by H_2 and CO_2) and a liquid effluent. The process provides several advantages over steam reforming (SR): a significant reduction in energy consumption (as it is carried out under milder operating conditions and in liquid phase, therefore avoiding the vaporization of the feed stream), easier separation of the H_2 generated (since no significant amount of CO is usually present in gas product due to the water-gas shift reaction is highly favoured at process operating conditions), etc. However, most of the studies published in the literature were performed using model compounds (or mixtures of them) as process feedstock.

The main objective of this Doctoral Thesis was the treatment and valorization to H_2 of the AFB from lignocellulosic biomass pyrolysis by APR process. Initially, a representative composition of AFBs was established, based on the relevant literature in the field. Then, the APR of each individual compound and mixtures of them was studied, selecting the optimal operating conditions. In addition, the stability of the catalyst was evaluated, as well as the possible relationship between the structure of the catalyst metal phase and the H_2 production. On the other hand, a technical-economic study of the APR of AFB was carried out, evaluating different approaches to the process according to the gas valorization possibilities. Finally, the APR of real AFBs was studied and the H_2 production obtained was related to the catalytic pyrolysis operating conditions.

Results

The first section of this Thesis was reported as the paper entitled "Aqueous-phase reforming of water-soluble compounds from pyrolysis bio-oils" [1], and it was focused on the APR of levoglucosan, hydroxyacetone, furfural and acetic acid (compounds usually present in AFBs), under different operating conditions. The experiments were carried out in

batch mode and using Pt impregnated at 3 wt% on ENSACO250 carbon black (CB) as catalyst. Different initial organic matter concentrations (1-5 wt%), temperatures (175-220 °C) and reaction times (0.5-4 h) were studied. The best results were obtained at 1 wt%, 220 °C and 4 h. The highest carbon-to-gas conversion (CCgas) and H_2 production and selectivity values were obtained for hydroxyacetone, which was mainly converted to H_2 , CO_2 and CH_4 . However, levoglucosan was mostly transformed to H_2 and CO_2 , while furfural and acetic acid mainly yielded CO_2 and different alkanes. These results were explained through different proposed reaction mechanisms. The catalyst exhibited high stability during five successive 4 h reaction cycles, using levoglucosan as feedstock, with only a slight decrease in Total Organic Carbon (TOC) conversion.

In the second section, presented as "Valorization to hydrogen of bio-oil aqueous fractions from lignocellulosic biomass pyrolysis by aqueous phase reforming over Pt/C catalyst" [2], the APR of several binary and multicomponent mixtures, as models of different AFB compositions, was studied. A strong dependence between the feedstock composition and H_2 production was observed, as the presence of furfural and acetic acid hindered APR, while the highest H_2 yields were obtained with levoglucosan- and hydroxyacetone-rich AFBs. In addition, the presence of minority compounds such as formic acid enhanced the reforming of the whole AFB, increasing H_2 production by more than 50 %. On the other hand, the catalyst activity remained almost constant over 5 consecutive reaction cycles. TPD characterization of the used catalysts showed an increasing mass loss with reaction cycles, related to the cumulative adsorption or deposition of reaction products. In addition, the Pt nanoparticles underwent morphological changes during reaction cycles, increasing the prevalence of low-coordination active sites (located at structural defects, step-edges, etc.), yielding higher H_2 production during cycles 2 and 3. It was found that, the presence of the H_2 generated in the first cycles, the acidic medium and the APR operating conditions led to these morphological changes.

The third chapter, "Energy and economic analysis of alternatives for the valorization of hydrogen rich stream produced in the aqueous phase reforming of pyrolysis bio-oil aqueous fraction" [3], was aimed at evaluating the potential feasibility of the APR technology. The process modelling was performed

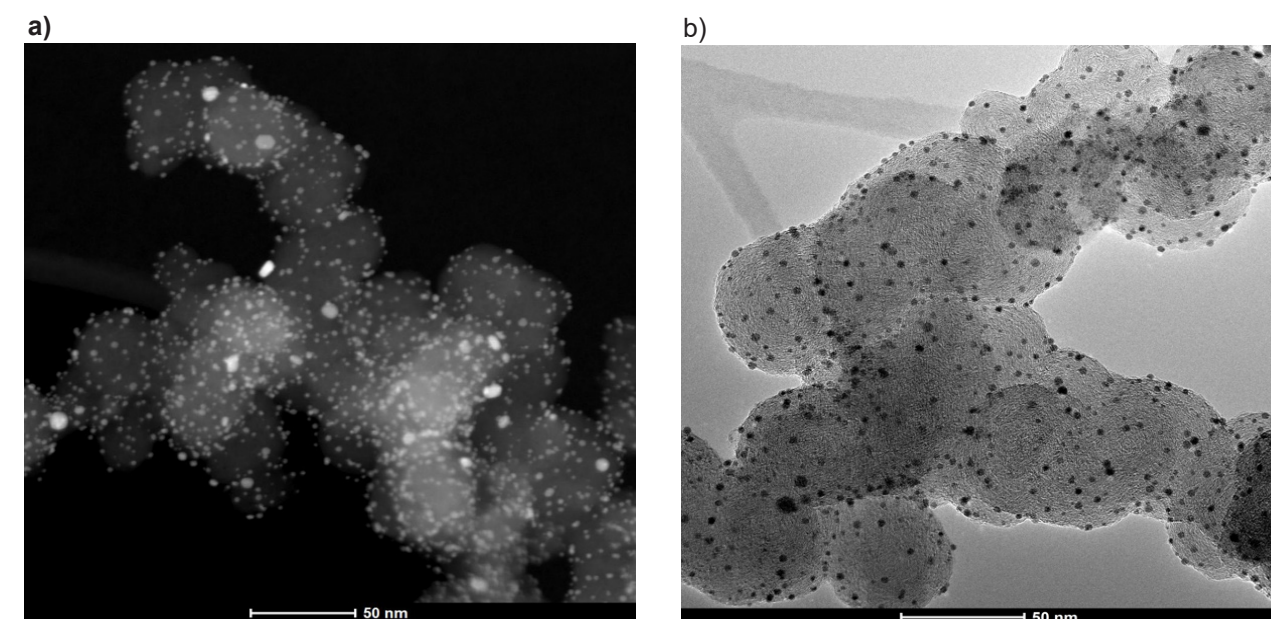


Figure 1. STEM/TEM images of fresh Pt/CB catalysts with a metal load of: a) 3 and b) 5 wt%.

using computational simulation tools (Aspen HYSYS), based on the experimental results reported in the previous paper for the most complex AFB composition. For this purpose, a specific thermodynamic model was developed to properly estimate the properties and phase equilibria of the AFB. Different process alternatives for the valorization of the APR gas stream, based on its commercialization, energy recovery or a combination of both, were technically and economically evaluated, detecting a significant energy cost reduction by means of an adequate heat integration. The economic optimum was achieved using a small fraction of the APR gas for energy self-covering and commercializing the rest as crude H_2 . For this case, a production cost of ca. 1.5 €/kg H_2 was estimated, suggesting the H_2 produced by APR as potentially competitive with green H_2 .

The fourth and last section of the Thesis, was published as "Understanding the relationship between catalytic pyrolysis conditions and hydrogen production by aqueous phase reforming of the water-soluble fractions of bio-oils" [4] and carried out in collaboration with the Thermochemical Processes Unit at IMDEA Energy Institute (Móstoles, Madrid). The main objective of the work was to study the APR of three real AFBs obtained by catalytic fast pyrolysis of oak woodchips at different conditions, using Pt contents in the catalyst of 3 and 5 wt% (Figure 1).

The best results were obtained for the AFB with the highest levoglucosan and the lowest acetic acid concentration, reaching up to 46 mol% H_2 in the APR gas. It was proved that the H_2 yield by APR was related to the AFBs composition and, in turn, to the catalytic pyrolysis conditions: more severe pyrolysis conditions provided with AFBs more favourable to the APR and, consequently, with a higher H_2 production and a treated effluent with a lower organic load. Moreover, as previously observed for synthetic AFBs, the addition of formic acid (0.04 %wt) led to a synergistic effect on the AFB reforming, increasing

H_2 production by 40 %. Finally, the stability of the 5 wt% Pt catalyst was evaluated over 3 consecutive reaction cycles. A small decrease in TOC conversion and CCgas was observed, although a more significant reduction in H_2 production. TPD analyses of the used catalysts showed an increasing mass loss with reaction cycles and TEM characterization, a small increase in the mean nanoparticle size after cycle 3.

Conclusions

The initially selected AFB representative compounds showed very different behaviour as individual APR substrates: hydroxyacetone provided the highest H_2 production, whereas furfural and acetic acid were transformed mainly to C_3H_8 and CH_4 , respectively. The Pt/CB catalyst showed a high stability in the levoglucosan APR after 20 h of use. Moreover, the reforming of synthetic binary mixtures suggested a possible selective adsorption of one of the compounds, preventing the reforming of the mixture. Minority compounds, such as formic acid, showed a synergistic effect on the APR of the mixtures, increasing TOC conversion, CCgas and H_2 production. Likewise, the presence of the H_2 generated over the cycles, the acidic medium and the operating conditions induced a higher prevalence of low-coordination centres in the metal nanoparticles of the catalyst and an increase in H_2 production. On the other hand, the energy and economic analysis of the process showed that the use of AFB as feedstock combined with an adequate integration and heat recovery results in a potentially feasible technology to produce bio- H_2 , at a competitive cost (1-2 €/kg). Finally, the APR of real AFBs improved with high concentrations of levoglucosan and was hampered by the presence of acids and ketones. The relationship between severe operating conditions of catalytic pyrolysis and a higher H_2 valorization of the AFB was established.

Related publications

[1] Justicia J, Baeza JA, Oliveira AS, Calvo L, Heras F, Gilarranz MA, Aqueous-phase reforming of water-soluble compounds from pyrolysis bio-oils, *Renewable Energy*, 2022; 199, 895-907. <https://doi.org/10.1016/j.renene.2022.09.021>

[2] Justicia J, Baeza JA, Calvo L, Heras F, Gilarranz MA, Valorization to hydrogen of bio-oil aqueous fractions from lignocellulosic biomass pyrolysis by aqueous phase reforming over Pt/C catalyst, *Chem Eng J*, 2023; 477, 146860. <https://doi.org/10.1016/j.cej.2023.146860>

[3] Heras F, Justicia J, Baeza JA, Gilarranz MA, Ferro VR, Energy and economic analysis of alternatives for the valorization of hydrogen rich stream produced in the aqueous phase reforming of pyrolysis bio-oil aqueous fraction, *Bioresour Technol*, 2024; 399, 130572. <https://doi.org/10.1016/j.biortech.2024.130572>

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Full thesis can be downloaded from: <https://repositorio.uam.es/handle/10486/715234>

Efficient catalysts with fibrillar morphology for the Fischer-Tropsch reaction with synthesis gas from residual biomass

Miguel Ángel Rodríguez-Cano

Defended in 2023, Department of Chemical Engineering, Faculty of Science, University of Málaga, 29010, Málaga, Spain

Supervisors: Prof. José Rodríguez-Mirasol (Department of Chemical Engineering, School of Industrial Engineering, University of Málaga, 29010, Málaga, Spain) and Prof. Tomás Cordero (Department of Chemical Engineering, Faculty of Science, University of Málaga, 29010, Málaga, Spain)

marodriguez@uma.es

Objectives and novelty

Biorefineries are a promising alternative to fossil fuels as they allow to obtain fuels but also substitutes for petrochemicals (e.g. olefins). In this sense the Fischer-Tropsch synthesis with synthesis gas -syngas- (H_2 and CO) produced from biomass waste represents an interesting route. However, this process present unsolved problems such as the heat evacuation from the reactor, the high pressure drop in fixed bed reactors and the necessity of catalysts active with syngas with low H_2/CO ratio.

The objective here is to study the preparation and use in reaction a catalyst that can amend the aforementioned problems. In this sense, the catalysts were structured with fibrillar morphology with the aid of the electrospinning technique. This morphology enhances the mass and heat transference, reducing the limitations in the reactor. They are also active for low H_2/CO ratio syngas. Two kinds of materials were studied: inorganic fibers based on ZrO_2 and Fe and carbon fibers prepared from a solution of Alcell® lignin and iron. The Figure 1 summarizes the objectives and the process.

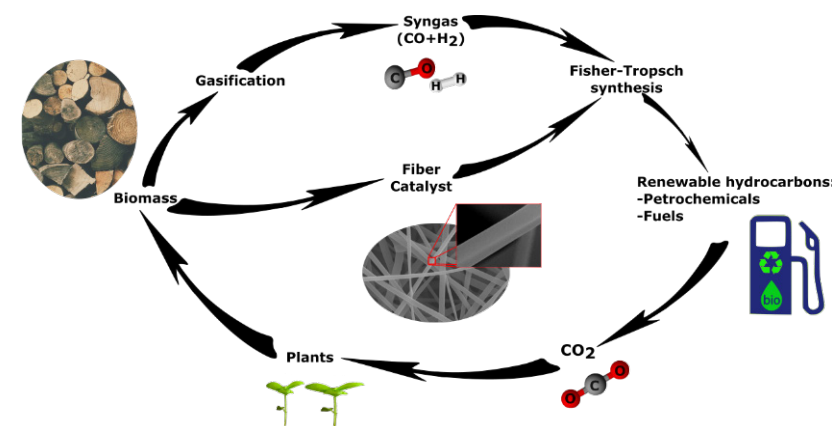


Figure 1. Overview of the overall process for Fischer-Tropsch synthesis and catalysts preparation from biomass.

Results

Two kinds of materials with fibrillar morphology were prepared, on the one hand with ZrO_2 and iron loadings from 20 to 30 (w/w) %; and on the other hand, carbon fibers with Alcell® lignin as precursor, carbonized at three different temperatures (500, 650 and 800 °C). Both were used as catalysts for Fischer-Tropsch synthesis with a simulated syngas produced via biomass gasification ($H_2/CO=1$).

Study of the carbonaceous fraction in inorganic fibers catalysts

The catalysts with different loadings of Fe in ZrO_2 presented a high activity which was increased with the iron loading. The products were mainly gaseous products (from methane to butane), but liquids (up to C20) were also obtained in all the cases. The main product distribution is collected in Table 1. The C5+ compounds were calculated by difference between consumed reactants (CO) and products, so solid carbonaceous materials produced in the reaction, due to Boudouard process, was included.

The carbonaceous fraction was deeply analyzed by different techniques in this thesis work. First, the

coke amount was quantified with thermogravimetric analyses (TGA) giving rise to a c.a. 17 (w/w) % of carbonaceous materials for the catalyst with 20 (w/w) % of Fe, and a c.a. 62 (w/w) % of burning material for the catalyst with 25 and 30 (w/w) % of iron. The higher production of coke could be related to the highest conversion or the later catalysts, however, the carbon productivity was also obtained with values $1 \text{ g}_C \text{ g}_{cat}^{-1} \text{ mol}_{CO}^{-1}$ for F20Fe@ ZrO_2 and c.a. $3.2 \text{ g}_C \text{ g}_{cat}^{-1} \text{ mol}_{CO}^{-1}$ for F25Fe@ ZrO_2 and F30Fe@ ZrO_2 .

The used catalysts were also analyzed by scanning and transmission electronic microscopy, SEM and TEM respectively. The images can be observed on Figure 2. The catalyst with 20 (w/w) % of iron showed the original fibrillar morphology with low carbonaceous deposits, on the other hand, the catalysts with 25 and 30 (w/w) % presented a high accumulation of carbonaceous materials. However, in the former, the fibrillar morphology was maintained while in the later it was difficult to differentiate the catalysts from the deposits. Thanks to TEM images, it was possible to observe that the fibers with 30 (w/w) % were broken due to the carbon deposits (Figure 2.c).

Table 1. CO conversion and selectivity of the Fischer-Tropsch synthesis with the catalysts with 20, 25 and 30 (w/w) of iron on ZrO₂ at 340 °C, 20 bar and 150 ml/min of syngas H₂/CO=1.

	Conversion (%)	Selectivity (%)			
	CO	CO ₂	CH ₄	C2-C4	C5+
F20Fe@ZrO ₂	38.5	31.6	11.1	25.9	31.4
F25Fe@ZrO ₂	92.7	42.5	9.9	23.5	24.1
F30Fe@ZrO ₂	95.9	41.2	8.1	20.9	29.7

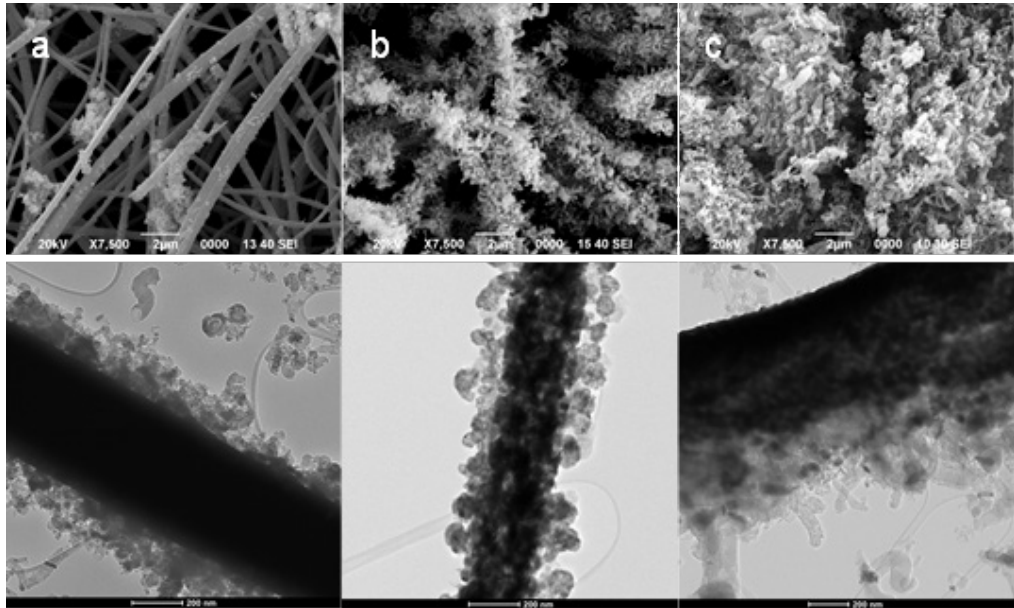


Figure 2. Up: SEM and down: TEM micrographs of the used catalyst a) F20Fe@ZrO₂, b) F25Fe@ZrO₂ and c) F30Fe@ZrO₂

The catalysts were also analyzed by Raman spectroscopy. The D and G bands were detected in the three used catalysts, evidencing low structured carbonaceous deposits. However, in the case of F25Fe@ZrO₂ and F30Fe@ZrO₂ catalysts, the radial breathing modes were also detected, which means that single or doble walled carbon nanotubes were also formed on these two catalysts.

Finally, a regeneration study was carried out with a used catalyst with a 25 (w/w) % of iron. An isothermal gasification study at 300, 325, 350, 375 and 400 °C, with air was performed in a thermobalance in order to develop a kinetic model. After trying to adjust different simple models a dual model was proposed with a very good fitting to the experimental data. The model includes a volumetric and a shrinking core model. There was a fraction of c.a. 70 % that reacted through the first model type. The two gasification models could be related with the different types of carbon detected by Raman spectroscopy.

Carbon fibers catalysts

An important section of this thesis work was a review article about different carbonaceous supports (powder, fibers, nanotubes, spheres, graphene oxide, etc.) as catalysts for the Fischer-Tropsch synthesis. Three of the main conclusions of this review paper were that carbon materials presented a low metal-support interaction; a high thermal conductivity,

that enhances the heat evacuation; and finally, the possibility of recovering the metals from the deactivated catalyst by gasifying the support. On the other hand, most of the carbon fibers used nowadays as catalysts supports are obtained from fossil fuel (e.g. oil). For that reason, an important objective of this thesis was the preparation of carbon fibers from a more sustainable source, in this case it was the lignin.

Carbon fibers were obtained with the electrospinning technique from a solution of lignin, iron nitrate and ethanol. Once the fibers were stabilized the effect of the carbonization temperature was studied carrying out the process at 500, 650 and 800 °C. The materials treated at high temperature showed an important development of the mesoporosity compared to the rest of the materials treated at lower temperatures. This phenomenon was attributed to an interaction between the iron and de carbon support, which was confirmed with X-ray diffraction. In the case of the fibers carbonized at 800 °C iron carbides were detected, while in the rest of the materials iron oxides were present.

These materials were used as Fischer-Tropsch catalysts with the same conditions than the inorganic fibers (340 °C, 20 bar). The catalyst treated at the highest temperature showed the best result in terms of conversion (c.a. 10 %) but also the product distribution was the most interesting. A higher quantity of hydrocarbons longer than methane was

obtained with a lower selectivity to CH₄ and CO₂ than the catalysts treated at lower temperatures. In the case of these last catalysts the narrow microporosity hindered the chain growing of the hydrocarbons promoting methane and carbon dioxide. Furthermore, in the case of the catalyst treated at 800 °C a high selectivity to olefins was obtained with a ratio of propene to propane of 4.

Conclusions

In this thesis work the electrospinning technique was proved as a feasible procedure to generate inorganic but also lignin fibers in just one step with the active phase already loaded. These catalysts showed a good activity in terms of conversion and an interesting product distribution such as olefins. In the case of the inorganic catalyst, a relationship between the carbon production and the iron loading was found, provoking in the worst case the damage of the fibrillar morphology due to coke production. That coke was of two kinds, including carbon nanotubes. On the other hand, it was also proved that the use of lignin is a useful carbon source to prepare carbon fibers loaded with iron as catalysts for the Fischer-Tropsch process. The temperature of carbonization was an important matter due to the porosity development which conditioned the conversion and product distribution.

Related Publications

[1] Cordero-Lanzac T, Rodríguez-Cano MA, Palomo J, Valero-Romero MJ, Aguayo AT, Bilbao J, et al. Binderless ZrO₂/HZSM-5 fibrillar composites by electrospinning as catalysts for the dimethyl ether-to-olefins process. *Microporous Mesoporous Mater* 2022;342:1–11. doi:10.1016/j.micromeso.2022.112102.

[2] Valero-Romero MJ, Rodríguez-Cano MÁ, Palomo J, Rodríguez-Mirasol J, Cordero T. Carbon-Based Materials as Catalyst Supports for Fischer–Tropsch Synthesis: A Review. *Front Mater* 2021;7:1–27. doi:10.3389/fmats.2020.617432.

Full Thesis can be downloaded from: <https://hdl.handle.net/10630/30788>

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