UNIVERSIDAD DE OVIEDO

Programa de Doctorado en Ingeniería de Procesos y Ambiental

RECICLADO DE CO_2 MEDIANTE REFORMADO DE GAS DE COQUERÍA PARA LA PRODUCCIÓN DE METANOL

TESIS DOCTORAL

JOSÉ MIGUEL BERMÚDEZ MENÉNDEZ
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RESUMEN DEL CONTENIDO DE TESIS DOCTORAL

1.- Título de la Tesis	
Español: Reciclado de CO_2 mediante reformado de gas de coquería para la producción de metanol	Inglés: CO_2 recycling by means of reforming of coke oven gas for methanol production

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RESUMEN (en español)

La industria siderúrgica es el sector productivo con mayor consumo energético en el mundo. Debido a esto, sus emisiones de CO_2 suponen entre el 5 y el 7% de las emisiones totales de origen humano. Por este motivo se está trabajando en la búsqueda de soluciones que permitan disminuir esas emisiones, así como mejorar la eficiencia energética. Una de esas soluciones es la mejorara en la gestión y el aprovechamiento de los excedentes de gas de batería. El reformado con CO_2 de los excedentes de gas de batería, que se estudia en este trabajo, puede suponer una salida rentable para esos gases, ya que permitiría la obtención de un gas de síntesis con una composición adecuada para la producción de metanol. Esto implicaría obtener un producto muy valioso a partir de dos corrientes gaseosas residuales: el propio excedente de gas de batería y el CO_2. De hecho, realizando un balance global al proceso, éste puede dar lugar a un reciclado parcial del CO_2, ya que parte del CO_2 que se produce tras la utilización del metanol se consume en la producción.

Un estudio termodinámico del proceso de reformado con CO_2 de gas de batería permitió determinar que es necesario trabajar a temperaturas superiores a 800 °C y a presiones tan bajas como la economía del proceso permita. Además, la relación de CH_4/CO_2 alimentada debe ser lo más próxima posible a la estequiométrica. En otras condiciones el rendimiento del proceso sería muy bajo y/o el gas de síntesis obtenido no tendría la composición adecuada para la producción de metanol.

El reformado de metano con CO_2 es una reacción catalítica heterogénea, por lo que es necesario encontrar catalizadores adecuados para llevarla a cabo. Se han evaluado diferentes catalizadores, siendo la mezcla física de carbón activo y un catalizador convencional Ni/Al_2O_3 el que ha dado lugar a resultados más prometedores. Esto se debe a que esta mezcla presenta un efecto sinérgico que permite alcanzar conversiones mayores a las que predice la ley de las mezclas y producciones de subproductos (en concreto agua) menores a las predichas por dicha ley. Asimismo, se ha determinado que la reacción puede tener lugar a través de dos posibles mecanismos. Por un lado, la vía clásica del reformado seco, formada por la descomposición de metano seguida de la gasificación de los depósitos de carbono. Por el otro, debido a la elevada proporción de H_2 presente en la alimentación, se produciría la reacción inversa de la *water gas shift* seguida del reformado con vapor de agua. Esta segunda vía parece ser la principal, lo que permitiría disminuir el elevado grado de desactivación de los catalizadores que tiene lugar en el reformado seco.

Analizando el proceso completo, la producción de metanol a partir de gas de batería presenta varias ventajas con respecto a la producción convencional. La mayor ventaja es la disminución de las emisiones de CO_2 que, dependiendo de la localización geográfica de la planta, puede alcanzar hasta el 30 % de reducción. Además, este proceso permite maximizar el aprovechamiento de las materias prima y minimizar los costes de purificación. Desde el punto de vista energético, los consumos son menores, aunque la producción convencional permite mayores recuperaciones de energía, lo que puede dar lugar a menores necesidades energéticas si se realiza una correcta integración energética del proceso.

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RESUMEN (en Inglés)

The steelmaking industry is the largest energy-consuming manufacturing sector. As a consequence of this, the CO_2 emissions from this sector account for about 5-7 % of the total anthropogenic CO_2 emissions. For this reason, increasing efforts are being made to find solutions that might help diminish these emissions and increase energy efficiency. A better management of the coke oven gas (COG) surplus is one of the proposed solutions. This study deals with the CO_2 reforming of COG surplus. By means of this technology it is possible to obtain a synthesis gas with a composition suitable for use in the production of methanol. Thus, a highly valuable product, with many applications in different industries is obtained from two residual streams: the surplus of coke oven gas and CO_2. Examined from a more global perspective this process constitutes a partial recycling of CO_2, since part of the CO_2 emitted when methanol is used is consumed in the production process.

It has been established that, from the thermodynamic point of view, the most favourable operating conditions for carrying out the CO_2 reforming of COG are temperatures higher than 800 °C and the lowest possible pressures. In addition, the CH_4/CO_2 ratio must be as near to the stoichiometric ratio as possible. Otherwise, the process yield will be very low and/or the syngas thus obtained will not be suitable for methanol production.

Since the CO_2 reforming of methane is a heterogeneous catalytic reaction, it is necessary to use an appropriate catalyst. Several catalysts have been tested, and the physical mixtures of activated carbon and a conventional Ni/Al_2O_3 catalyst have been found to be the most promising. Such mixtures have a synergetic effect that leads to higher conversions of methane and carbon dioxide than those predicted by the law of mixtures. Moreover, the production of by-products, such us water, are lower than what is predicted by this law. It has been found that the CO_2 reforming of COG can take place via two different reaction mechanisms: on the one hand, the classical dry reforming, consisting of methane decomposition followed by gasification of the carbon deposits and on the other hand, due to the large amount of H_2 present in the feed, the reverse water gas shift followed by steam reforming. This latter reaction path seems to be the main mechanism, diminishing the high deactivation rate characteristic of dry reforming.

An assessment of the whole process, from the coke oven gas to the use of the methanol produced, has shown that this novel technology has certain advantages over conventional methanol production, the most important being lower CO_2 emissions. Indeed, these emissions can be reduced by as much as 30%, depending on the location of the plant and the energy integration of the process. Moreover, COG-based production allows the exploitation of the raw materials to be maximized while keeping purification costs down to a minimum. From the energy point of view, COG-based production entails less energy consumption than conventional production, whereas conventional production allows a higher energy recovery, which could eventually result in lower energy requirements as long as an adequate energetic integration strategy is adopted.

SR. DIRECTOR DE DEPARTAMENTO DE INGENIERÍA QUÍMICA Y TECNOLOGÍA DEL MEDIO AMBIENTE

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RESUMEN

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ABSTRACT

The steelmaking industry is the largest energy-consuming manufacturing sector. As a consequence of this, the CO_2 emissions from this sector account for about 5-7 % of the total anthropogenic CO_2 emissions. For this reason, increasing efforts are being made to find solutions that might help diminish these emissions and increase energy efficiency. A better management of the coke oven gas (COG) surplus is one of the proposed solutions. This study deals with the CO_2 reforming of COG surplus. By means of this technology it is possible to obtain a synthesis gas with a composition suitable for use in the production of methanol. Thus, a highly valuable product, with many applications in different industries is obtained from two residual streams: the surplus of coke oven gas and CO_2. Examined from a more global perspective this process constitutes a partial recycling of CO_2, since part of the CO_2 emitted when methanol is used is consumed in the production process.

It has been established that, from the thermodynamic point of view, the most favourable operating conditions for carrying out the CO_2 reforming of COG are temperatures higher than 800 ºC and the lowest possible pressures. In addition, the CH_4/CO_2 ratio must be as near to the stoichiometric ratio as possible. Otherwise, the process yield will be very low and/or the syngas thus obtained will not be suitable for methanol production.

Since the CO_2 reforming of methane is a heterogeneous catalytic reaction, it is necessary to use an appropriate catalyst. Several catalysts were tested, and the physical mixtures of activated carbon and a conventional Ni/Al_2O_3 catalyst were found to be the most promising. Such mixtures have a synergetic effect that leads to higher conversions of methane and carbon dioxide than those predicted by the law of mixtures. Moreover, the production of by-products, such us water, are lower than what is predicted by this law. It was found that the CO_2 reforming of COG can take place via two different reaction mechanisms: on the one hand, the classical dry reforming, consisting of methane decomposition followed by gasification of the carbon deposits and on the other hand, due to the large amount of H_2 present in the feed, the reverse Water Gas Shift followed by steam reforming. This latter reaction path appears to be the main mechanism, which would result in a lower deactivation rate than that of dry reforming.

An assessment of the whole process, from the coke oven gas to the use of the methanol produced, has shown that this novel technology has certain advantages over conventional methanol production, the most important being lower CO_2 emissions. Indeed, these emissions can be reduced by as much as 30%, depending on the location of the plant and the energy integration of the process. Moreover, COG-based production allows the maximum exploitation of the raw materials while purification costs are kept down to a minimum. From the energy point of view, COG-based production entails lower energy consumption than conventional production, whereas conventional production allows a higher energy recovery, which could eventually result in lower energy requirements provided that an adequate energetic integration strategy is adopted.

1. INTRODUCCIÓN

La industria del acero es el sector productivo con mayor consumo energético [1, 2]. Debido a esto, las emisiones de CO_2 de esta industria suponen entre el 5 y el 7 % de las emisiones totales de CO_2 debidas al ser humano [1, 2]. Si a esto le unimos el constante incremento de la producción de acero durante los últimos años (al margen del actual periodo de crisis económica) y que esta tendencia alcista se espera que continúe durante las próximas décadas, estas emisiones de CO_2 seguirán aumentado, suponiendo un serio problema medioambiental [1-4].

Desde los años 60, la industria del acero ha realizado grandes esfuerzos y progresos en busca de la sostenibilidad, centrándose especialmente en aspectos energéticos así como en la reducción de emisiones de gases de efecto invernadero [1]. De hecho, los procesos productivos han alcanzado unos niveles de eficiencia que los acercan a sus límites en utilización de carbono, por lo que la industria del acero está buscando nuevas alternativas para mejorar su eficiencia [1, 2, 5-7].

Una de las alternativas más prometedoras es una mejor gestión y aprovechamiento del gas de coquería [2, 3, 6-8]. Un material imprescindible para la producción del acero es el coque metalúrgico, cuya labor es actuar como combustible, reductor y, sobre todo, como soporte permeable de la carga que se está tratando en el alto horno [9]. El coque se produce en baterías de hornos, las cuales suelen ser una instalación anexa a las industrias siderúrgicas o encontrarse dentro de la propia acería, debido al elevado consumo de este material [3, 10]. En la Figura 1 se muestra un esquema del funcionamiento de una acería, en el cual se puede localizar el punto del proceso en el cual se encuentran las baterías de hornos de coque.

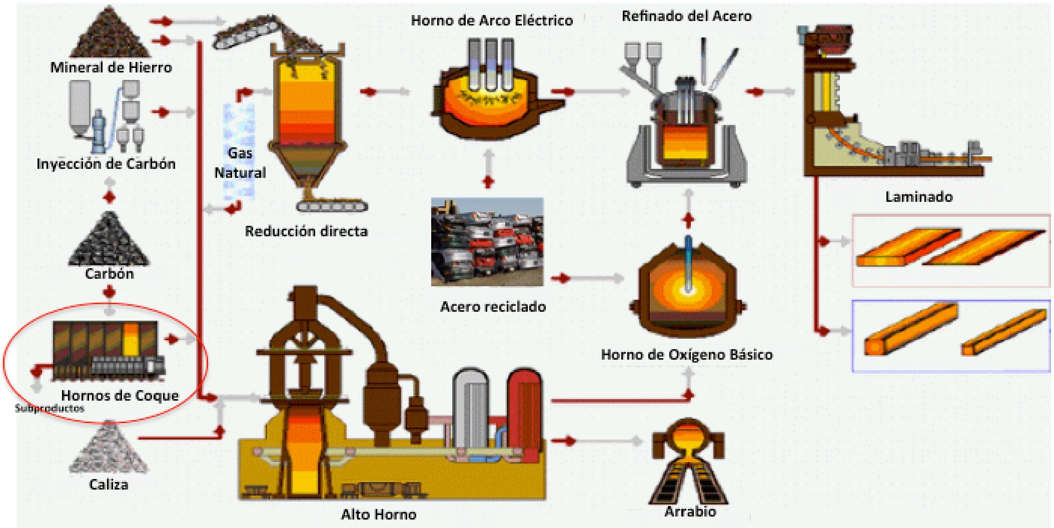
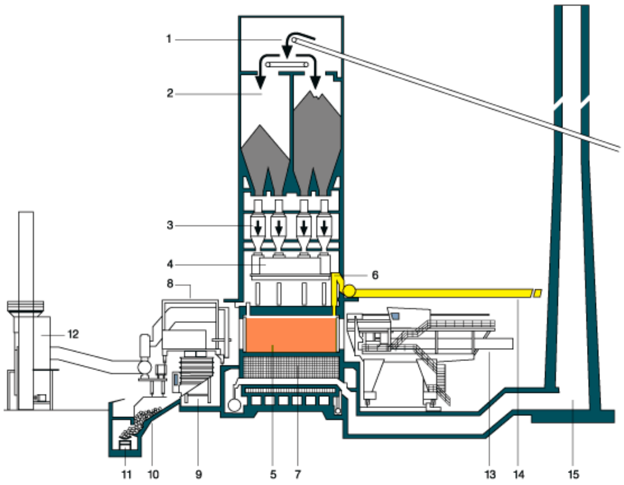


Figura 1. Diagrama de flujo de una acería. Detalle de las baterías de hornos de coque.

1. INTRODUCCIÓN

La coquería, como se conoce a la instalación en donde se produce el coque, es en sí misma una compleja planta industrial. El equipamiento principal de estas plantas son las baterías de hornos, una serie de hornos situados en paralelo en los que se introducen los carbones bituminosos para obtener el coque, a través de un proceso de calentamiento a elevadas temperaturas en ausencia de oxígeno. En la Figura 2 se puede ver un esquema de este tipo de hornos.



1. Entrada del carbón
2. Carbonera
3. Dosificadores
4. Carro de carga
5. Cámara del horno
6. Riser
7. Regenerador
8. Equipo de transferencia
9. Carro de extinción
10. Muelle
11. Coque producido
12. Recolector de partículas
13. Descargador
14. Salida de gases de coquización
15. Chimenea

Figura 2. Esquema de un horno de coque.

En la producción del coque, además del propio coque, se producen otras dos fracciones, una gaseosa que es el gas de coquería y otra líquida, las breas. Ambas fracciones, antes de enfriarse, abandonan la batería de hornos en forma de gases de coquización a través de tubos situados en la parte superior de la batería, como los que se pueden observar en la Figura 3.

Figura 3. Detalle de una batería de hornos de coque con los tubos de recogida de los gases de coquización.

El gas de coquería es una mezcla de gases altamente energética, con una composición bastante compleja en el momento de abandonar el horno de coquización. Al salir del horno se enfría y se separa de la fracción líquida, las breas. Posteriormente, el gas es tratado en un proceso de limpieza donde se eliminan el H_2S, el NH_3 y los BTX (benceno-tolueno-xileno) [3]. Tras todo este proceso, el gas de coquería está compuesto básicamente de H_2, CH_4, CO, N_2, CO_2 y otros hidrocarburos en pequeñas proporciones [3, 10-18]. Las proporciones en las que se suelen encontrar los principales componentes del gas de coquería se muestran en la Tabla 1.

Tabla 1. Proporción de los componentes mayoritarios del gas de coquería [3, 10-18]

Componente	Proporción (% vol.)
H_2	55-60
CH_4	23-27
CO	5-8
N_2	3-6
CO_2	>2
C_nH_m	>1

La situación de las baterías de hornos de coque en la acería permite el aprovechamiento de los subproductos de la producción del coque en la propia industria siderúrgica [3, 10]. Aproximadamente, entre el 20 y el 40 % del gas de coquería se aprovecha como combustible en el propio proceso de coquización [8, 16, 19, 20]. El gas restante se utiliza como combustible en otros procesos de la acería [3, 8, 21]. Sin embargo, normalmente existen grandes excedentes que, al no poder ser aprovechados, se queman en antorchas e, incluso, en algunos países llegan a ser emitidos directamente a la atmósfera [3, 8, 20-22]. Teniendo en cuenta que el gas de coquería supone en torno al 18 % de la energía saliente de una planta de coquización, esto además de suponer un problema ambiental, constituye un importante desperdicio energético que acaba derivando en una baja eficiencia económica [3, 5, 8, 23]. Por estos motivos, existe un enorme interés hoy en día, por parte de la industria siderúrgica, en mejorar el aprovechamiento de los excedentes de gas de coquería. Prueba de ello es esta Tesis, en la que se intenta desarrollar una alternativa para el aprovechamiento de esos excedentes de gas de coquería, y que se enmarca dentro de un proyecto de investigación financiado por una gran multinacional del sector como Arcelor-Mittal.

Durante los últimos años, han ido apareciendo numerosas alternativas para la explotación de los excedentes de gas de coquería, que van desde su aprovechamiento energético hasta su utilización directa en el alto horno como reductor [3, 8, 10-14, 16-22, 24-43]. Entre todas estas alternativas, destacan la separación de H_2, la producción de gas de síntesis a partir del gas de coquería para la producción de diferentes compuestos orgánicos y otras tecnologías, como la combustión en bucle químico (*chemical looping combustion*) que apenas están en sus fases iniciales de desarrollo [35].

Este trabajo, tal y como se detalla en los objetivos, está enmarcado en la segunda de estas alternativas: la producción de gas de síntesis. Este proceso puede realizarse mediante diferentes tecnologías: reformado con vapor de agua [44-50], oxidación parcial [44, 45, 51] y reformado seco [44, 47, 49, 52-55]. El reformado seco o reformado con CO_2 (Reacción 1), proceso en el que se centra este trabajo, presenta ciertas ventajas con respecto a las otras tecnologías [44, 55, 56].

$$CH_4 + CO_2 \leftrightarrow 2\ H_2 + 2\ CO \qquad \Delta H = 247\ \text{kJ/mol} \qquad \text{(Reacción 1)}$$

En el reformado seco, además del metano (presente también en el reformado con vapor de agua y en la oxidación parcial) se consume CO_2, principal gas responsable del efecto invernadero, con lo que se podría sacar provecho de otras corrientes residuales de la industria. Por otro lado, en comparación con el reformado con vapor de agua, el consumo energético necesario para llevar a cabo el reformado seco es considerablemente menor, mientras que en comparación con la oxidación parcial, el coste de utilizar O_2 como reactivo es considerablemente superior al de utilizar CO_2 [34, 44, 57]. Además, en el caso concreto del gas de coquería, la aplicación del reformado seco como tecnología para obtención de gas de síntesis, permite obtener un gas de coquería con una relación H_2/CO en torno a 2, sin necesidad de ninguna etapa extra de acondicionamiento [8, 10-14, 43]. Esta relación H_2/CO es la idónea para la utilización del gas de síntesis en reacciones de Fischer-Tropsch y, especialmente, en la producción de metanol [58-60]. En el caso del reformado con vapor de agua y la oxidación parcial, esta relación H_2/CO es considerablemente mayor, debido al H_2 que ya contiene el gas de coquería alimentado, por lo que el gas de síntesis obtenido de esta manera sería más aplicable a la producción de H_2 [61]. Por otro lado, uno de los gastos más importantes de los procesos de reformado es el derivado de la compresión del gas. Todos los procesos que utilizan gas de síntesis se realizan a altas presiones, por lo que el gas de síntesis debe ser comprimido una vez obtenido [44, 48, 50, 62]. Sin embargo, la práctica habitual consiste en realizar una primera compresión, hasta una presión intermedia, previa a la producción del gas de síntesis para, una vez obtenido, realizar una segunda compresión hasta la presión de trabajo [44, 48, 50, 62]. A pesar de que al duplicarse el número de moles en la reacción, termodinámicamente es mejor para el rendimiento del reformado llevar a cabo el proceso a bajas presiones, ese incremento en el número de moles hace que el gasto de compresión se dispare si se realiza de una sola vez tras obtener el gas de síntesis. Por ello, es más rentable hacer una primera compresión a una cantidad de moles mucho menor y, posteriormente, una segunda compresión ya con la cantidad de moles duplicada [8, 44, 48, 50, 62]. Asimismo, esto permite trabajar en reactores de menor tamaño y reducir los costes de operación [44, 48, 50, 62]. Sin embargo, en el caso del gas de coquería, aún logrando conversiones del 100 %, el incremento del número de moles se sitúa en torno al 40 %, con lo que no resulta tan rentable esa compresión previa, pudiendo llevarse a cabo el reformado seco a bajas presiones, logrando así mayores conversiones [8, 10].

Lo apuntado en esta breve introducción, así como otros datos de interés sobre el gas de coquería y las diferentes alternativas existentes hoy en día para el aprovechamiento de sus excedentes, tratados en mucha más profundidad, se pueden encontrar en el artículo *An overview of novel technologies to valorise coke oven gas surplus*, incluido en esta Sección, y que se encuentra a continuación. Este artículo, publicado en Fuel Processing Technology, en prensa (2013), es una revisión en la que se detallan pormenorizadamente las alternativas que, hasta el día de hoy, se han propuesto para el aprovechamiento de los excedentes de gas de coquería, centrándose en los logros alcanzados y en las perspectivas de futuro de cada una de ellas.

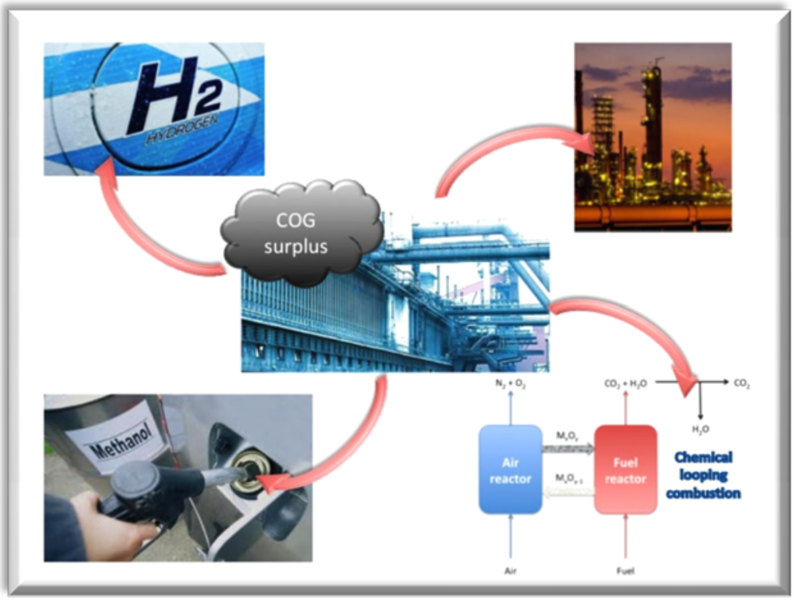


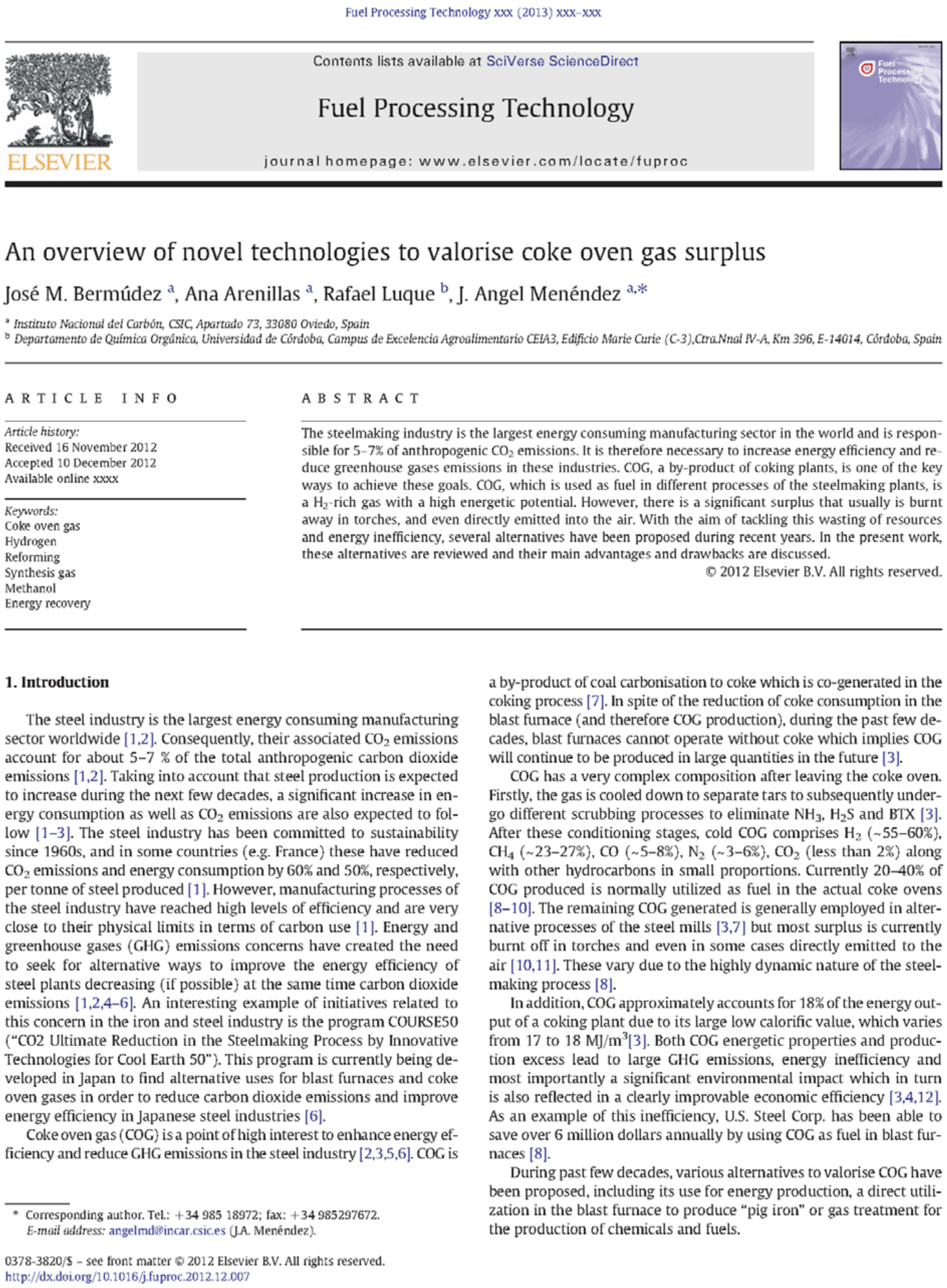
Figura 4. *Graphical abstract* del artículo *An overview of novel technologies to valorise coke oven gas surplus*.

Fuel Processing Technology

Artículo 1

An overview of novel technologies to valorise coke oven gas surplus

Fuel Processing Technology, en prensa (2013)



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An overview of novel technologies to valorise coke oven gas surplus

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ABSTRACT

The steelmaking industry is the largest energy consuming manufacturing sector in the world and is responsible for 5–7% of anthropogenic CO_2 emissions. It is therefore necessary to increase energy efficiency and reduce greenhouse gases emissions in these industries. COG, a by-product of coking plants, is one of the key ways to achieve these goals. COG, which is used as fuel in different processes of the steelmaking plants, is a H_2-rich gas with a high energetic potential. However, there is a significant surplus that usually is burnt away in torches, and even directly emitted into the air. With the aim of tackling this wasting of resources and energy inefficiency, several alternatives have been proposed during recent years. In the present work, these alternatives are reviewed and their main advantages and drawbacks are discussed.

1. Introduction

The steel industry is the largest energy consuming manufacturing sector worldwide [1,2]. Consequently, their associated CO_2 emissions account for about 5–7 % of the total anthropogenic carbon dioxide emissions [1,2]. Taking into account that steel production is expected to increase during the next few decades, a significant increase in energy consumption as well as CO_2 emissions are also expected to follow [1–3]. The steel industry has been committed to sustainability since 1960s, and in some countries (e.g. France) these have reduced CO_2 emissions and energy consumption by 60% and 50%, respectively, per tonne of steel produced [1]. However, manufacturing processes of the steel industry have reached high levels of efficiency and are very close to their physical limits in terms of carbon use [1]. Energy and greenhouse gases (GHG) emissions concerns have created the need to seek for alternative ways to improve the energy efficiency of steel plants decreasing (if possible) at the same time carbon dioxide emissions [1,2,4–6]. An interesting example of initiatives related to this concern in the iron and steel industry is the program COURSE50 ("CO2 Ultimate Reduction in the Steelmaking Process by Innovative Technologies for Cool Earth 50"). This program is currently being developed in Japan to find alternative uses for blast furnaces and coke oven gases in order to reduce carbon dioxide emissions and improve energy efficiency in Japanese steel industries [6].

Coke oven gas (COG) is a point of high interest to enhance energy efficiency and reduce GHG emissions in the steel industry [2,3,5,6]. COG is a by-product of coal carbonisation to coke which is co-generated in the coking process [7]. In spite of the reduction of coke consumption in the blast furnace (and therefore COG production), during the past few decades, blast furnaces cannot operate without coke which implies COG will continue to be produced in large quantities in the future [3].

COG has a very complex composition after leaving the coke oven. Firstly, the gas is cooled down to separate tars to subsequently undergo different scrubbing processes to eliminate NH_3, H_2S and BTX [3]. After these conditioning stages, cold COG comprises H_2 (~55–60%), CH_4 (~23–27%), CO (~5–8%), N_2 (~3–6%), CO_2 (less than 2%) along with other hydrocarbons in small proportions. Currently 20–40% of COG produced is normally utilized as fuel in the actual coke ovens [8–10]. The remaining COG generated is generally employed in alternative processes of the steel mills [3,7] but most surplus is currently burnt off in torches and even in some cases directly emitted to the air [10,11]. These vary due to the highly dynamic nature of the steelmaking process [8].

In addition, COG approximately accounts for 18% of the energy output of a coking plant due to its large low calorific value, which varies from 17 to 18 MJ/m^3[3]. Both COG energetic properties and production excess lead to large GHG emissions, energy inefficiency and most importantly a significant environmental impact which in turn is also reflected in a clearly improvable economic efficiency [3,4,12]. As an example of this inefficiency, U.S. Steel Corp. has been able to save over 6 million dollars annually by using COG as fuel in blast furnaces [8].

During past few decades, various alternatives to valorise COG have been proposed, including its use for energy production, a direct utilization in the blast furnace to produce "pig iron" or gas treatment for the production of chemicals and fuels.

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This work is aimed to provide an overview of some of the most promising and challenging technologies from the research viewpoint. Proposed alternatives can be grouped into three main categories: hydrogen separation, synthesis gas production and other technologies.

Each of these alternatives requires different preconditioning stages as the presence of some COG components (especially H_2S and NH_3) may be highly damaging for the processes [3,4,13]. This will be described in detailed in each section.

2. Hydrogen separation

Hydrogen is the main and most valuable component in COG, which is the reason why COG has been proposed as an alternative hydrogen source. Pressure swing adsorption and membrane separation have been the two main technologies proposed for this purpose, although other possibilities have also been investigated including hydrate formation and cryogenic separation.

2.1. Pressure swing adsorption

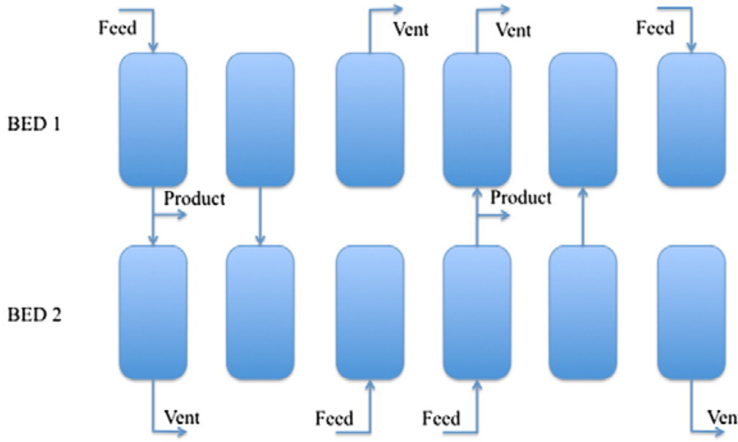
The leading technology to efficiently separate hydrogen from COG is pressure swing adsorption (PSA) [6,7,11,14–23]. This technology is a low-cost, low-energy and highly efficient gas separation process [24]. PSA processes employ several parallel units that operate in consecutive steps. Fig. 1 shows a schematic representation of the operating steps in a system comprising two adsorption beds. The process commences with an adsorption step, in which the crude gas flows through a PSA unit filled with adsorbent materials at the highest operation pressure. The adsorbable substances are retained by the adsorbents and the rest of the gas leaves the unit. After a period of time, the adsorbent saturates and the operation is stopped. At this point, the adsorbent needs to be regenerated at the lowest pressure, so the unit needs to be depressurised. The depressurisation cycle is terminated by counter-flow expansion down to the lowest pressure, called dump step. The adsorber is regenerated with a gas stream which purges all the adsorbed impurities. Finally, the adsorber is brought back to high pressure conditions to resume adsorption. These cycles operate at constant temperature, requiring no heating or cooling steps [24,25]. Different adsorbent materials are utilized for hydrogen recovery, most commonly carbonaceous materials, alumina oxides or zeolites [16,17,19,24].

Other components in COG (e.g. higher hydrocarbons, H_2S or NH_3) have to be removed before reaching the adsorption bed owing to issues associated to bed saturation (as they cannot be desorbed by decreasing the pressure in the systems) [3,18]. For this reason, COG needs to undergo complete preconditioning prior to its utilization in PSA processes.

Two different streams, namely a H_2-rich stream and a highly concentrated CH_4 gas, are generally obtained in PSA H_2 separation from COG. The methane-enriched stream can be considered as a substitute of natural gas (SNG), with the possibility to be employed as fuel in various plant processes in a similar way to COG. However, the loss of energetic power due to H_2 separation from COG needs to be compensated by other fuels if this methane-rich stream is used as fuel [7,15,16]. Other technologies should be obviously used in combination with PSA to achieve an optimum valorisation of COG.

Most studies published in the field of PSA have considered simple mixtures with two or three components, which cannot possibly have a similar behaviour to that of COG [18,19]. Yang and Lee [18] studied the dynamics of the system and proposed a mathematical model of PSA adsorption to recover H_2 from COG using a layered bed of activated carbon and zeolites. These authors claimed that the composition of the bed is a key parameter in the process, since the employed materials can influence the concentration of the major impurity in the final stream. In the particular case of a layered bed of activated carbon and zeolites, it is necessary to establish the optimum carbon ratio (defined as the ratio of activated carbon layer length to the bed length) [18,21]. Another interesting conclusion of these studies is that, although N_2 is a minor impurity in COG, it can play an important role in the process, giving rise to different breakthrough times for the rest of the components fed into the PSA column [21,22]. Ahn et al. [20] included a backfill step in the PSA process and found that this additional step increased H_2 purity in the final stream at the expense of decreasing H_2 recovery. However, H_2 purities higher than 99.99 % were very difficult to achieve.

Further studies beyond fundamental research have also been conducted to ascertain a plausible implementation of this technology at industrial level. Joseck et al. [7] explored the possibility of H_2/COG separation by means of PSA technology, aiming to valorise COG for



BED 1	AD	DPE	DP	PG	PPE	FP
BED 2	PG	PPE	FP	AD	DPE	DP

Fig. 1. Scheme of the operation steps of a pressure swing adsorption system composed of two adsorption beds (AD, adsorption; DPE, depressurizing pressure equalization; DP, depressurization; PG, purge; PPE, depressurizing pressure equalization; FP, feed pressurization). Adapted from [20].

fuel cell vehicles (FCVs). The study was carried out in the Rust Belt (Mideast-Northeast US area with an important network of coking and steel plants) and showed that H_2 obtained from such a large concentration of plants could fuel ca. 1.7 million FCVs. The economics of the project however need to be thoroughly examined but the project can in principle offer a significant potential in terms of energy savings and reduction of GHG emissions.. A similar study conducted by Hwang and Chang [23] assessed the possibility to use hydrogen from different sources in fuel cell scooters in Taiwan. Life-cycle Analysis studies revealed that FC scooters fueled with hydrogen from COG accounted for the most efficient technology, resulting in remarkably reduced GHG emissions together with a improved energy efficiencies.

2.2. Membrane separation

Another recently proposed technology for hydrogen recovery from COG is membrane separation [11]. Membrane gas separation is a pressure-driven process which entails several advantages compared to other technologies (i.e. easy operation, low capital and operating costs and low-energy requirements) [26]. In a membrane separation process, a gaseous mixture at high pressure is forced to pass through the surface of a membrane which is selectively permeable to one or more of the gas components. As a result, the permeate (stream obtained after it has passed through the membrane) can be enriched in these components while the retentate (stream that does not pass through the membrane) is therefore enriched in the rest of the components. A basic scheme of the process is shown in Fig. 2 [25,27]. Shen et al. reported that a H_2-rich stream ($>95\%$ maximum H_2 concentration) and a CH_4-rich stream (70% maximum CH_4 concentration) could both be obtained using an organic membrane [11]. However, membrane technologies have been mostly applied in the form of membrane reactors to syngas production processes, to increase conversions and selectivities, as detailed in Section 3.

2.3. Other technologies

Other hydrogen separation technologies including cryogenic separation [28] and hydrate formation [29] have been proposed as alternatives to PSA and membrane separation for COG valorisation. Cryogenic separation processes proposed by Chang et al. [28] comprising four steps, namely 1) separation of heavier compounds (hydrocarbons like ethylene and propane) 2) methane separation 3) O_2–CO–N_2 separation and 4) eventual separation-liquefaction of hydrogen. While the principles of the proposed methodology are sound, this technology is still in its infancy and needs to undergo further developments and studies prior to a potential implementation at industrial scale.

Comparatively, hydrate separation has the advantage of being a simple process which can be operated at mild conditions. Hydrates are non-stoichiometric crystalline compounds formed by small molecules of gas and water under certain temperature and pressure conditions [29,30]. A maximum H_2 concentration of 80 vol. % in the final product has been obtained using this hydrate methodology, with recovering yields in the 72–90% range [29]. Apart from a low hydrogen concentration, the technology has associated drawbacks including the need to use additives such as tetrahydrofuran (to decrease pressure operation) or sodium dodecyl sulfate (to increase reaction rates). The proposed technology has promising prospects of application in hydrogen recovery from COG but it is currently at a very low stage of development compared to alternative available technologies.

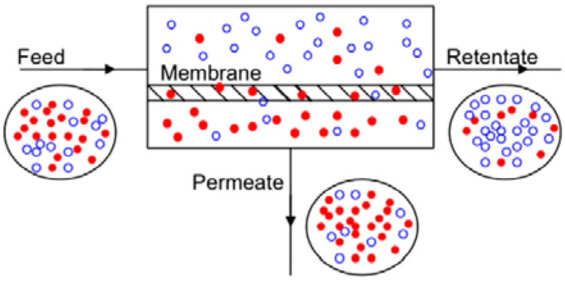


Fig. 2. Scheme of the operation of a separation membrane system.

3. Synthesis gas production

Synthesis gas (syngas) is a H_2 and CO enriched mixture utilized as raw material for the large scale production of hydrogen and a wide variety of organic products and fuels [31]. Syngas has been extensively produced from natural gas and oil, but the limited supply of fossil fuels and concerns on climate change and GHG emissions have intensified the search for alternative processes of syngas production including biomass gasification [32], biogas reforming [33] and the thermal upgrading of COG [5,9,10,34–55]. The main thermal upgrading technologies studied for COG valorisation include steam [34–39,43–45,49] and dry reforming [9,40–42,46–48] as well as partial oxidation [10,50–55]. Turpeinenet al. [56] reported an interesting thermodynamic analysis of COG conversion into hydrogen using these three different technologies as compared to other potential hydrogen sources (e.g. natural gas, biogas and refinery gas). This study conveys an idea of the remarkable potential of COG as a source of syngas, particularly related to the use of the produced syngas for hydrogen generation. COG is clearly the best source in terms of energy consumption and CO_2 emissions when steam and especially dry reforming is conducted. Partial oxidation of COG still gives rise to the lowest CO_2 emissions but syngas production from natural and refinery gas is less energy consuming [56].

All proposed methodologies employ a catalyst which can be severely poisoned by the presence of some COG components. For this reason, a cleaning process (e.g. scrubbers or absorbers)is required prior to reaction [3,57,58]. In the case of dry reforming, the development of the SPARG process (where the catalyst is partially poisoned with H_2S to avoid coke formation) may avoid the need to remove H_2S [59,60].

3.1. Steam reforming

The steam reforming of methane (Reaction 1) is currently the main process for hydrogen or syngas production. This process involves the heterogeneously catalysed reaction of methane and steam to obtain a syngas with high H_2/CO ratio (theoretically 3/1). Nearly all metals from Group VIII have been investigated as supported on various supports. Ni has attracted most interest due to its greater availability and lower cost compared to the other metals. Normally, the reaction takes places in tubular reactors, the catalyst being placed inside the tubes. The process is carried out at high temperatures (700–1000 °C) as the steam reforming of methane is a highly endothermic reaction. The pressure is normally mild (20–30 bar), although the reaction produces an increase in the net number of moles and, therefore, high pressures lead to a reduction in the conversion of the systems. This is assumed because the products are normally used in processes at high pressure and it is cheaper to compress the methane and the steam than the synthesis gas produced. Moreover, carrying out the process under pressure allows smaller reactors to be used [57,61–63].

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \text{(Reaction 1)}$$

Side reactions may take place between the different species present in COG. This may affect the selectivity of the process and the final product composition. Some examples of side reactions include water gas shift (WGS), reverse WGS chemistries (Reaction 2) and dry reforming processes (Reaction 3), as well as CH_4 decomposition (Reaction 4) and the Boudouard equilibrium (Reaction 5).

$$H_2O + CO \leftrightarrow H_2 + CO_2 \qquad \text{(Reaction 2)}$$

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2\,CO \qquad \text{(Reaction 3)}$$

$$CH_4 \rightarrow 2H_2 + C \qquad \text{(Reaction 4)}$$

$$C + CO_2 \leftrightarrow 2\,CO \qquad \text{(Reaction 5)}$$

One of the most critical factors in the steam reforming of methane is H_2O/CH_4 ratio. Steam is generally injected in excess over the stoichiometric value of the reaction ($H_2O/CH_4 > 1$) as it prevents catalyst deactivation caused by carbon deposits on the catalyst [57,61]. Excess steam is used to prevent the formation of coke, while additional heat is needed, so a lower H_2O/CH_4 ratio is desired to improve the energy efficiency of the process. In the case of the steam reforming of COG, this ratio may differ from that used in the steam reforming of methane, as the presence of H_2, CO_2 and CO in COG influences the equilibriums of the different reactions involved in the process. Zhang et al. [38,45] reported that the thermodynamically permissible H_2O/CH_4 value should be in 1.1–1.3 range, at temperatures between 950 and 1000 °C. A kinetic model for the steam reforming of COG was also proposed taking into consideration the combination of steam and dry reforming (due to the presence of carbon dioxide in COG). Results revealed that both reactions were of first order from methane, steam and carbon dioxide, with kinetic parameters shown in Table 1. Changing the H_2O/CH_4 ratio to 1.0 was also found to be possible using a NiO/MgO catalyst due to excellent coking resistance of the catalyst [43].

The use of hot COG (no conditioning processes prior to leaving the coke oven) in the steam reforming process has been widely proposed to reform methane as well as the tarry components, taking advantage of the high temperatures of the gas to promote the desired reactions [34–37,39,44,49]. As hot COG contains ca. 10–15% steam, the energy efficiency and cost of the process can be improved as lower quantities of steam need to be injected in the system. Tars usually account for 30 wt% of hot COG, the main components being naphthalene, benzene, pyrene and toluene [34,35]. These species compete with each other and with methane in steam reforming processes, especially naphthalene (the only component which reacts at temperatures below 750 °C while at higher temperatures the other compounds react once naphthalene has been completely converted) [34]. Steam reforming of hot COG can be carried out in the presence or absence of catalysts, but the presence of a catalyst significantly improves the results obtained. The main disadvantage of using hot COG is related to the lower ratio H/C obtained as compared to conditioned COG which in turn leads to a very important production of carbonaceous deposits of different nature in the system (i.e. well-ordered graphite, non-oriented carbon forms, carbon filaments and metal carbides) depending on the working temperatures [49]. The generation of carbonaceous deposits also increases the deactivation rate of the catalyst. The presence of hydrogen, an adequate load of active metal as well as an appropriate steam/carbon ratio could contribute to reduce such deactivation rate [39,44,49]. The presence of H_2S is also highly undesirable due to its poisoning effects on catalysts (e.g. Ni) but generally this deactivation effect is low and the catalyst can easily be regenerated [34,49]. Remarkably, this technology can potentially generate 3–5 times more H_2 to that of the COG before undergoing the reforming process, making the steam reforming of hot COG one of the most promising alternatives for H_2 production from COG. Reports may indicate that hydrogen can be produced by combining steam reforming and partial oxidation of hot COG, reducing by 30% production costs as compared to PSA mediated direct hydrogen separation from the COG [37].

Table 1
Kinetic parameters of the steam reforming of COG [38].

	A	E_a (J/mol)
Steam reforming rate (K_{SR})	4.56×10^9	21373.4
Dry reforming rate (K_{DR})	8.06×10^8	20843.7
Kinetic equation	$r_{CH4} = A_{SR}\cdot\exp(-E_{aSR}/T)\times C_{CH4}\times C_{H2O} + A_{DR}\times \exp(-E_{a\,DR}/T)\times C_{CH4}\times C_{CO2}$	

3.2. Dry reforming

CO_2 reforming or dry reforming of methane (Reaction 3) has been widely proposed as an alternative process to steam reforming of methane [64–68]. The increasing interest in this process is based on the lower energy requirements compared to steam reforming together with the consumption of two commonly extended greenhouse gases such as CH_4 and CO_2, with an eventual generation of highly valuable products. CO_2 reforming also allows the production of a low H_2/CO ratio syngas (theoretically 1/1, although the presence of side reactions, such as reverse WGS slightly reduces it), which is suitable for the production of higher hydrocarbons and oxygenated derivatives [31,66].

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2\,CO \qquad \text{(Reaction 3)}$$

As in the case of steam reforming, dry reforming must be carried out in the presence of a catalyst. Once again, Ni has been the most commonly metal utilized as catalyst in dry reforming chemistries, but the drawback to this process is the intense formation of carbonaceous deposits which leads to a rapid catalyst deactivation. This drawback should be addressed prior to technology implementation at industrial scale. Consequently research efforts related to dry reforming of methane have been focused on the development of commercial catalysts able to achieve high and stable conversions, being at the same time resistant to deactivation [64,65,69–71]. To date, only two processes based on methane dry reforming have been industrially implemented: the SPARG process [59,60] and the CALCOR process for CO production [72].

The SPARG process could be especially interesting in the application of dry reforming methodologies to COG. This technology is based on the addition of H_2S to the process stream which leads to a partial poisoning of the catalyst but prevents at the same time the formation of carbonaceous deposits in the active centers of the catalyst, keeping high conversions of CH_4 and CO_2 in the systems [59,60]. In this way, the previous scrubbing step required to remove H_2S from COG can be eliminated in the conditioning stages, improving the economics of COG valorisation.

Until now, the application of dry reforming to COG has received less attention than steam reforming or partial oxidation [9,4042,46–48]. Nevertheless, results reported in these works are encouraging, pointing to a potentially optimum way to transform COG into syngas with a close to optimum $H_2/CO = 2$ ratio to be employed in Fischer–Tropsch (FT) synthesis of chemicals as well as in methanol production. Comparatively, steam reforming of COG gives rise to H_2/CO ratios that are considerably higher than 3 (ratio obtained with methane) [47]. In the case of partial oxidation, the H_2/CO ratio obtained with methane is ca. 2, so that an expected H_2/CO ratio of 2.5–3 will be likely to be the case in COG partial oxidation due to its hydrogen content. These values are not close to the optimal requirements for FT processes and methanol synthesis [47] and entail the addition of further conditioning stages which are not required in the case of dry reforming of COG [9,40–42,47].

Side reactions may also influence the theoretical results in COG dry reforming as observed in other processes. In this case, the reverse WGS (reaction 2) is the most critical. acting as a step in the process, rather than as a side reaction [40], leading to two different alternative pathways:

1. *Direct dry reforming*: methane is decomposed into hydrogen and carbon through reaction 4 and then carbon is gasified to CO through the Boudouard equilibrium (reaction 5).

$$CH_4 \rightarrow 2H_2 + C \qquad \text{(Reaction 4)}$$

$$C + CO_2 \leftrightarrow 2\,CO \qquad \text{(Reaction 5)}$$

2. *Reverse WGS followed by steam reforming (SR)*: the large amount of hydrogen contained in COG promotes the RWGS reaction (reaction 2), producing water which subsequently reacts with methane (steam reforming) to generate CO and H_2 (reaction 1).

$$H_2 + CO_2 \leftrightarrow H_2O + CO \qquad \text{(Reaction 2)}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \text{(Reaction 1)}$$

The direct dry reforming generates carbon as by-product as CO_2 is not generally able to convert all carbon produced to CO, resulting in the deactivation of the catalyst [9,41,47]. Comparatively, the RWGS + SR pathway generates water as by-product which influences H_2 selectivity (reduced) and consequently H_2/CO ratios differ from 2 [9,40–42,47].

Three different types of catalysts have been studied for dry reforming processes. These include carbonaceous materials, Ni supported catalysts and mixtures of both catalysts. Table 2 summarises the best conversion and selectivity results obtained for the different literature reported catalysts.

The most interesting results have been obtained with mixtures of activated carbon and Ni/Al_2O_3 catalysts, since these have been reported to have a synergetic effect [40], which was previously observed in the dry reforming of methane [73]. Interestingly, this synergism that leads to higher activities and selectivities was more noticeable in COG dry reforming [40], with catalysts also being more stable (in terms of BET surface area reduction) and generating less water [40]. CO was found to have a negative influence on such synergetic effect, pointing out that these catalysts will be more efficient in processing COG of low CO content.

3.3. Partial oxidation

The partial oxidation of methane (Reaction 6) is a mildly exothermic reaction which yields a syngas with an intermediate H_2/CO ratio between those obtained with steam and dry reforming [74].

$$CH_4 + {}^1\!/_2O_2 \leftrightarrow 2H_2 + CO \qquad \text{(Reaction 6)}$$

In this case, side reactions (Reactions 7 and 8) may also affect the process, changing the H_2/CO ratio and reducing its selectivity and efficiency [75].

$$CH_4 + 2\,O_2 \leftrightarrow 2H_2O + CO_2 \qquad \text{(Reaction 7)}$$

$$CH_4 + O_2 \leftrightarrow 2H_2 + CO_2 \qquad \text{(Reaction 8)}$$

The partial oxidation of methane can be carried out in two different ways: non catalytic and catalytic [76]. The non-catalytic method is an established industrial process which operates at high temperatures (>1100 °C) and mild pressures (50–70 atm, mainly due to the high pressure downstream process, as in the case of steam reforming) and which requires very complex equipment. This normally makes the process even less energy efficient to that of methane steam reforming [62,74,76,77].

The catalytic method has a long history (like steam reforming) but has attracted significantly less attention until the past decade. However, its importance will most probably increase during the next few years due to several advantages [76,77]:

- It is a mildly exothermic process. This will increase the energetic efficiency of the process in addition to the lower operating temperatures needed due to the use of catalyst (750–1000 °C). This is probably the most important advantage of the partial oxidation of methane.
- The final H_2/CO ratio is generally 2, that required for methanol production and FT processes. However, this advantage disappears in COG valorisation practises if hydrogen contained in COG is not previously removed (otherwise, the final H_2/CO ratio will exceed 2, making it less suitable than in the case of the dry reforming for the synthesis of chemicals such us methanol or dimethyl ether [9]).
- Product gases have a very low CO_2 concentration, which often needs to be removed prior to the use of syngas in downstream processes.
- Reaction rates are higher compared to those of steam or dry reforming under otherwise identical operating conditions, giving rise to a faster process.

Most research efforts in the field of partial oxidation have been focused on the development of appropriate catalysts for the process, that overcome drawbacks including carbon deposition or loss of active compound during the reaction [75,77]. Three main types of catalysts have been proposed based on transition metals (nickel, cobalt and iron), and noble metal supported catalysts as well as transition metal carbide catalysts [75,77]. Due to their lower price and wider availability, Ni, Co and Fe, have been the focus of most studies in spite of the improved resistance to deactivation of noble metal supported catalysts. Nickel has been reported to be highly active and selective for syngas production, but it also efficiently catalyses carbon formation. The use of this particular type of catalyst requires O_2 excess working conditions to work with an excess of O_2 to reduce carbon formation. Modification of the support has been reported to improve the stability of the catalyst, but its deactivation is unavoidable with time due to a reduction in the surface area of nickel and carbon deposition. The addition of Co and Fe has been reported to enhance the resistance of the catalyst to deactivation. Iron addition stabilises nickel, as compared to a reduction in carbon formation strongly promoted by cobalt addition (which makes possible to work at lower temperatures in Co-promoted catalysts) [77].

Reports focusing on the application of partial oxidation to COG have been mostly catalytic [10,50,51,53,78,79], with only a few reports on

Table 2
Conversions and selectivities of the catalysts studied in the dry reforming of COG.

Catalyst	Temperature (°C)	VHSV (L/g×h)	Conversions (%)		Selectivity (%)	Ref.
			CH_4	CO_2		
Charcoal	1000	7.5	70	90	n.d.	[48]
Activated carbon	1000	0.75	82	95	90–100	[42]
Ni/SiO_2	800	30	75	80	100	[9]
Ni/Al_2O_3	900	9	90	95	94	[41]
Ni/Al_2O_3 (67%) Activated Carbon (33%)	800	3,75	85	93	85	[40]

non-catalyzed partial oxidation [54,55], mostly related to numerical simulations. Chen et al. [80] performed a theoretic thermodynamic analysis of the partial oxidation of cold preconditioned COG to study the influence of two critical parameters on conversions and yields: temperature (studied in interval from 500 to 1750 °C) and O_2/CH_4 molar ratio (studied in interval from 0.25 to 1). They also studied the possibility of adding an additional step to the process, a WGS reaction of syngas, aiming to increase H_2 yield. The optimal operating conditions found comprised an O_2/CH_4 molar ratio of 0.5 and temperatures higher than 1000 °C. Under these conditions, carbon deposition was negligible [80]. A related thermodynamic study reached almost the same conclusions (namely an ideal O_2/CH_4 molar ratio in the range of 0.46–0.47), but suggested temperatures could be reduced to 800–900 °C for a carbon deposition-free process [81].

A deep analysis of the influence of different reaction conditions on the final syngas produced using Ni/SiO_2 catalysts indicated that oxygen was completely consumed at temperatures from 600 to 900 °C, and H_2 and CO selectivities increased (H_2/CO ratio decreased) at increased temperatures [9]. This behaviour was claimed to be influenced by methane combustion at low temperatures, whereas partial oxidation processes prevailed at high temperatures. The influence of O_2/CH_4 ratio was also studied and shown to be of critical importance in the process [80]. Conversion increased dramatically when O_2/CH_4 ratio was increased from 0.125 to 1.0 at a temperature of 750 °C. Selectivities to H_2 and CO decreased at O_2/CH_4 ratios higher than 0.5. The authors suggested that these results were a consequence of the consumption of the surplus of oxygen in the complete oxidation of methane (reaction 8) and/or the complete oxidation of the produced H_2 and CO (reactions 9 and 10):

$$H_2 + {}^1/_2 O2 \leftrightarrow H_2O \qquad \text{(Reaction 9)}$$

$$CO + {}^1/_2 O_2 \leftrightarrow CO_2 \qquad \text{(Reaction 10)}$$

An increase in space velocity favoured the combustion of methane in detriment to partial oxidation. Therefore, the value of the space velocity was suggested to play an important role in order to be able to treat as much gas as possible while avoiding high rates of methane combustion, which will lead to a lower selectivity.

One of the most important issues in the industrial implementation of partial oxidation technologies relates to its elevated cost (in both economic and energetic terms) to supply pure oxygen to carry out the reaction. In fact, as much as 40% of the expenses of a partial oxidation plant come from oxygen production processes [82]. To overcome this problem, the use of membrane reactors has become an attractive alternative to conventional technologies. In the particular case of COG partial oxidation, membrane reactors have been pretty much the only technology to be investigated in recent years [10,39,50,51,53,78,79,81,83]. These reactors offer the possibility to feed air directly instead of the need for previous separation processes to feed pure oxygen. Inside the reactor, an oxygen permeable membrane exclusively allows oxygen to reach the catalyst, but not the other components present in the air. A scheme of this system is shown in Fig. 3. This technology has shown promising results to date, with yields, conversions and selectivities being as high as those reported using the conventional technology. It can therefore be considered as a potential future alternative for syngas production from COG valorisation [10,78,81,83]. The presence of other species different from methane influences the performance of the membrane in terms of stability and oxygen flux. Hydrogen is a particularly interesting compound which behaves as a "pseudo-catalyst" and favours the oxygen permeation through the membrane when BCFNO membranes (composed of Ba, Co, Fe, Nb and O) are employed [84]. These membranes also show excellent long-term stability. In the light of these premises, research into this type of membrane technologies and reactors for the partial oxidation of COG are likely to take over during the next few years. In fact, such technology has also been applied to hot COG and results were even more interesting to those of cold preconditioned COG [52]. Quantitative conversions could be achieved for heavy components (e.g. toluene)at methane conversions higher than 90% [52].

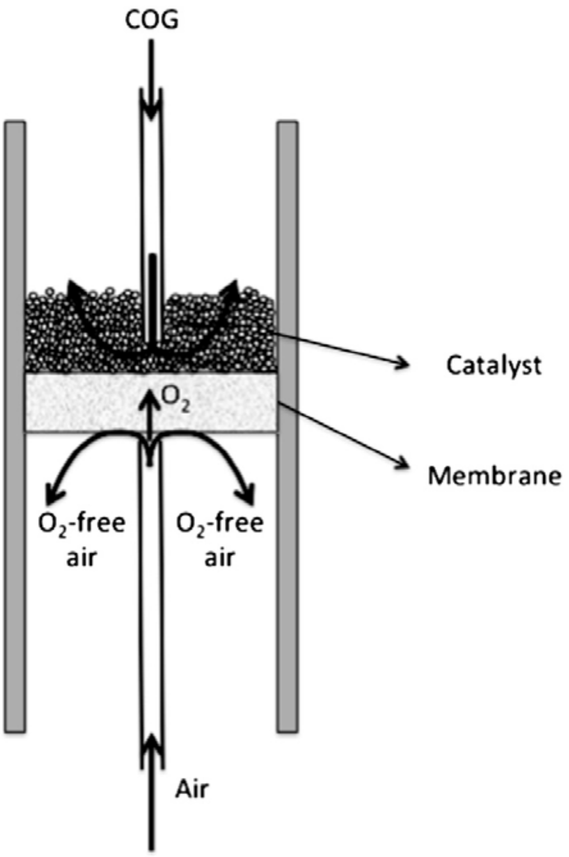


Fig. 3. Scheme of a membrane reactor for the partial oxidation of coke oven gas.

3.4. Methanol production

Most of the published works on the transformation of COG into syngas focused on the final production of hydrogen. However, an interesting alternative reported in some work deals with the use of COG-derived syngas for the synthesis of organic chemicals including methanol. The production of methanol from COG-derived syngas has been widely investigated due to its practicality in obtaining a liquid fuel instead of a gaseous product [40–42,46,85,86] as well as to the recent interest in methanol over the past years [2]. Methanol has been proposed to potentially play a key role in the future energetic model as a raw material for biofuels production of biofuels and/or hydrogen carrier in the Hydrogen Economy. Indeed it has acquired so much importance that the Nobel Prize winner, Prof. George A. Olah, has proposed Methanol Economy as an alternative to Hydrogen Economy [87,88].

In the case of COG, the most evident example of the increased interest in methanol production from COG is the construction of several industrial plants in China to manufacture 1.2 million ton/year of methanol from COG, China being world leader in coke production (and therefore COG) [89].

COG dry reforming can be considered as the most interesting syngas production technology for methanol synthesis due to the possibility to obtain an optimum H_2/CO ratio of 2 in just one step (without the need for any preconditioning stage), as long as such dry reforming is conducted under stoichiometric conditions of CH_4 and CO_2 [40–42,47]. Moreover, the process also involves a partial recycling of the CO_2 (Fig. 4) [40–42], as half of the CO_2 produced upon methanol consumption is recycled in the dry reforming process.

There are two reactions taking place in the synthesis of methanol (Reaction 11 and Reaction 12).

$$2H_2 + CO \leftrightarrow CH_3OH \qquad \text{(Reaction 11)}$$

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O \qquad \text{(Reaction 12)}$$

The presence of Reaction 12 imposes an additional restriction to that of H_2/CO ratio, as represented in Eq. (1) [31,46,87,88,90–93]. The optimal ratio for the R parameter has been established to being the 2.03–2.05 range [88,93]

$$R = (H_2 - CO_2)/(CO + CO_2) \qquad (1)$$

This R parameter gives values slightly lower than 2 when COG-derived syngas is produced by means of dry reforming [40–42]. However, as conversions in methanol synthesis are very low, the gas purge in the recycling loop that needs to be included in the process [31,90], gives rise to a hydrogen-rich gas, which can be recovered and used as fuel for the plant or to adjust the value of the R parameter [90]. A detailed thermodynamic analysis of this process was carried out by our research group [94]. Results showed that it is possible to obtain H_2/CO ratios very close to 2 and R parameter values slightly lower than 2, at high conversions and selectivities, working at temperatures higher than 800 °C and under stoichiometric conditions of CH_4 and CO_2 [94].

Further techno-economic studies of methanol production from COG in a Swedish plant show that this can be economically competitive with other methanol production technologies and, annual production could meet as much as 58 % of the methanol demand in the region where the plant is situated [86].

Maruoka and Akiyama [85] also studied the potential of methanol production from COG, in this case, from the exergetic point of view. They proposed an energetic integration, using the latent heat from the exhaust gases from the LD converter of the steel mill, in the reforming process of COG to produce syngas for methanol synthesis. Methanol could be produced with only 28 % of the total exergy loss experienced by the conventional methanol production process.

4. Other technologies

The feasibility of the aforementioned technologies has been demonstrated by their already existing applications in current industrial plants [8,89]. Interestingly, there are other emerging technologies that could become important alternatives in the near future.

For example, the chemical looping combustion (CLC) of COG, with the objective to improve combustion efficiency and facilitating the capture of the CO_2 produced in the system has been proposed [95]. This technology is an elegant and energy efficient method to capture CO_2 from fuels combustion. It consists of two reactors and a circulating metal oxide that works as oxygen carrier (Fig. 5). The metal oxide is reduced in the fuel reactor, then circulates to the air reactor where it is oxidised to its initial state. In this process, H_2O and CO_2 are the only combustion products and CO_2 is easier to capture as these products are not diluted with N_2 from air.

In this work, different oxygen carriers were studied, the best results being obtained with that comprising 45% of Fe_2O_3, 15% of CuO and 40% of $MgAl_2O_4$. This carrier showed a high and stable activity over 15 reduction-oxidation cycles and achieved a maximum fuel conversion of 92% [95].

Other systems proposed during recent years are based on the combination of more than one technology. Single technologies will not be able to achieve an optimal utilization of COG. However, combinations of such systems could possibly produce the needed synergy to improve single technologies. Several authors have recently proposed the combination of these techniques. A system in which PSA-mediated separation of hydrogen was combined with subsequent thermal upgrading of COG to produce syngas (and more H_2) was recently proposed by Wang et al. [96]. This study also included the necessary CO_2 adsorption technology to improve hydrogen production. Such combination led to an H_2 production increase of about 9 %.

Comparatively, Jin et al. [97] proposed a multifunctional energy technology in which COG and coal were utilized to produce hydrogen and energy in the same system. Improved hydrogen recoveries and energy efficiencies at reduced CO_2 emissions could be obtained in the combined technology as compared to those of individual systems.

A polygeneration system in which three different chemicals (methanol, dimethyl ether and dimethyl carbonate) were produced from COG and coal gasification gas by means of an integrated catalytic synthesis

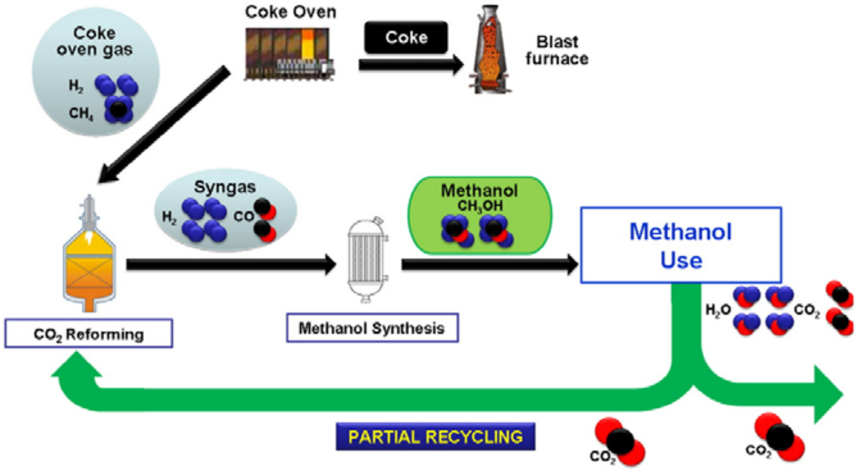


Fig. 4. Partial recycling of CO_2 in the dry reforming of coke oven gas to produce methanol for energy generation.

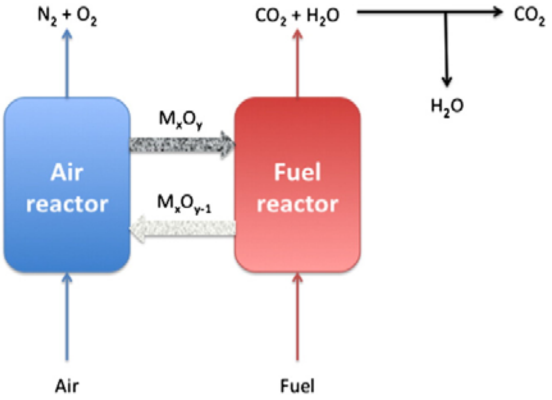


Fig. 5. Scheme of the process of chemical looping combustion.

procedure was also recently reported [98]. A simulation of the proposed system (with comments on improvements needed in syngas conversion and reformer design) was also included as part of this work to demonstrate the potential of the technology to efficiently produce high added value chemicals.

5. Future prospects and outlook

The steelmaking industry is the largest energy consuming manufacturing sector in the world and, therefore, it is responsible for 5–7% of the total anthropogenic CO_2 emissions. Consequently, it is necessary for this industry to achieve the highest possible energetic efficiency and to reduce GHG emissions. A point of high interest for this purpose is coke oven gas (COG). Although this gas is used as fuel in different processes of the steelmaking plants, there is an important surplus, which needs to be treated in order to obtain a better energetic efficiency, diminish GHG emissions and achieve higher economic benefits.

During recent years, alternative technologies for exploiting the COG surplus have attracted much attention due to the environmental, energetic and economical benefits that can be obtained from them. Table 3 summarizes the main advantages and disadvantages of all the technologies reviewed in this work. These alternatives can be divided in three main blocks: hydrogen separation, synthesis gas production and other technologies. Hydrogen separation has a huge potential since COG is a H_2-rich gas, which would allow a "green" production of H_2, since, instead of the pollution and GHG emissions characteristic of conventional H_2 production technologies, using COG as H_2 source, would eliminate the pollution resulting from its combustion. Hydrogen separation has been one of the most studied alternatives for using the COG surplus. Moreover, some of these technologies, such as PSA and membrane separation are already in use in other industrial processes, so their implantation in coking plants would not present any special difficulty. However, the H_2 recovery from COG surplus has an important drawback that needs to be overcome. With these technologies, no advantage is taken of the other gases, especially those containing carbon, i.e. CH_4, CO, CO_2 and light hydrocarbons. For this reason, H_2 separation needs to be combined with other technologies in order to exploit all of the components of the COG surplus.

Table 3
Advantages and disadvantages of the different technologies for COG use.

Process	Technology	Advantages		Disadvantages	
Hydrogen separation	PSA	• Well developed • Easy industrial implementation	• Low energy requirement • Low operating cost • High H_2 purity	• Need of other technologies for whole exploitation of COG surplus	• Previous separation of tar, BTX, H_2S, NH_3 and light hydrocarbons
	Membranes	• Well developed • Easy industrial implementation	• Easy operation • Low capital and operating costs • Low energy requirement		• H_2 purity limited to 95 % • Less studied for H_2 separation from COG
	Hydrates	• Mild operating conditions	• No need of removing light hydrocarbons		• Low stage of development • Low H_2 concentration • Needs additives
	Cryogenic	• High purity of H_2			• Complicated process • Low stage of development
Syngas Production	Steam reforming	• Lower CO2 emissions than conventional processes • Whole exploitation of COG surplus • High versatility for the production of chemicals	• Most used and known technology • Catalysts well developed • High H_2/CO ratio • Possible use of hot COG (but quick catalyst deactivation)	• High energy requirements • High operation and capital costs	• The high H_2O/CH_4 ratios avoiding catalyst deactivation decrease energy efficiency • Mild pressures • With cold COG the complete elimination of BTX, NH_3 and H_2S is needed
	Dry reforming		• Requires lower pressure and energy • Consumption of CO_2 • $H_2/CO \approx 2$ (Fischer–Tropsch) • Possible to avoid total H_2S elimination		• Needs complete elimination of BTX and NH_3 • No commercial catalyst
	Partial oxidation		• High energy efficiency • Higher reaction rates • Possible use of hot COG (but quick catalyst deactivation)		• Cold COG needs complete elimination of BTX, NH_3 and H_2S • High temperatures • High costs (reduced with membrane technology) • Low operation margin in the O_2/CH_4 ratio
	Methanol production		• Possible partial recycling of CO_2 • Industrially implanted • Economically competitive • Easier to handle than H_2		• Recovery of unreacted H_2 to adjust the H_2/CO ratio • Higher cost and more complex facilities
Other technologies	Chemical Looping Combination	• Easier CO2 capture • Optimal use of COG surplus		• Low stage of development	

For syngas production, COG is upgraded by means of the different technologies currently available (steam reforming, dry reforming and partial oxidation), making these processes interesting alternatives for H_2 amplification of the original COG or for the production of chemicals, thereby supplanting conventional production from natural gas or petroleum. Synthesis gas production from COG surplus seems to be the most interesting alternative for the use of this interesting source. The large number of processes available (steam reforming, dry reforming, partial oxidation) allows obtaining a wide variety of H_2/CO ratios (from 2 in dry reforming to nearly 5 in steam reforming), making the COG alternative highly versatile for obtaining different final chemical products. Moreover, even for the production of H_2, COG is a more interesting alternative than H_2 separation, since the hydrocarbons (CH_4 and C_nH_m) are also used. However, reforming processes are energy intense technologies, so their industrial implantation needs to study in depth the energetic requirements and benefits. Besides, the construction of reforming plants requires a high level of capital investments.

Special attention has been paid to methanol production, due to the interest of this product as a gasoline substitute or H_2 carrier. In this case, dry reforming of COG seems to be the preferable technology, since it will require fewer process units than the other thermal upgrading technologies. In the particular case of methanol, it is already industrially implanted and. Besides, by using dry reforming as the method for the production of synthesis gas, it will be possible to partially recycle the CO_2 produced when methanol has been consumed. Moreover, the economic studies carried out on this matter, suggest that it would be economically competitive with classical methanol synthesis processes. Even so, the complete process of methanol production will require a higher level of investment and more complex facilities.

Other interesting alternatives, such as COG chemical looping combustion or the combination of two or more of the previous technologies have been proposed, though research into these systems is still in its initial stages and will need further research before considering their implantation at industrial level.

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2. OBJETIVOS

La presente Tesis se enmarca dentro del contexto de búsqueda de soluciones eficientes para los excedentes de gas de coquería en las industrias siderúrgicas. Más concretamente, el objetivo principal se centra en **estudiar el proceso de reformado seco del gas de coquería procedente de la producción de coque, con el propósito de obtener un gas de síntesis que pueda ser empleado para la producción de metanol de forma viable, eficiente y respetuosa con el medio ambiente**.

La idea de utilizar el gas de síntesis obtenido mediante reformado seco del gas de coquería para la producción de metanol se debe a que, realizando un balance al CO_2 a lo largo de todo el proceso, esta tecnología da lugar a un *"reciclado parcial"* de CO_2, como muestra la Figura 5[10-14]. En esta figura se detalla como, por cada dos moléculas de metanol consumido (en cualquiera de los diferentes usos que puede tener esta molécula orgánica) se generan dos moléculas de CO_2, y que por cada dos moléculas de metanol generadas mediante el proceso aquí propuesto, se consume una molécula de CO_2. Por esto, en el balance global sólo se genera la mitad del CO_2 que se produce en la utilización de metanol sintetizado mediante tecnologías convencionales, reutilizándose la otra mitad y dando lugar de esta manera al *"reciclado parcial"*.

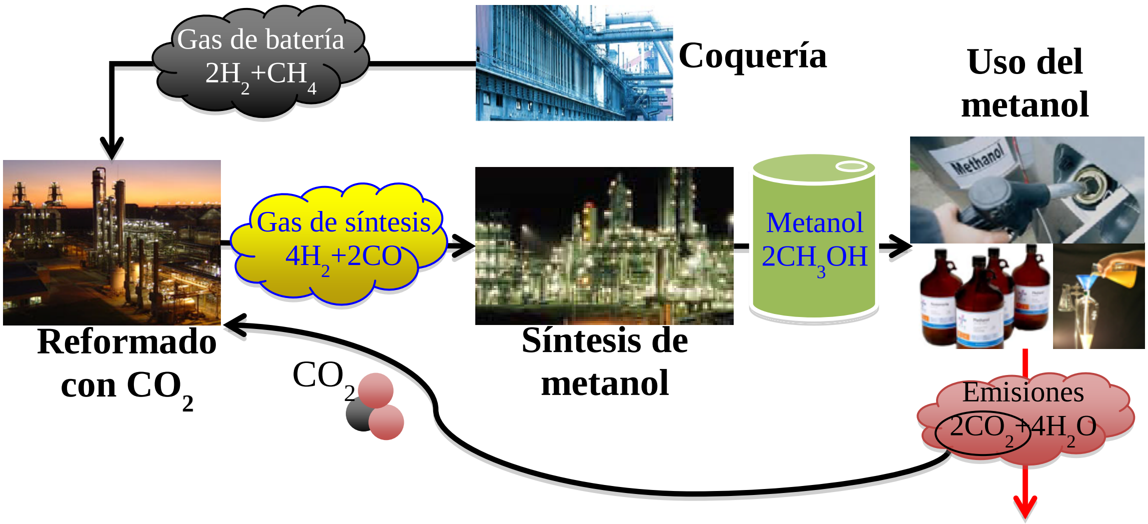


Figura 5. Reciclado parcial de CO_2 en la producción de metanol a partir de gas de coquería utilizando reformado seco.

Para la consecución de este objetivo general, se plantean cuatro objetivos parciales, que se encuentran desarrollados en cada una de las Secciones en los que se divide el Capitulo 3 de Resultados:

1. Estudiar el equilibrio termodinámico del proceso de reformado seco de gas de coquería. El equilibrio termodinámico fija los límites de conversión y rendimiento que se pueden alcanzar en la reacción de reformado, por lo que se ha determinado el equilibrio termodinámico en un amplio rango de temperaturas y presiones. Este objetivo está tratado en la Sección 3.1 *Equilibrio termodinámico del reformado con* CO_2 *de gas de coquería*.

2. Estudiar diferentes catalizadores para el proceso. El catalizador utilizado tiene un papel clave, de la misma forma que el equilibrio, por lo que resulta fundamental encontrar un catalizador que permita obtener conversiones lo más elevadas posible, que sea estable y resistente a la desactivación. Por esto, se han estudiado diferentes catalizadores con el propósito de determinar el más adecuado para el proceso. Este objetivo se ha estudiado en la Sección 3.2 *Catalizadores para el reformado con* CO_2 *de gas de coquería*.

3. Estudiar el proceso con calentamiento microondas. Las microondas han demostrado ser capaces de mejorar los rendimientos en reacciones heterogéneas como la que nos ocupa en esta Tesis, y en concreto, se han alcanzado grandes resultados en el reformado de metano. Es por esto que se ha estudiado el proceso, con los catalizadores más adecuados, utilizando el calentamiento microondas, intentando evaluar si existen mejoras sobre el proceso con calentamiento convencional. Este objetivo se trata en la Sección 3.3 *Reformado con* CO_2 *de gas de coquería asistido con microondas*.

4. Comparar el proceso desarrollado con procesos convencionales. Aunque sobre el papel el proceso presenta múltiples ventajas sobre procesos convencionales de producción de metanol, es necesario comprobar que esto se cumple en la realidad. Para ello se ha comparado, utilizando herramientas informáticas de simulación de procesos, un proceso convencional de producción de metanol con el propuesto en esta Tesis, estudiando sus consumos energéticos, emisiones de CO_2 y la calidad del metanol obtenido. Este objetivo se desarrolla en la Sección 3.4 *Comparación con procesos convencionales de producción de metanol*.

La presente memoria de Tesis se ha confeccionado como un compendio de publicaciones, en las cuales se muestran los resultados obtenidos gracias al trabajo experimental realizado para tratar de dar respuesta a los objetivos planteados. En la Tabla 2 se muestran dichas publicaciones, la Sección de la memoria en la que se encuentran, las revistas en la que se han publicado y el factor de impacto de dichas revistas.

Tabla 2. Publicaciones incluidas en la memoria

Capítulo/Sección	Publicación	Revista	Factor de impacto
1. Introducción	An overview of novel technologies to valorise coke oven gas surplus	Fuel Processing Technology	2.945
3.1. Equilibrio termodinámico del reformado con CO_2 de gas de coquería	Equilibrium prediction of CO_2 reforming of coke oven gas: Suitability for methanol production	Chemical Engineering Science	2.431
3.2. Catalizadores para el reformado con CO_2 de gas de coquería	Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis	Fuel	3.248
	CO_2 reforming of coke oven gas over a Ni/γAl_2O_3 catalyst to produce syngas for methanol synthesis	Fuel	3.248
	Syngas from CO_2 reforming of coke oven gas: Synergetic effect of activated carbon/ Ni-γAl_2O_3 catalyst	International Journal of Hydrogen Energy	4.054
3.3. Reformado con CO_2 de gas de coquería asistido con microondas	Microwave-assisted CO_2 reforming of coke oven gas: An exception to the general rule?	Afinidad	0.138
3.4. Comparación con procesos convencionales de producción de metanol	New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process	Applied Energy	5.106

3. RESULTADOS

En este capítulo se presenta con detalle el trabajo realizado en esta Tesis, así como los resultados obtenidos y su discusión.

Cada una de las Secciones de este capítulo consta de una introducción en la que se responde, de forma resumida y concisa, a cuatro preguntas:

- ¿Qué se ha hecho? Se indica el trabajo realizado.

- ¿Por qué se ha hecho? Se explica el objetivo que se persiguió en ese trabajo así como las motivaciones que plantearon dicho objetivo.

- ¿Cómo se ha hecho? Se explica someramente el procedimiento experimental utilizado para la obtención de los resultados.

- ¿Qué se concluye? Se enumeran las principales conclusiones derivadas del trabajo y qué implicaciones tienen para el objetivo global de la Tesis.

A continuación de esta introducción se adjuntan los artículos correspondientes a cada Sección que han sido realizados como consecuencia del trabajo experimental llevado a cabo. En estos artículos se recoge con mayor detalle el trabajo realizado, los resultados obtenidos y las conclusiones derivadas de los mismos.

3.1. EQUILIBRIO TERMODINÁMICO DEL REFORMADO CON CO_2 DE GAS DE COQUERÍA

¿Qué?

En esta Sección se estudia el equilibrio termodinámico del reformado con CO_2 del gas de coquería en un amplio rango de temperaturas y presiones. Los rendimientos del proceso y las características del gas de síntesis obtenido han sido evaluados y se han determinado las condiciones de operación en las que se obtiene un gas de síntesis que puede ser adecuado para la producción de metanol. Además, se ha estudiado la influencia que tienen la composición del gas de coquería y la relación CH_4/CO_2 utilizada en el reactor sobre el equilibrio termodinámico. La descripción detallada del trabajo realizado y de los resultados se encuentran recogidos en el artículo *Equilibrium prediction of* CO_2 *reforming of coke oven gas: Suitability for methanol production*, publicado en Chemical Engineering Science, 82 (2012), 95-103.

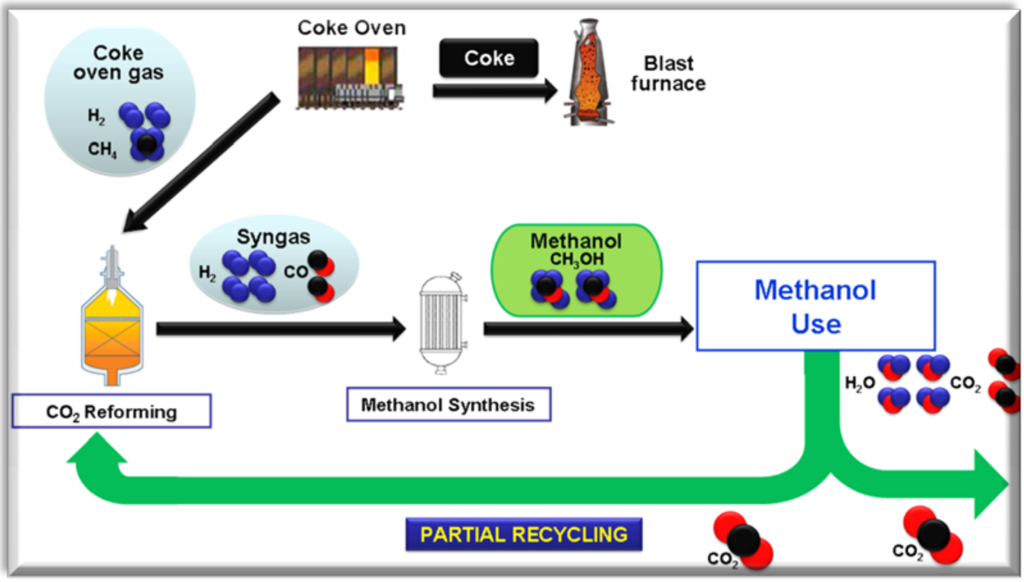


Figura 6. *Graphical abstract* del artículo *Equilibrium prediction of* CO_2 *reforming of coke oven gas: Suitability for methanol production*.

¿Por qué?

Como se indicó en la introducción, es esencial conocer el equilibrio termodinámico de un proceso previamente a su estudio. Esto se debe a que el equilibrio termodinámico es el que marcará los límites del proceso y, por lo tanto, determinará los rendimientos máximos que se pueden obtener y composición del gas se salida. Todo esto permite que se pueda determinar el rango de condiciones de operación en el que se optimiza tanto el rendimiento como la composición de los productos para su posterior aprovechamiento.

¿Cómo?

Para realizar este estudio se ha utilizado el software comercial de simulación de procesos Aspen Plus ®. Aunque no es necesario utilizar programas de este tipo para la determinación del equilibrio de un proceso, la complejidad del sistema que se está analizando (se pueden dar varias decenas de reacciones simultáneamente) y la gran versatilidad de este programa, permiten realizar el análisis más fácilmente.

Se definió un modelo en Aspen Plus compuesto por dos corrientes de entrada (una de gas de coquería y otra de CO_2), un reactor de Gibbs (que calcula el equilibrio minimizando la energía libre de Gibbs) y una corriente de salida con los productos de reacción. El equilibrio se estudió a temperaturas entre 600 y 1200 ºC y a presiones entre 1 y 20 bar. Para evaluar la influencia de la composición del gas de coquería (más concretamente la presencia de hidrocarburos ligeros) y de la relación CH_4/CO_2 en el equilibrio, se definieron 4 escenarios:

- Caso base: se tomó una composición típica del gas de coquería, sin C_2, y se fijó un flujo para la corriente de CO_2 que asegura una relación estequiométrica de CH_4 y CO_2 (es decir CH_4/CO_2=50%/50%).

- Exceso de CO_2: manteniendo la composición del gas de coquería anterior se aumentó el flujo de la corriente de CO_2 para obtener una relación CH_4/CO_2=40%/60%.

- Exceso de CH_4: manteniendo la composición del gas de coquería igual a la de los dos casos anteriores, se disminuyó el flujo de la corriente de CO_2 para obtener una relación CH_4/CO_2=60%/40%.

- Presencia de C_2: se incluyeron en la composición del gas de coquería pequeñas cantidades de C_2H_4 y C_2H_6, manteniendo la relación estequiométrica de CH_4 y CO_2 (es decir CH_4/CO_2=50%/50%)

Los parámetros estudiados para evaluar las mejores condiciones de operación, una vez alcanzado el equilibrio, fueron:

- Conversiones de CH_4 y CO_2.

- Producción de H_2: se comparó la producción de H_2 con respecto a la máxima que se podría obtener, es decir, que todo el hidrógeno del CH_4 reaccionado se transformase en H_2 y no en otros productos. En otras palabras, la selectividad de proceso hacia el H_2.

- Relación H_2/CO y parámetro R (Ecuación 1) del gas de síntesis: los valores de estos parámetros, que deben estar en torno a 2 para el primero y en el intervalo de 2.03 a 2.05 en el segundo [60, 63-65], son los que permiten evaluar la idoneidad del gas de síntesis para su posterior utilización en la producción de metanol.

$$R\text{, adimensional} = (H_2 - CO_2) / (CO + CO_2) \qquad \text{(Ecuación 1)}$$

- Producción de carbono, agua y otros subproductos: la presencia de estos subproductos tiene importantes consecuencias tanto en el reformado seco como en la posterior síntesis de metanol. El carbono, que forma depósitos en el catalizador, es el principal motivo de desactivación de los catalizadores utilizados en el proceso de reformado seco [47, 52, 53, 66, 67]. El agua también provoca la desactivación de los catalizadores pero, en este caso, los utilizados en la síntesis de metanol [63, 68]. Por último, el resto de posibles subproductos (hidrocarburos de cadena corta principalmente) serán inertes que disminuirán la concentración en el reactor de síntesis de metanol, provocando menores velocidades de reacción y, por tanto, menores conversiones. Además, debido a su acumulación en el bucle de recirculación, será necesario llevar a cabo purgas elevadas, con la consiguiente pérdida de reactivos y productos de interés.

Conclusiones

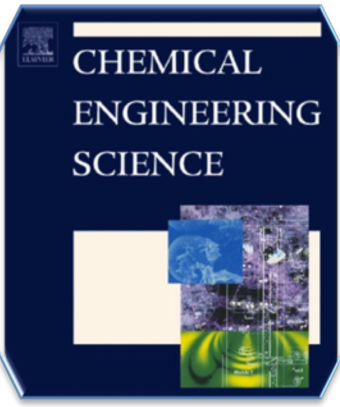
La conclusión más importante derivada de este estudio es el intervalo óptimo de temperaturas y presiones entre las que se debe operar para alcanzar un máximo rendimiento (máximas conversiones y selectividades posibles) del proceso y producir un gas de síntesis con las condiciones requeridas para la posterior producción de metanol. Para el caso de la temperatura, ésta debe encontrarse por encima de los 800 ºC, mientras que la presión debe de ser lo más baja posible, es decir, la más baja a la que la economía del proceso permita operar. En estas condiciones, se logran conversiones superiores al 80% para el caso del metano y al 90% en el caso del CO_2, mientras que la producción de H_2 alcanza valores que van desde el 70%, en el peor de los casos, hasta el 100%. En lo que a subproductos se refiere, bajo esas condiciones de operación se consigue minimizar su producción, llegando prácticamente a anularla en algunos casos. En el caso de los parámetros de gas de síntesis, se puede observar que la relación H_2/CO se mantiene en torno a 2 en estas condiciones, mientras que el parámetro R se encuentra ligeramente por debajo de 2. Esto, que a priori podría suponer un problema, tiene fácil solución debido a las particularidades de la síntesis de metanol. Dado que las conversiones de esta reacción son muy bajas, es necesario trabajar con un bloque de recirculación que, debido a la acumulación de inertes, presenta una purga. Esa purga es una corriente muy rica en H_2, el cual suele ser recuperado dado su elevado valor. Este H_2 recuperado puede utilizarse para aumentar el parámetro R, ajustándolo de esta manera a sus valores óptimos.

En cuanto a las diferentes proporciones de CH_4/CO_2 en el reactor, se ha comprobado que es imprescindible mantenerse lo más cerca de la proporción estequiométrica (50%/50%) para que el proceso sea viable ya que, a pesar de que las conversiones y la producción de H_2 se mantienen elevadas, los valores de los parámetros del gas de síntesis se alejan en gran medida de los deseados. Incluso, en el caso del exceso de CH_4, la producción de carbono es muy elevada convirtiéndose, por tanto, en un problema, ya que afectaría muy severamente a la desactivación del catalizador utilizado.

Finalmente, en el caso de la presencia de hidrocarburos de cadena corta (C_2) en la composición del gas de coquería, se puede observar que disminuye muy ligeramente la conversión de CH_4 (ya que los C_2 compiten con el CH_4 para reaccionar con el CO_2) mientras que la conversión de CO_2 y la producción de H_2 se mantienen prácticamente constantes. Respecto a los parámetros de gas de síntesis, sus valores se acercan más si cabe a los ideales, por lo que la presencia de pequeñas proporciones de C_2 en la alimentación tiene un efecto positivo en este aspecto. Sin embargo, también se observó un incremento en la producción de carbono que contrarresta este efecto positivo, favoreciendo la desactivación del catalizador.

En resumen, para lograr un gas de síntesis adecuado para la producción de metanol mediante el reformado seco de gas de coquería, las mejores condiciones de operación son temperaturas superiores a 800ºC y presiones lo más bajas posibles (dependiendo de la economía del proceso). Es necesario trabajar lo más cerca posible de las condiciones estequiométricas de CH_4 y CO_2 (para evitar valores de los parámetros del gas de síntesis inadecuados) y utilizar gases de coquería con muy bajas proporciones de hidrocarburos de cadena corta para evitar una pronta desactivación del catalizador utilizado.

Artículo 2



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Equilibrium prediction of CO_2 reforming of coke oven gas: Suitability for methanol production

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Equilibrium prediction of CO_2 reforming of coke oven gas: Suitability for methanol production

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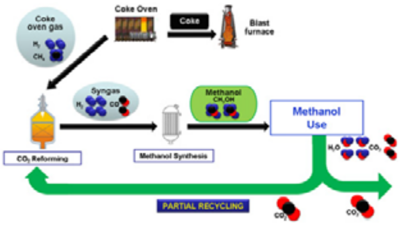
HIGHLIGHTS

- ► The CO_2 reforming of coke oven gas was studied using Aspen Plus software.
- ► The syngas produced was found to be suitable for methanol synthesis.
- ► Stoichiometric conditions of CH_4/CO_2 are mandatory for obtaining a suitable syngas.
- ► Temperatures above 800 °C and the lowest possible pressures are preferred.
- ► Presence of C_2H_x improves syngas quality but promotes catalyst deactivation.

GRAPHICAL ABSTRACT



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ABSTRACT

A thermodynamic study of the equilibrium of the CO_2 reforming of coke oven gas (COG) was carried out with the aid of Aspen Plus® software. The influence of various operation conditions (temperature, pressure, COG composition and CO_2/CH_4 ratio) upon different parameters (conversions, yields, outlet composition, carbon production, by-products) was studied in order to evaluate the suitability of the process for producing a synthesis gas appropriate for methanol production. It was established that it is necessary to work at temperatures higher than 800 °C, at the lowest possible pressures and in stoichiometric conditions of CH_4 and CO_2. It was also found that the presence of light hydrocarbons in the COG gives rise to a syngas that is more suitable for methanol production than when they are absent. However, they were also observed to promote deactivation of the catalyst.

1. Introduction

One of the most important materials consumed by the steel industry is metallurgical coke, since it performs several functions in the blast furnace (Loison et al., 1989). In order to produce it, bituminous coals are carbonized, giving rise to three different fractions: coke, tar and coke oven gas (COG). COG, after a series of cleaning treatments, consists mainly of H_2 (~55–60%), CH_4 (~23–27%), CO (~5–8%), N_2 (~3–6%) and CO_2 (less than 2%) along with other hydrocarbons, H_2S and NH_3 in small proportions (Bermúdez et al., 2010, 2011b; Wang et al., 2010; Zhang et al., 2008). Part of this gas is used to fuel the coke oven itself. However, there is an important surplus of gas which is employed as a fuel in other processes in the coking plant and in the associated steel industry or which is just burnt away in torches. As a consequence, environmental problems arise, mainly in the form of greenhouse gases emissions and there is also a large

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waste of energy resources (Bermúdez et al., 2010, 2011b; Shen et al., 2007; Wang et al., 2010).

In order to solve these problems and to find a more sustainable way of utilizing this highly energetic gas, different solutions have been proposed. The most relevant are the separation of H_2 with PSA (Diemer et al., 2004; Joseck et al., 2008), the direct use of COG as a reduction agent in the blast furnace (Diemer et al., 2004) and the production of synthesis gas (Bermúdez et al., 2010, 2011b; Bermúdez et al., 2011a; Diemer et al., 2004; Zhang et al., 2008; Zhang et al., 2010). The last alternative is especially interesting, since it makes use of a pollutant gas to produce several organic products, which would otherwise have to be obtained from fossil resources, such as natural gas. Synthesis gas can be produced by means of several different processes including the steam reforming, partial oxidation or dry reforming of hydrocarbons (Wender, 1996). In the case of coke oven gas, the dry reforming option (reaction 1 in Table 1) has a peculiar feature which makes it more interesting than the other processes.

Apart from consuming two harmful greenhouse gases (CO_2 and CH_4), the dry reforming of coke oven gas under stoichiometric conditions of methane and carbon dioxide gives rise to a syngas with a H_2/CO ratio of close to 2, which is the ratio suitable for methanol production (Olah et al., 2006; Yin et al., 2005). This is another environmental benefit, since it involves the consumption of CO_2 and the use of a pollutant gas (COG), instead of a valuable fossil resource (natural gas), for the synthesis of an organic product. What is more, methanol is an organic product which will play a key role in the future energy model due to its several applications (as a gasoline substitute, for biodiesel production, and as a hydrogen carrier). Moreover, this process involves the partial recycling of carbon dioxide, since it consumes half of the CO_2 generated by the use of methanol at the end of its life cycle (Bermúdez et al., 2010, 2011a, 2011b). The CO_2 balance of the process is illustrated in Fig. 1.

Dry reforming is a catalytic process and most research efforts so far have focused on the search for effective commercial catalysts (Fidalgo et al., 2010). The production of carbon deposits, which is very intense in the dry reforming, rapidly deactivates the catalyst, blocking the active centers, which prevents the reactant gases gaining access to them (Wang et al., 1996). Other species that can be harmful for the catalysts is H_2S, since it can act as a poison for the catalyst, being necessary a previous cleaning step. However, the SPARG process developed by Haldor Topsoe could be an interesting solution for both problems (Udengaard et al., 1992). In this process a partial poisoning of the catalyst with H_2S is proposed, keeping high conversions of CH_4 and CO_2 and reducing carbon formation. Another problem for the catalyst is that dry reforming is carried out at such high temperatures, that sintering of the metal particles of the catalyst occurs, a process which promotes the carbon deposition. But the catalyst is not the only critical factor for the viability of the process. The thermodynamic equilibrium must also be carefully studied, since it is this that establishes the limits of the process (conversions, yields, by-products) and will determine, together with the catalyst, the most appropriate conditions (temperature, pressure, inlet concentrations) for optimizing the process. Process modeling software, such us Aspen Plus®, is a very useful tool in chemical engineering for performing thermodynamic equilibrium calculations, as it offers the possibility of tackling complicated problems on user-friendly interfaces. The use of modeling software to predict thermodynamic behavior of chemical processes is already widespread (Murat Sen et al., 2012; Sadhukhan et al., 2010), but in the concrete case of the CO_2 reforming of COG there are no exhaustive works about the influence of the different operation conditions (pressure, temperature, compositions) upon the performance of the system, upon the formation of carbon blocking the active centers of the catalyst and other byproducts (light hydrocarbons or water) or about the suitability of the resulting syngas for applications in subsequent processes.

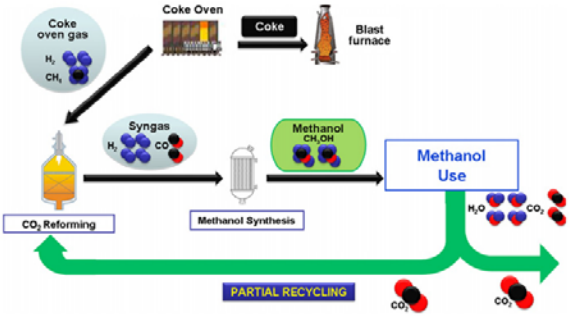

Fig. 1. Partial recycling of CO_2 by means of the CO_2 reforming of COG for methanol production.

Table 1
Possible reactions in the CO_2 reforming of coke oven gas.

Number	Reaction	ΔH (kJ/mol)
1	$CH_4+CO_2 \leftrightarrow 2H_2O+2\ CO$	247
2	$H_2+CO_2 \leftrightarrow H_2O+CO$	42
3	$H_2O+CH_4 \leftrightarrow 3H_2+CO$	205
4	$CH_4 \leftrightarrow C+2H_2$	76
5	$CO_2+C \leftrightarrow 2CO$	173
6	$C+H_2O \leftrightarrow CO+H_2$	131
7	$C+2H_2O \leftrightarrow CO_2+2H_2$	90
8	$CH_4+2H_2O \leftrightarrow CO_2+4H_2$	165
9	$CO+2H_2 \leftrightarrow CH_3OH$	−91
10	$CO_2+3H_2 \leftrightarrow CH_3OH+H_2O$	−41
11	$C_2H_6 \leftrightarrow C_2H_4+H_2$	136
12	$C_nH_m \leftrightarrow nC+(m/2)H_2$	
13	$C_nH_m+nH_2O \leftrightarrow nCO+(n+m/2)H_2$	
14	$C_nH_m+nCO_2 \leftrightarrow 2nCO+(n/2)H_2$	
15	$3CO+3H_2 \leftrightarrow CH_3OCH_3+CO_2$	−258
16	$CH_3OCH_3+H_2O \leftrightarrow 2CH_3OH$	37
17	$CH_3OCH_3+3H_2O \leftrightarrow 2CO+6H_2$	136

The aim of the present work is to study the dry reforming of the coke oven gas from a thermodynamic equilibrium point of view in order to determine the influence of different operation conditions (temperature, pressure, inlet gas composition, CO_2/CH_4 ratio) upon several process parameters (conversions, yields, outlet composition, carbon production, by-products). The suitability of the synthesis gas has been studied with a view to the production of methanol, with the objective of determining the best operation conditions. The study was conducted with Aspen Plus® software and is focused just in the determination of the thermodynamic equilibrium, without developing any information about reaction rates.

2. Materials and methods

2.1. *Thermodynamic equilibrium prediction*

There are two main ways to calculate the thermodynamic equilibrium: via the equilibrium constants or by minimizing the free energy (Chan and Wang, 2000; Seo et al., 2002; Turpeinen et al., 2008). Calculations based on equilibrium constants become very complex and tedious in systems where several simultaneous reactions may take place (Perry and Green, 1999), as in this case (Table 1 shows the most typical reactions that could occur between the species involved in the CO_2 reforming of COG). Moreover, with this approach it is very difficult to analyze the presence of solid phases, such us solid graphite (Bermúdez et al., 2011b; Seo et al., 2002). Consequently, the minimization of free energy is the preferred method in chemical systems like the one proposed here (Chan and Wang, 2000; Gordon and McBride, 1994; Seo et al., 2002).

The condition for equilibrium can be stated in terms of thermodynamic functions such as the minimization of Gibbs free energy or Helmholtz free energy or the maximization of entropy (Chan and Wang, 2000; Gordon and McBride, 1994). For this study, we selected the minimization of Gibbs free energy, since it is easier to minimize when the temperature and pressure are specified (Chan and Wang, 2000; Gordon and McBride, 1994).

The minimization of the Gibbs free energy was accomplished with Aspen Plus software. The Peng–Robinson equation with the Boston–Mathias alpha function was selected as the equation of state (Mathias et al., 1984), since the Peng–Robinson equation is the preferred equation of state in gas processing at high temperatures and pressures while the Boston–Mathias alpha function gives more accurate results when there are some species with critical temperatures lower than the operating temperature. The species that were considered in the simulations were H_2, CH_4, CO, CO_2, N_2, C_2H_4, C_2H_6, H_2O, C, dimethyl ether (DME) and methanol.

2.2. *Description of the model*

The model consists of two feeding streams (COG and CO2), a mixer (MIX), a Gibbs reactor (GIBBS) and a stream of products (PROD) (Fig. 2). These components are defined as follows:

1. COG: a stream representing the coke oven gas. In the basic scenario it includes H_2, CH_4, CO, CO_2 and N_2, and in the final case it also includes other hydrocarbons (C_2H_4 and C_2H_6) that may appear in small proportions.
2. CO2: a stream representing the CO_2 added to the coke oven gas to reform it.
3. MIX: a block used to mix both feeding streams. The software makes a flash equilibrium calculation in it that has a negligible effect on the results of the simulation.
4. GIBBS: a block that represents a Gibbs Reactor which applies the minimization of the Gibbs free energy with phase splitting to calculate the equilibrium. A Gibbs Reactor does not require the reaction stoichiometry to be specified and is also able to calculate the chemical equilibrium between any number of conventional solid components and fluid phases.

2.3. *Description of the simulations*

The influence of temperature and pressure was studied in the ranges of 600–1200 °C and 1–20 bar. Four different scenarios were considered: a basic scenario, in which CO_2 and CH_4 were introduced in stoichiometric conditions and light hydrocarbons (C_2H_4 and C_2H_6) were excluded from the fed-in streams; a second scenario in which an excess of CO_2 over the estequiometric conditions (the CO_2/CH_4 ratio was 60%/40%) was included since it has been found that, in these conditions, the resistance to deactivation of the catalyst increases (Fidalgo et al., 2008); a third scenario in which an excess of CH_4 over the stoichiometric conditions (the CO_2/CH_4 ratio was 40%/60%) was introduced in order to obtain a syngas with a higher content in H_2; and a final scenario with stoichiometric conditions of CO_2 and CH_4 and the presence of light hydrocarbons in the feeding streams. The feeding stream conditions employed in each scenario are summarized in Table 2.

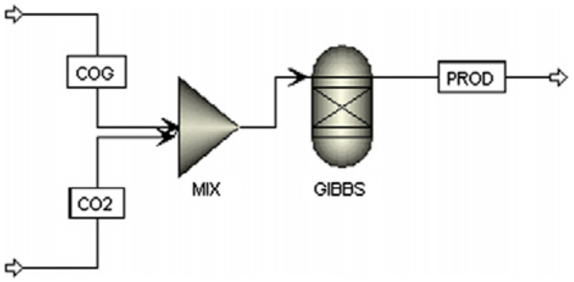

Fig. 2. Scheme of the model.

In order to determine the influence of these operation conditions on the process, variations in the following eight parameters were studied:

1. CH_4 and CO_2 conversions (Eqs. (1) and (2)), which express the amount of each species reacted. These parameters were calculated as follows:

$$CH_4\ \text{conversion},\% = 100 \cdots (CH_4\text{in} - CH_4\text{out})/CH_4\text{in} \quad (1)$$

$$CO_2\ \text{conversion},\% = 100 \cdots (CO_2\text{in} - CO_2\text{out})/CO_2\text{in} \quad (2)$$

2. H_2 production (Eq. (3)), which expresses how much hydrogen was produced as a percentage of the maximum amount of hydrogen that could be produced (i.e., all the hydrogen present in the CH_4 and the light hydrocarbon is converted to H_2). This parameter was calculated as follows:

$$H_2\ \text{conversion},\% = 100 \cdots (H_2\text{prod}/H_2\text{max}) \quad (3)$$

3. The H_2/CO ratio of the synthesis gas.
4. The *R* parameter of the synthesis gas (Eq. (4)), which expresses the relation between the H_2, CO and CO_2 present in the synthesis gas and which is used to evaluate the suitability of the syngas for producing methanol. This should take on values slightly higher than 2 (Olah et al., 2006; Tjatjopoulos and Vasalos, 1998).

$$R,\text{dimensionless} = (H_2 - CO_2)/(CO + CO_2) \quad (4)$$

5. Carbon production, which is the parameter mainly responsible for the deactivation of the catalyst.
6. Water production, which is the main byproduct of the CO_2 reforming of coke oven gas (Bermúdez et al., 2010, 2011a, 2011b) and has a deactivating effect upon the catalyst used in the subsequent methanol synthesis stage (Sun et al., 1999).
7. Byproducts, included in this parameter is the sum of the molar fractions of all the other resultant products which may have a negative effect on the subsequent stages of the methanol production process (C_2H_2, C_2H_4, C_2H_6, DME and methanol).

The results obtained have been represented using Matlab®, but only the most representative results have been included in the

Table 2
Feed streams conditions.

Scenario		Composition of COG (vol%)							CO_2/COG	CO_2/CH_4
		H_2	CH_4	CO	CO_2	N_2	C_2H_6	C_2H_4		
1	Base case	61.0	26.0	6.0	1.5	5.5	0	0	0.245	50/50
2	CO_2 excess	61.0	26.0	6.0	1.5	5.5	0	0	0.375	60/40
3	CH_4 excess	61.0	26.0	6.0	1.5	5.5	0	0	0.158	40/60
4	C_2 presence	61.0	26.0	6.0	1.5	3.0	0.5	2.0	0.245	50/50

text. The rest of the figures have been included as Supplementary Material.

3. Results and discussion

3.1. CO_2 reforming of COG: Scenario 1

The results relating to the conversions of methane and carbon dioxide and the production of hydrogen in scenario 1 (stoichiometric conditions of CH_4/CO_2 and absence of light hydrocarbons) are shown in Fig. 3. The figure shows the 3D surfaces and the contour plots obtained for these parameters as a function of temperature and pressure.

As can be seen, all of these parameters are favored at high temperatures and low pressures. However, temperature is the operation condition which has the greater effect, since pressure produces only slight variations in these parameters. The conversion of CO_2 exceeds 60% over the entire range of temperatures and pressures studied whereas the conversion of CH_4 is more affected by these operation conditions, even displacing negative values at low temperatures and high pressures. This could be due to a shift in some of the equilibriums towards the reactants (reactions 3 and 8 in Table 1). Pressure has a greater influence in the conversion of CH_4 possibly because in the main reactions of CH_4 (reaction 1, 3, 4 and 8 in Table 1) there is in every case an increase in the number of moles. However, there are some reactions involving CO_2 (reaction 2 and 5 in Table 1) in which the number of moles remains unchanged. In the case of temperature, it can be seen that reactions involving CH_4 have higher enthalpies than those involving CO_2, so an increase in temperature favors a greater increase in the conversion of CH_4.

For the production of H_2 high temperatures are necessary and it is possible to work in a wide range of pressures (depending on the temperature selected). As in the case of methane conversion, negative values in the production of hydrogen can be found, possibly due to the aforementioned equilibrium shift but more probably due to the influence of the reverse water gas shift reaction (reaction 2 in Table 1), which has been found to be a critical reaction in the CO_2 reforming of COG (Bermúdez et al., 2010, 2011a, 2011b; Zhang et al., 2010). These suppositions are confirmed by the results in Fig. 4, for the production of carbon, water and other byproducts that may affect the subsequent processes in which the synthesis gas produced can be used.

As can be seen, the production of water is very high at low temperatures and high pressures. This is mainly due to the lower endothermic character of the reverse water gas shift (reaction 2 in Table 1), compared to the reactions in which the water acts as a reactant (reactions 3, 6–8 in Table 1), such as the steam reforming of methane or gasification. A similar situation occurs in the production of carbon. Although the decomposition of CH_4 is favored at high temperatures and low pressures, both steam and CO_2 gasification are enhanced by the increase in temperature. The combination of all these reactions allows finding a wide range of temperatures and pressures where the carbon production is very low. This is an important point, since the plugging of the active centers of the catalyst due to carbon deposition is the main reason for the deactivation of the catalysts. In the case of the other byproducts, they can be ignored since, even in the worst conditions, the concentration of the sum of all of them is less than 25 ppm.

As already mentioned, the most interesting application of the CO_2 reforming of COG is the use of the resulting synthesis gas to produce methanol. In order to determine the suitability of the syngas for the synthesis of methanol, the H_2/CO and the R parameter (Eq. (4)) were evaluated. The H_2/CO ratio of the syngas needs to be 2 for the synthesis of methanol, whereas the R parameter must have a value equal to, or slightly higher than, 2 (Olah et al., 2006; Tjatjopoulos and Vasalos, 1998). When R is lower than 2 there is an increase in the byproducts formed in the synthesis of methanol and when the values are higher than 2 an increase in the recycling rate is required due to an excess of H_2, as a result of which the process becomes less efficient.

As can be seen in Fig. 5, the H_2/CO ratio is close to 2 at temperatures higher than 800 °C over almost the entire range of pressures studied and reaches very high values (up to 9) when the temperature is lower than 800 °C. In the case of the R parameter, there is only a very small range within which values are slightly higher than 2 (around 700 °C and pressures lower than 3 bar). Under these operating conditions the value of the H_2/CO ratio is very high, the conversions are very low and H_2 production is almost zero, as a result of which these conditions should be

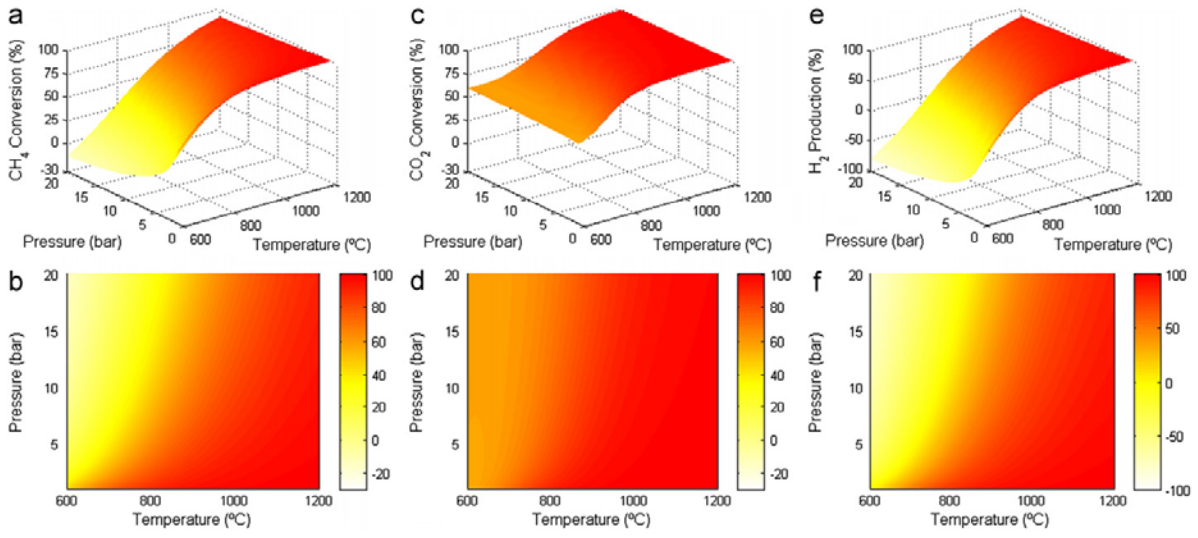

Fig. 3. Results for the conversion of methane (a, b), the conversion of carbon dioxide (c, d) and hydrogen production (e, f) obtained in the scenario 1.

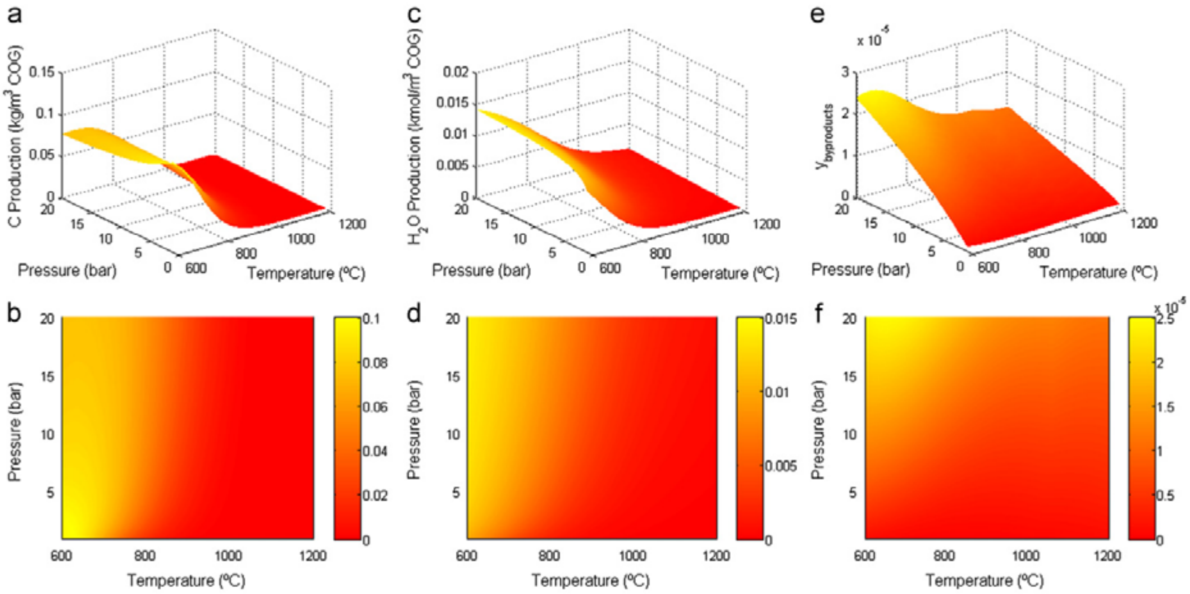

Fig. 4. Results for carbon production (a, b), water production (c, d) and molar fraction of byproducts (e, f) obtained in scenario 1.

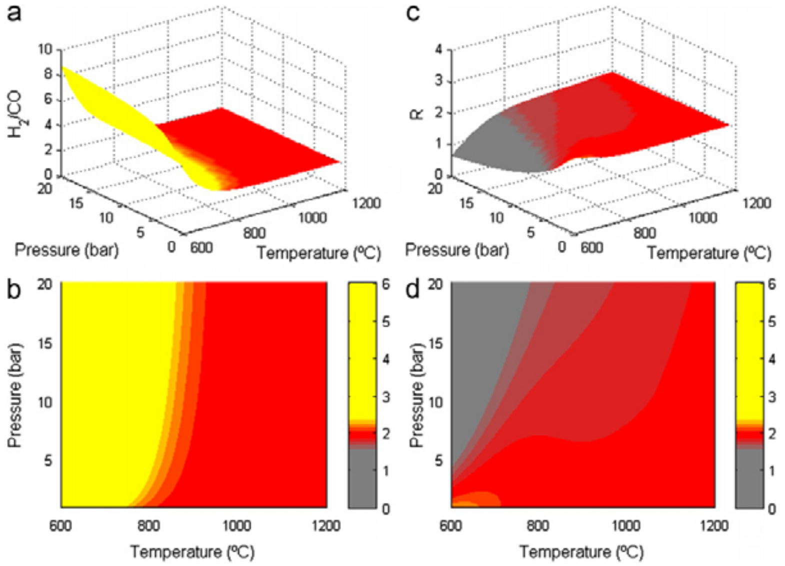

Fig. 5. Results for the H_2/CO ratio (a, b) and the *R* parameter (c, d) obtained in the scenario 1.

discarded. However, the *R* parameter values are slightly lower than 2 over a very wide range of operating conditions. In the synthesis of methanol there is a very low conversion of H_2 (Aasberg-Petersen et al., 2010; Wender, 1996), so the reaction products are separated from the reactants, which are recycled. Due to the presence of inert species (such as N_2 or CH_4) it is necessary to include a purge in the recycling loop, which gives rise to a H_2-rich stream. Usually the H_2 present in this stream is recovered and can be used to adjust the value of the *R* parameter (Aasberg-Petersen et al., 2010) in order to increase its value.

In conclusion, there is a very wide range of temperatures and pressures which can be used for the CO_2 reforming of COG, but it is necessary to work at temperatures higher than 800 °C, and at the lowest possible pressures (the higher the temperature, the lower the pressure required). Reforming processes are usually carried out at mild pressures (15–30 bar) for economic reasons, since the subsequent processes are carried out at high pressures (Rostrup-Nielsen et al., 2002). Working at high pressures before reforming makes it possible to use smaller reactors and compress less volume of gas, because both steam reforming and dry reforming double the number of moles. However in this case the increase in the number of moles is less than 1.4 times, which means that the benefit from pressurizing before the reforming step is reduced.

3.2. *Influence of the CO_2/CH_4 ratio: Scenarios 2 and 3*

The CO_2/CH_4 ratio in the feed gases has a significant effect on the behavior of the system. When there is an excess of CO_2, it is possible to achieve higher conversions during longer periods of time, since the excess of CO_2 allows the gasification of more carbon deposits (Fidalgo et al., 2008). With an excess of CH_4, it should be possible to obtain a synthesis gas with a higher H_2/CO ratio and *R* parameter. With this in mind, the same analysis as in the case of the scenario 1 was carried out, but varying the proportions of CO_2 and CH_4 in the feed. Table 3 shows the differences in the results of conversions and H_2 production between the simulations of the base case (CO_2/CH_4=50/50), the case with an excess of CO_2 (CO_2/CH_4=60/40) and the case with an excess of CH_4 (CO_2/CH_4=40/60). Fig. 6 compares the different carbon and water productions for the three CO_2/CH_4 ratios while Fig. 7 shows the H_2/CO ratios and the *R* parameters of the synthesis gas produced for each CO_2/CH_4 ratio. The CO_2/CH_4 ratio was found to have no significant influence on the byproducts, and the concentration of the sum of all of them was too low for them to be of significance.

3.2.1. *Excess of CO_2*

When the CO_2 reforming of COG is carried out with an excess of CO_2 in the feed, the conversions are noticeably affected. In the case of CH_4 conversion, it can be seen that the values are higher than those of the base case over the whole interval of pressures and temperatures studied. Yet it is difficult to establish a general tendency with pressure and temperature, since the results reflect ups and downs. In other words, depending on the operating temperature and pressure, different reactions govern the process. A similar situation arises, but with the opposite results, with CO_2 conversion. In this case, the results are worse than those obtained in the base case. The excess of CO_2 has increased the amount of methane reacted, with almost 100% of methane conversion being achieved, but there is still a surplus of CO_2 that could not react. A significant part of the CO_2 reacts via the reverse water gas shift (reaction 2 in Table 1), since the production of water increases, whereas the H_2 production decreases, despite the improvement in methane conversion. Nevertheless the CO_2 that reacts through the reverse water gas shift is not enough to overcome the CO_2 surplus introduced into the system via the feed gases, giving rise to these lower conversions.

The amount of carbon produced depends on the operating temperature (pressure has very little influence). At low temperatures, the production of carbon is higher than in the base case. This is due to a combination of effects promoted at low temperatures: the increase in methane conversion, which in turn causes an increase in the carbon deposits (reaction 4 in Table 1), an increase in the CO_2 reacting through the reverse water gas shift instead of through the gasification of the carbon deposits (reaction 5 in Table 1) and the probable displacement in the equilibrium of reaction 7 (see Table 1) to the side of the reactants. However, when the temperature reaches higher values, the opposite effects are observed. The production of carbon is lower than in the base case mainly due to the lower increase in methane conversion. This lower increase in methane conversion combined with the increase in CO_2 reacted through the Boudouard equilibrium (reaction 5 in Table 1, which is favored at high temperatures), and the decrease in the CO_2 reacted via the reverse water

Table 3
Comparison between the conversions of CH_4 and CO_2 and the H_2 production achieved in the base case (scenario 1) and the other cases (scenarios 2, 3 and 4). The results are expressed in differences of percentages as a function of temperature (*T* in °C) and pressure (*P* in bar).

Scenario 2—Excess of CO_2							
Difference in CH_4 conversion (%)							
T	600	700	800	900	1000	1100	1200
P							
1	7.2	3.2	5.2	3.9	2.0	0.8	0.3
5	12.8	8.4	4.7	8.5	7.8	4.4	2.3
10	14.5	10.7	7.0	7.0	10.9	7.8	4.4
15	15.4	12.0	8.4	5.3	12.0	10.2	6.3
20	15.9	12.8	9.4	6.3	12.2	11.9	7.9
Difference in CO_2 conversion (%)							
T	600	700	800	900	1000	1100	1200
P							
1	−6.5	−4.4	−6.5	−9.3	−8.9	−7.9	−7.0
5	−7.5	−6.2	−4.1	−5.3	−7.2	−7.2	−6.7
10	−7.7	−6.7	−5.0	−3.7	−5.8	−6.5	−6.3
15	−7.8	−6.9	−5.5	−3.3	−5.1	−5.9	−6.0
20	−7.9	−7.1	−5.8	−3.8	−4.6	−5.5	−5.7
Difference in H_2 production (%)							
T	600	700	800	900	1000	1100	1200
P							
1	−2.8	−2.2	−3.1	−10.5	−15.2	−17.9	−19.3
5	−1.2	−1.7	−1.3	−0.8	−6.7	−12.8	−16.6
10	−0.8	−1.2	−1.2	−0.2	−1.5	−8.0	−13.5
15	−0.6	−0.9	−1.0	−0.4	−0.7	−4.6	−10.8
20	−0.5	−0.8	−0.9	−0.4	−1.6	−2.2	−8.6

Scenario 3—Excess of CH_4							
Difference in CH_4 conversion (%)							
T	600	700	800	900	1000	1100	1200
P							
1	−6.4	−2.8	−1.1	−0.5	−0.3	−0.4	−0.3
5	−11.3	−7.4	−4.1	−2.1	−1.1	−1.0	−1.0
10	−12.7	−9.4	−6.1	−3.5	−2.0	−1.7	−1.6
15	−13.4	−10.5	−7.3	−4.6	−2.7	−2.2	−2.2
20	−13.8	−11.1	−8.2	−5.4	−3.3	−2.7	−2.7
Difference in CO_2 conversion (%)							
T	600	700	800	900	1000	1100	1200
P							
1	5.9	4.0	1.5	0.4	0.1	0.1	0.1
5	6.6	5.5	3.5	1.5	0.5	0.3	0.2
10	6.7	5.9	4.4	2.3	0.9	0.5	0.3
15	6.8	6.1	4.8	2.8	1.3	0.6	0.4
20	6.8	6.2	5.1	3.2	1.5	0.8	0.5
Difference in H_2 production (%)							
T	600	700	800	900	1000	1100	1200
P							
1	2.5	2.0	0.7	0.1	0	−0.2	−0.1
5	1.1	1.6	1.2	0.3	−0.1	−0.4	−0.5
10	0.7	1.1	1.1	0.4	−0.1	−0.6	−0.8
15	0.6	0.9	0.9	0.4	−0.2	−0.7	−1.1
20	0.5	0.7	0.8	0.4	−0.2	−0.8	−1.3

Scenario 4—Presence of light hydrocarbons							
Difference in CH_4 conversion (%)							
T	600	700	800	900	1000	1100	1200
P							
1	−2.8	−1.4	−0.6	−0.3	−0.2	−0.3	−0.3
5	−4.6	−3.3	−2.0	−1.1	−0.6	−0.8	−0.8
10	−5.1	−4.1	−2.9	−1.8	−1.0	−1.2	−1.3
15	−5.3	−4.5	−3.4	−2.3	−1.4	−1.5	−1.8
20	−5.5	−4.7	−3.7	−2.7	−1.7	−1.8	−2.2
Difference in CO_2 conversion (%)							
T	600	700	800	900	1000	1100	1200
P							
1	−0.8	−0.4	−0.1	0	0	−0.1	−0.1
5	−0.9	−0.7	−0.3	−0.1	0	−0.1	−0.1
10	−0.9	−0.8	−0.5	−0.2	−0.1	−0.1	−0.2
15	−0.9	−0.8	−0.5	−0.2	−0.1	−0.2	−0.2
20	−1.0	−0.8	−0.6	−0.3	−0.1	−0.2	−0.3
Difference in H_2 production (%)							
T	600	700	800	900	1000	1100	1200
P							
1	2.8	1.3	0.5	0.2	0	−0.1	−0.1
5	4.6	3.0	1.6	0.7	0.3	−0.1	−0.3
10	5.2	3.8	2.3	1.2	0.5	−0.1	−0.5
15	5.6	4.3	2.8	1.6	0.7	0	−0.6
20	5.8	4.6	3.2	1.9	1.0	−0.1	−0.7

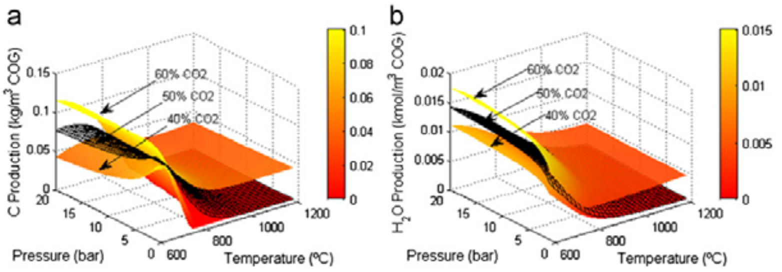

Fig. 6. Comparison between the results for carbon production (a) and water production (b) obtained in scenarios 1 (50% CO_2/50% CH_4), 2 (60% CO_2/40% CH_4) and 3 (40% CO_2/60% CH_4).

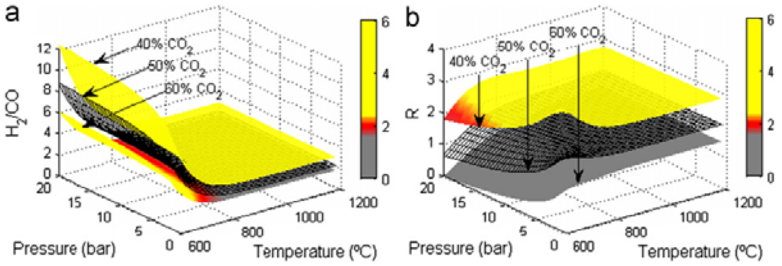

Fig. 7. Comparison between the results for the H_2/CO ratio (a) and R parameter (b) obtained in scenarios 1 (50% CO_2/ 50% CH_4), 2 (60% CO_2/ 40% CH_4) and 3 (40% CO_2/ 60% CH_4).

gas shift (which is disfavored at high temperatures) leads to a decrease in carbon production. Hence, the excess of CO_2 increases the resistance of the catalyst to deactivation at high temperatures.

With respect to the use of the synthesis gas for the production of methanol, there is only a limited range where the H_2/CO ratio has suitable values, and the *R* parameter never exceeds 1.4. In other words, there is no combination of temperature and pressure which can be used to obtain directly syngas suitable for methanol production, when the feed has an excess of CO_2.

3.2.2. *Excess of CH_4*

When an excess of CH_4 is introduced in the feed gases, the conversions exhibit the opposite behavior to when there is an excess of CO_2. Now, the conversion of CH_4 is lower than in the base case, whereas the conversion of CO_2 is higher. Contrary to when there is an excess of CO_2, a general tendency is observed. The increase in CO_2 conversion and decrease in CH_4 conversion are lower as the temperature increases and the pressure decreases. Thus, it appears that in this case there is a reaction that governs the process over the entire range of temperatures and pressures. This reaction seems to be the decomposition of CH_4 (reaction 4 in Table 1), since the production of carbon is very high. At low temperatures the production of carbon is lower than in the other cases, probably due to the decrease in CH_4 conversion and the increase in CO_2 conversion, as a result of which the carbon deposits formed through reaction 4 (see Table 1) are gasified. However, at high temperatures the carbon production is much higher than in the base case because, although the conversions are very similar to those of the base case, the amount of CO_2 fed is too low to gasify all the carbon deposits formed from the decomposition of CH_4. Moreover, the reduction in the CO_2 fed in leads to a lower production of water through the reverse water gas shift. As a consequence, the production of H_2 is very similar to that of the base case (with a range of variation lower than ±3%).

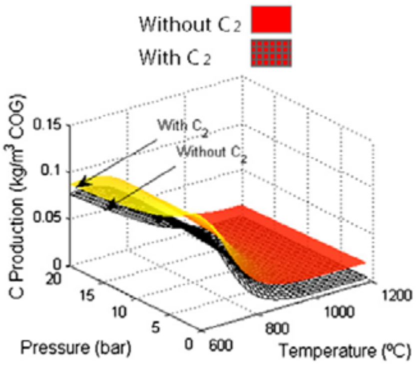

Fig. 8. Comparison between the results for carbon production obtained in scenarios 1 (without light hydrocarbons) and 4 (with light hydrocarbons).

With respect to the composition of the syngas, once again, if the feed composition diverges from stoichiometric conditions, the H_2/CO ratio and the *R* parameter do not acquire suitable values for the production of methanol. Only at low temperatures and high pressures does the *R* parameter have values close to 2, but under these operating conditions the H_2/CO ratio is higher than 8. Therefore the synthesis gas obtained will not be suitable for the production of methanol.

3.3. *Influence of the presence of light hydrocarbons: Scenario 4*

The influence of certain light hydrocarbons present in the COG (usually C_2H_4 and C_2H_6) also needs to be studied, since some of the reactions in which they are involved (reactions 11–14 in Table 1) may play an important role in the process. The different results for conversions and H_2 production between the base case and when light hydrocarbons are present are shown in Table 3. As

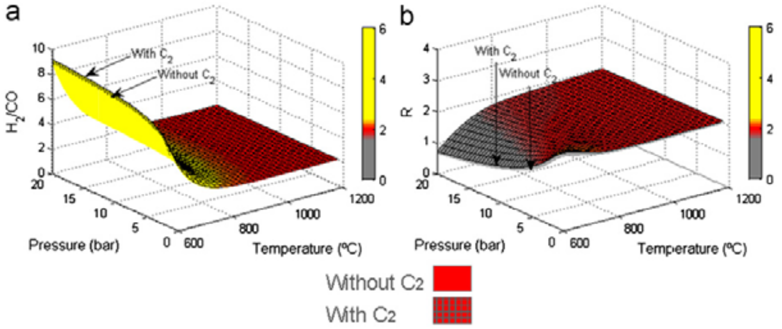

Fig. 9. Comparison between the results for the H_2/CO ratio (a) and the *R* parameter (b) obtained in scenarios 1 (without light hydrocarbons) and 4 (with light hydrocarbons).

can be seen, the variation in CO_2 conversion is negligible (lower than 1% over the entire range of temperatures and pressures) whereas the conversion of CH_4 and the production of H_2 are more vulnerable to change, especially at low temperatures. Under these conditions, the conversion of methane is lower than in the base case whereas H_2 production is greater. This could be due to the reforming of light hydrocarbons at the expense of CH_4, since these compounds compete with the CH_4 to react with CO_2 and H_2O (reactions 13 and 14 in Table 1).

Fig. 8 compares the production of carbon in the base case and when light hydrocarbons are present. The results for the concentration of the sum of all the byproducts and the difference in water production with the base case were negligible. The production of carbon is higher over the entire range of temperatures and pressures. This is due to the thermal decomposition of light hydrocarbons (reaction 12 in Table 1), which results in a higher carbon deposition. This may render the catalyst more vulnerable to deactivation at high temperatures than in the base case where there is almost no carbon production at high temperatures.

The presence of light hydrocarbons has almost no influence on the parameters of the syngas produced. Fig. 9 shows the differences in the H_2/CO ratio and the *R* parameter of this synthesis gas both with and without the presence of light hydrocarbons. As can be seen there is a slight increase in the values of the H_2/CO ratio and the *R* parameter. This increase is more positive in the case of the *R* parameter, since it is possible to achieve suitable values over a wider range of operating conditions than in the base case. However, this positive result cannot compensate for the faster deactivation of the catalysts caused by the greater number of carbon deposits. In the light of these results, the possibility of removing these light hydrocarbons before the reforming process should be considered.

4. Conclusions

The thermodynamic analysis carried out in this work has revealed that, in order to achieve high conversions of methane and carbon dioxide and high productions of hydrogen, it is necessary to work at temperatures higher than 800 °C and pressures as low as the economics of the process allows. It is necessary to work with high temperatures to minimize, and even prevent, the production of water and carbon. The production of the other byproducts included in the study is also minimized at high temperatures and low pressures, but in all the cases, their presence is so low that they can be considered negligible. The synthesis gas parameters (H_2/CO ratio and *R* parameter) acquire suitable values for methanol production at temperatures higher than 800 °C and over a wide range of pressures, but these values should be adjusted later with the hydrogen recovered at the end of the process of methanol production.

Using CO_2/CH_4 ratios different from the stoichiometric proportion (50:50) yield worse results, since the conversions and H_2 production are affected. The effect is especially negative on the formation of carbon and on the syngas parameters, which have values that are far from suitable for methanol production.

The presence of light hydrocarbons has a slightly negative effect on the conversion of methane, since they compete with the methane to react with CO_2 and H_2O in the reforming processes. However, the values of the synthesis gas parameters are slightly better in the presence of light hydrocarbons than in their absence. The main problem resulting from the presence of light hydrocarbons is the increase in carbon formation, since the carbon deposits are able to deactivate the catalyst.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ces.2012.07.012.

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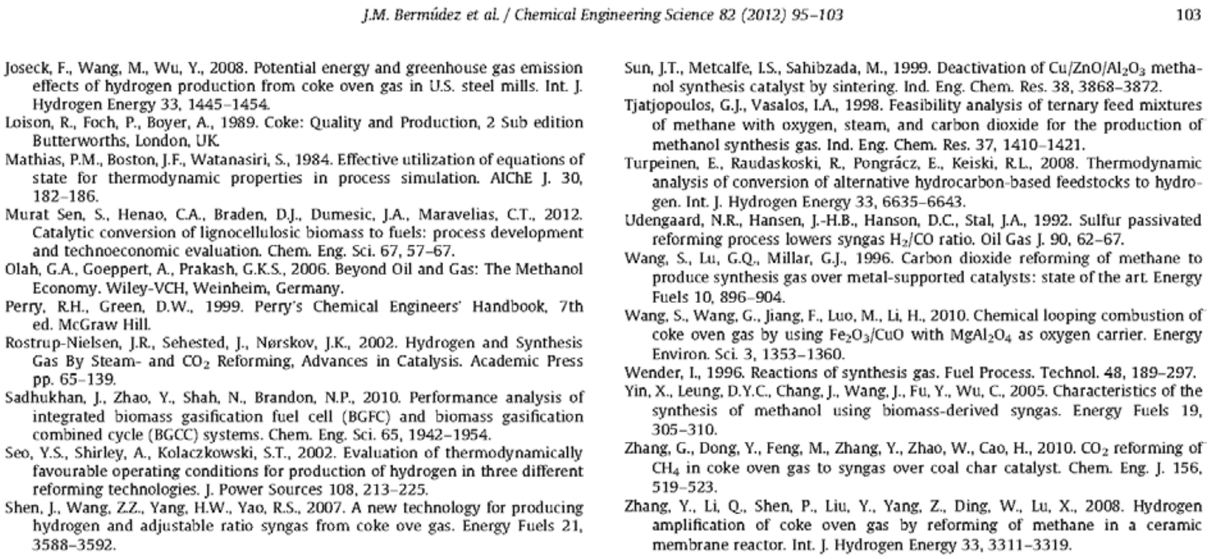

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3.2. CATALIZADORES PARA EL REFORMADO CON CO_2 DE GAS DE COQUERÍA

¿Qué?

En esta Sección se muestra el estudio de distintos tipos de catalizadores utilizados para llevar a cabo el proceso de reformado con CO_2 del gas de coquería. Se han estudiado tres tipos de catalizadores: un carbón activo (AC), catalizadores convencionales de níquel soportado en alúmina (Ni/Al_2O_3) y mezclas físicas de ambos. Se han evaluado en función de las conversiones alcanzadas, su selectividad en la conversión de metano hacia hidrógeno, su resistencia a la desactivación y la adecuación del gas de síntesis obtenido para la producción de metanol. Los resultados obtenidos en este estudio se recogen en una serie de tres artículos:

1. *Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis*, publicado en Fuel (2010), 89 (10), 2897-2902.

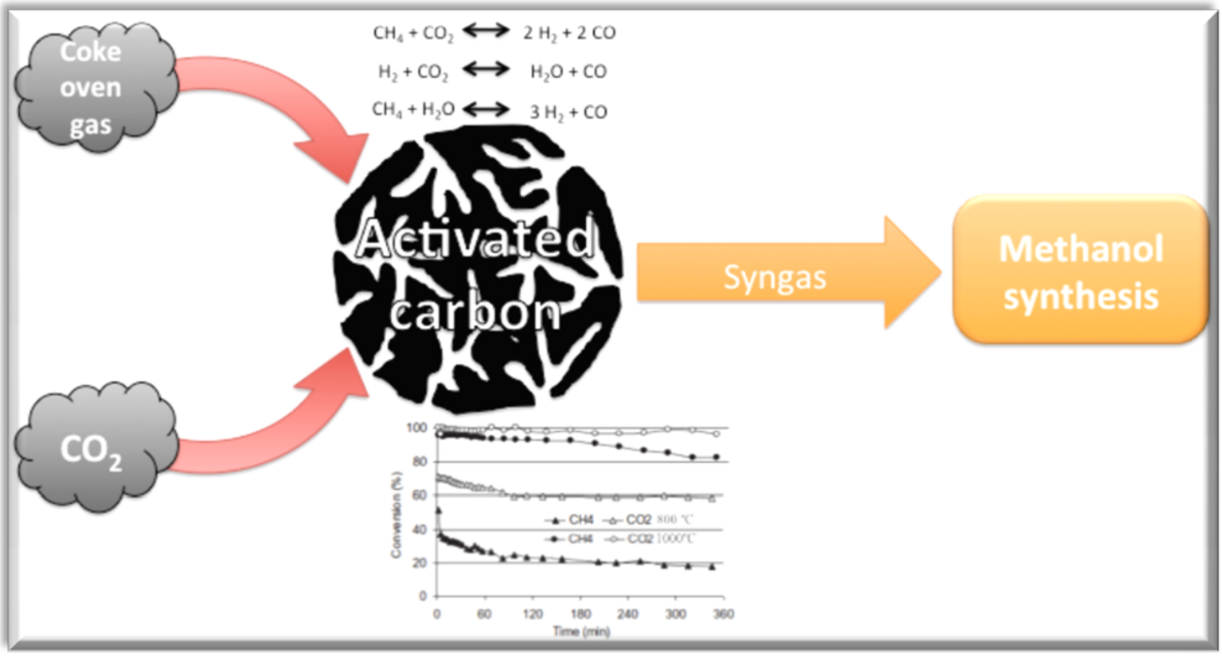

Figura 7. *Graphical abstract* del artículo *Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis*.

2. *CO_2 reforming of coke oven gas over a Ni/γAl_2O_3 catalyst to produce syngas for methanol synthesis*, publicado en Fuel (2012), 94, 197-203.

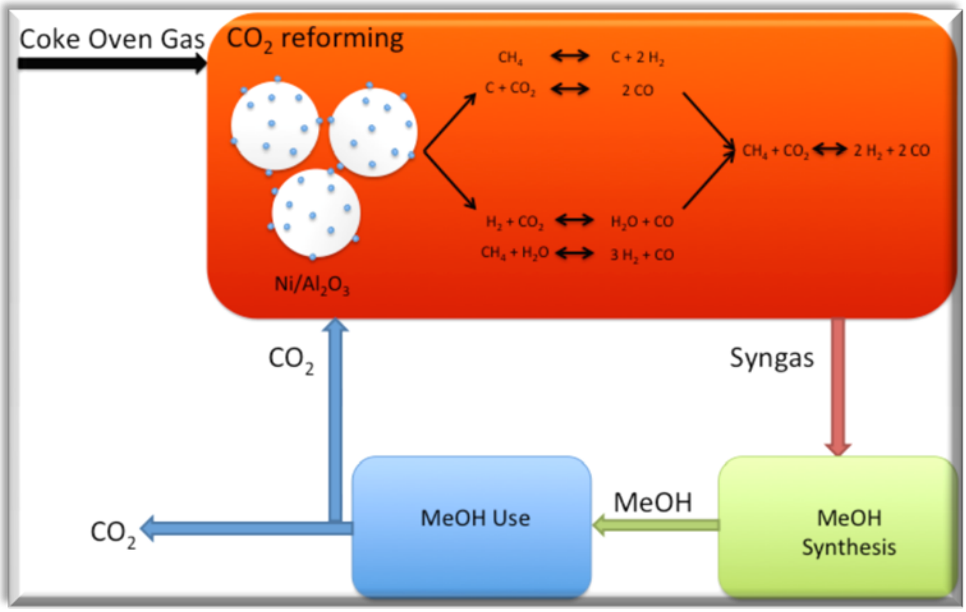

Figura 8. *Graphical abstract* del artículo *CO_2 reforming of coke oven gas over a Ni/γAl_2O_3 catalyst to produce syngas for methanol synthesis*.

3. *Syngas from CO_2 reforming of coke oven gas: Synergetic effect of activated carbon/Ni-γAl_2O_3 catalyst*, que ha sido publicado en International Journal of Hydrogen Energy (2011), 36 (21), 13361-13368.

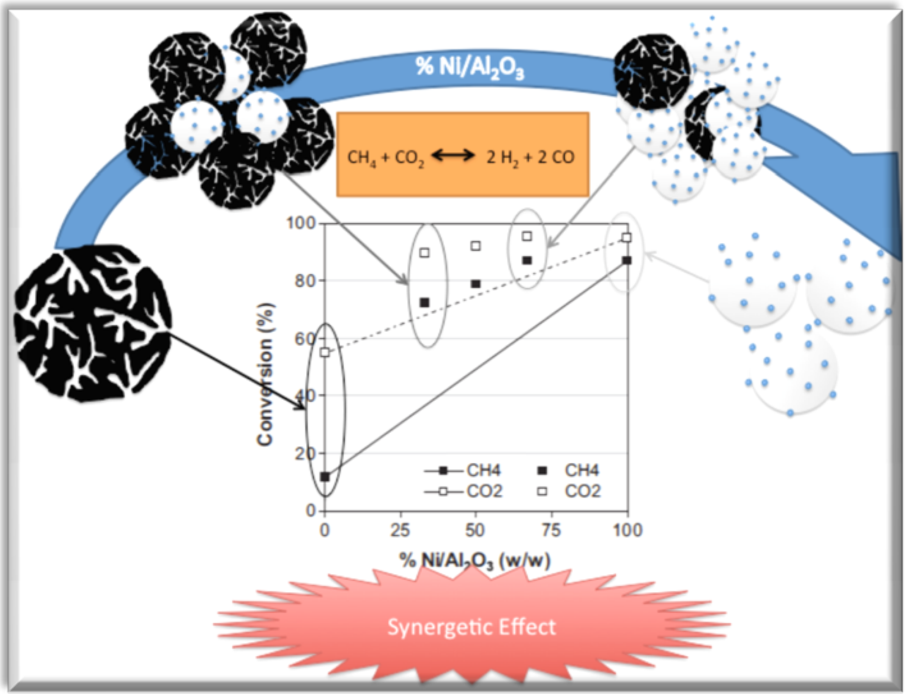

Figura 9. *Graphical abstract* del artículo *Syngas from CO_2 reforming of coke oven gas: Synergetic effect of activated carbon/Ni-γAl_2O_3 catalyst*.

¿Por qué?

El reformado de metano con CO_2 es un una reacción catalítica heterogénea que aún hoy en día se encuentra en desarrollo [52, 53, 55, 56, 66, 69-78]. A pesar de las importantes ventajas que presenta sobre el proceso convencional de producción de gas de síntesis (reformado con vapor de agua), como son el aprovechamiento del CO_2 y el menor consumo de energía, su implementación a escala industrial aún no está muy extendida. Tan solo un par de procesos industriales utilizan actualmente el reformado seco de metano: el proceso CALCOR para obtención de CO y el proceso SPARG para la producción de gas de síntesis de baja relación H_2/CO, en el que se utiliza un catalizador parcialmente envenenado con azufre [79-81]. Esto se debe a la dificultad para vencer el principal hándicap del reformado con CO_2 de metano: la desactivación del catalizador a consecuencia de la formación de depósitos carbonosos, que impiden el acceso de los reactivos gaseosos a los centro activos del catalizador [54, 55, 69, 70, 82-85].

¿Cómo?

Dispositivos

Para este estudio se han utilizado dos tipos de dispositivos experimentales: un reactor de cuarzo calentado por un horno eléctrico convencional y un microrreactor comercial PID Microactivity-Reference.

El dispositivo convencional (Figura 10) está compuesto por un horno eléctrico, en cuyo interior se introduce un reactor de cuarzo que contiene el catalizador a utilizar para la reacción. La salida se encuentra calefactada con una manta eléctrica para evitar la condensación del agua, que se puede formar por la reacción inversa de la *Water Gas Shift* (Reacción 2), la cual se recoge mediante un absorbente (perclorato de magnesio anhidro). Finalmente, los productos gaseosos de la reacción se recogen en bolsas Tedlar® para su posterior análisis mediante cromatografía de gases.

$H_2 + CO_2 \leftrightarrow H_2O + CO$ $\Delta H = 41$ kJ/mol (Reacción 2)

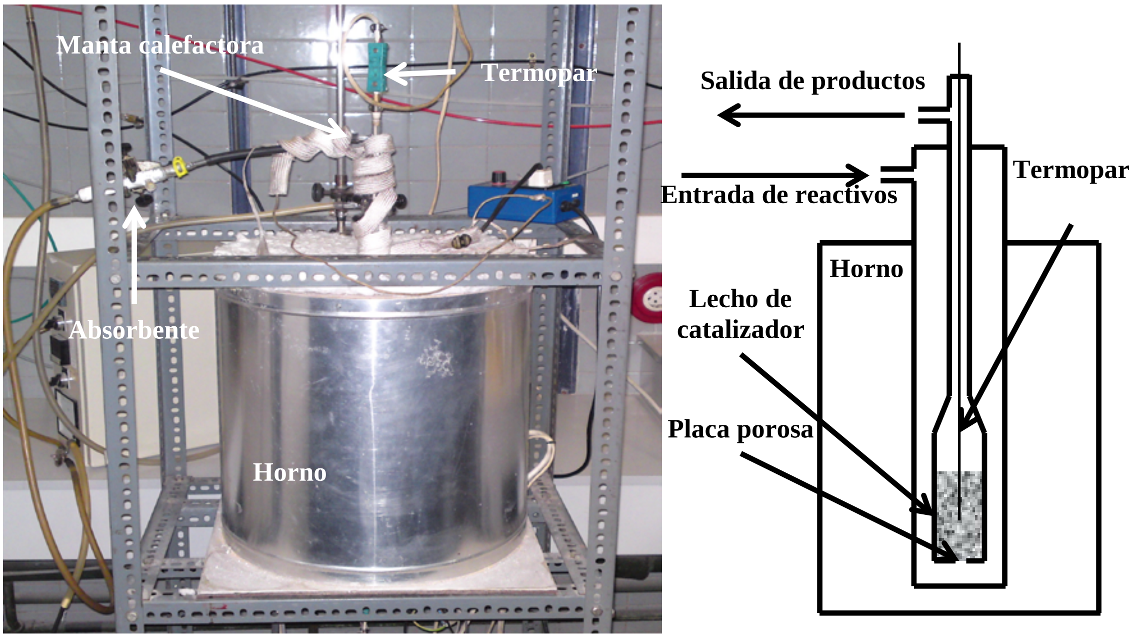

Figura 10. Dispositivo convencional utilizado en el reformado con CO_2 de gas de coquería y esquema del reactor de cuarzo.

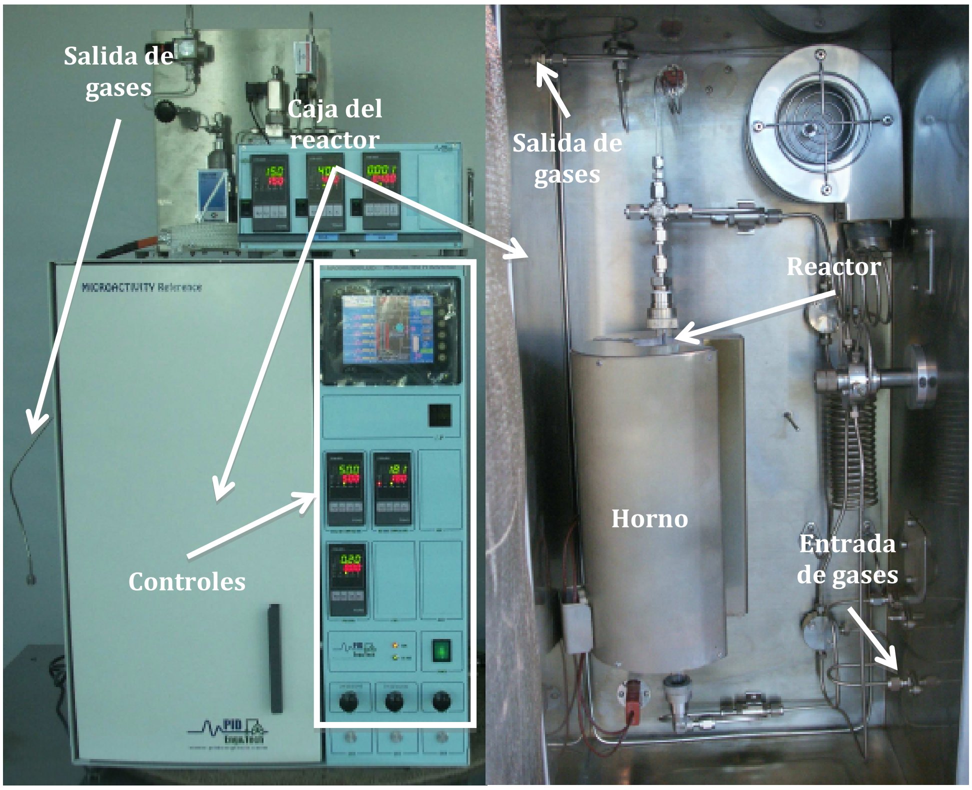

Figura 11. Microrreactor comercial PID Reference.

Por su parte, el microrreactor comercial PID Reference (Figura 11) consiste en un horno eléctrico en el cual se introduce un reactor de cuarzo con una placa porosa sobre la que se sitúa el catalizador. Todo este dispositivo se encuentra en el interior de una caja caliente por la que discurren las conducciones gaseosas, para evitar la condensación de productos. A la salida del equipo se encuentra un absorbente de la misma forma que en el dispositivo convencional. Este microrreactor permite cargar cantidades de catalizador muy inferiores a las que se utilizan en el dispositivo convencional, trabajando así con mayores velocidades espaciales. Además, la salida de gases, tras pasar a través del absorbente, se encuentra conectada a un microcromatógrafo de gases, que permite el muestreo automático, pudiendo realizarse experimentos de larga duración.

Condiciones experimentales

Los ensayos del reformado con CO_2 del gas de coquería fueron realizados a presión atmosférica en todos los dispositivos utilizados. La reacción se estudió en un rango de temperaturas que va desde los 800 hasta los 1000 ºC, de acuerdo con los valores óptimos deducidos del estudio del equilibrio termodinámico. Por otro lado, también se estudió la influencia de la velocidad espacial del gas, la cual se varió desde los 0.75 L g^{-1} h^{-1} hasta los 9.30 L g^{-1} h^{-1}.

En cuanto a la composición del gas de alimentación, inicialmente y con el objetivo de facilitar el estudio, se utilizaron mezclas ternarias de 54% de H_2, 23% de CH_4 y 23% de CO_2 (los dos gases mayoritarios del gas de coquería, H_2 y CH_4, y el CO_2 para llevar a cabo la reacción de reformado seco). Estas mezclas conservan la relación H_2/CH_4 del gas de coquería (que está entre 2 y 2.7) y las condiciones estequiométricas de CH_4 y CO_2 para el reformado seco, que son las adecuadas para el proceso, tal y como se concluyó en el estudio del equilibrio termodinámico, descrito en la Sección 3.1. Finalmente, en algunos de los experimentos se añadió CO, que es el tercer gas mayoritario del gas de coquería, utilizando mezclas cuaternarias de 52% de H_2, 21% de CH_4, 21% de CO_2 y 6% de CO, manteniendo el ratio $H_2/CH_4/CO$ del gas de coquería y las condiciones estequiométricas de CH_4 y CO_2.

Catalizadores

Para este estudio se han utilizado tres catalizadores diferentes:

1. Carbón activo FY5: este carbón activo ha mostrado una gran actividad catalítica en la reacción del reformado seco del metano [56, 83, 86-91], tanto por sí mismo como actuando

como soporte de catalizador en el que se depositó Ni, como se puede ver en el Anexo 1. En este Anexo se presentan también otros catalizadores usados en el reformado de metano con CO_2 que no dieron lugar a buenas conversiones cuando se utilizaron en el reformado seco de gas de coquería, por lo que no se incluyen en esta parte de la memoria. El estudio relacionado con este catalizador se encuentra en el artículo *Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis*, publicado en Fuel (2010), 89 (10), 2897-2902.

2. Catalizador convencional Ni/Al_2O_3: el Ni depositado sobre alúmina es el catalizador más comúnmente utilizado en el reformado seco de metano [52-54, 70, 84, 85, 92-94]. Por este motivo se preparó este tipo de catalizador mediante la impregnación de una alúmina comercial (γ-Al_2O_3) con $Ni(NO_3)_2$. Los resultados obtenidos con este catalizador se encuentran en el artículo *CO_2 reforming of coke oven gas over a $Ni/\gamma Al_2O_3$ catalyst to produce syngas for methanol synthesis*, publicado en Fuel (2012), 94, 197-203.

3. Mezclas de FY5 y Ni/Al_2O_3: dado que uno de los objetivos de esta Tesis es el estudio del proceso asistido con microondas, es necesario que el catalizador pueda ser calentado por las microondas, algo que no sucede con el Ni/Al_2O_3. Por este motivo se prepararon mezclas físicas de FY5 (que sí puede ser calentado por las microondas) y el Ni/Al_2O_3, en diferentes proporciones (se denotarán como xxAC/yyNi, siendo xx e yy los porcentajes en masa de carbón activo y catalizador convencional en la mezcla, respectivamente). Este estudio, su experimental y los resultados obtenidos, se encuentran en el artículo *Syngas from CO_2 reforming of coke oven gas: Synergetic effect of activated carbon/Ni-γAl_2O_3 catalyst*, que ha sido publicado en International Journal of Hydrogen Energy (2011), 36 (21), 13361-13368.

Conclusiones

Se pudo observar la enorme influencia que tiene sobre el proceso de reformado seco de gas de coquería el H_2 presente en el propio gas de coquería alimentado. Normalmente, el reformado con CO_2 de metano suele darse como la descomposición de metano (Reacción 3) seguida de la gasificación del carbono (también conocida como equilibrio de Boudouard) generado en la descomposición del metanol (Reacción 4).

$CH_4 \leftrightarrow 2\,H_2 + C$ $\Delta H = 75$ kJ/mol (Reacción 3)

+

$C + CO_2 \leftrightarrow 2\,CO$ $\Delta H = 172$ kJ/mol (Reacción 4)

$CH_4 + CO_2 \leftrightarrow 2\,H_2 + 2\,CO$ $\Delta H = 247$ kJ/mol (Reacción 1)

Sin embargo, la presencia de ese H_2 en la alimentación, da lugar a un segundo posible camino de reacción compuesto por reacción inversa de la *Water Gas Shift* (Reacción 2) seguida del reformado de metano con vapor de agua (Reacción 5).

$H_2 + CO_2 \leftrightarrow H_2O + CO$ $\Delta H = 41$ kJ/mol (Reacción 2)

+

$H_2O + CH_4 \leftrightarrow 3\,H_2 + CO$ $\Delta H = 206$ kJ/mol (Reacción 5)

$CH_4 + CO_2 \leftrightarrow 2\,H_2 + 2\,CO$ $\Delta H = 247$ kJ/mol (Reacción 1)

En el caso de los ensayos con carbón activo o con las mezclas de carbón activo y catalizador convencional Ni/Al_2O_3 es difícil determinar cuál de las dos vías de reacción tiene lugar o, en caso de ocurrir ambas (lo más probable), cuál es la prioritaria, debido a que también puede darse la reacción de gasificación del carbono con el CO_2 (Reacción 4) sobre el propio material de partida y no sólo sobre los depósitos de carbono formados en la descomposición de CH_4, lo cual puede encontrarse en Bermúdez *et al.*, 2010, Fuel 89 (10), 2897-2902. Sin embargo, en el caso del catalizador convencional Ni/Al_2O_3, si fue posible determinar que la vía principal es la que combina la reacción inversa de la *Water Gas Shift* y el reformado de metano con vapor de agua, tal y como se muestra en Bermúdez *et al.*, 2012, Fuel 94, 197-203.

Cuando el catalizador utilizado es el carbón activo FY5, se observó una importante variación de las conversiones de CH_4 y CO_2 en el reformado seco de gas de coquería con respecto a las obtenidas en el reformado seco de metano. Además, debido al efecto de la reacción inversa de la *Water Gas Shift*, se produjeron importantes cantidades de agua. Es necesario reseñar la relevancia de este hecho, ya que la presencia de agua en la posterior síntesis de metanol es un problema, debido a su efecto desactivante en los catalizadores utilizados en dicho proceso. En el caso del gas de coquería, se observó una gran disminución de la conversión de CH_4 con respecto a la obtenida en el reformado seco de metano, mientras que la conversión del CO_2 fue considerablemente superior.

Un aumento en la temperatura de reacción permite mejorar las conversiones tanto de CH_4 como de CO_2, así como disminuir la diferencia existente entre ambas a menores temperaturas. Este hecho se debe a que el reformado seco es una reacción más endotérmica que la reacción inversa de la *Water Gas Shift* y a que también se promociona la reacción de reformado con vapor de agua. Por el contrario, al aumentar la velocidad espacial, se observan pérdidas de conversión que afectan de diferente medida al CH_4 y al CO_2, ya que el segundo sigue reaccionando a través de la reacción inversa de la *Water Gas Shift*.

Por su parte, la selectividad del catalizador sólo es alta a las temperaturas más elevadas, ya que menores temperaturas llevan asociadas bajos valores de selectividad debido a la producción de agua. De hecho, en algunas condiciones, la selectividad llega a ser negativa ya que, no sólo el H_2 proveniente del metano, sino que también una gran parte del H_2 alimentado reacciona a través de las reacción inversa de la *Water Gas Shift*, sin ser capaz de reaccionar a continuación a través de la reacción de reformado con vapor de agua. Todo esto está más ampliamente detallado en Bermúdez *et al.*, 2010, Fuel 89 (10), 2897-2902.

En el caso del catalizador convencional Ni/Al_2O_3, el descenso de la conversión de metano con respecto a la obtenida en el reformado seco de metano es mucho menos pronunciado, mientras que la conversión de CO_2 apenas se incrementa. De nuevo, el aumento en la temperatura de reacción dio lugar a incrementos en las conversiones, que llegaron a alcanzar valores del 100%. Así mismo, el aumento en la velocidad espacial del gas produjo descensos en las conversiones, si bien con este tipo de catalizadores se pudo multiplicar hasta más de 10 veces el valor de la velocidad espacial logrando que las conversiones no cayeran por debajo del 70% para el CH_4 y el 85% para el CO_2 a 800 ºC, ni del 90% para el CH_4 y el 95% para el CO_2 a 900 ºC. Esto provoca que este catalizador sea mucho más selectivo que el carbón activo.

Dado que las conversiones obtenidas con este catalizador se mantuvieron muy estables a lo largo de las 6 horas que duraban los experimentos, al contrario que en el caso del carbón activo FY5, se decidió estudiar su desactivación en experimentos de mayor duración (50 horas) tanto a 800 como a 900º C a una velocidad espacial intermedia. En ambos casos las conversiones se mantuvieron estables durante las 50 horas. Esto parece deberse a un proceso reactivo que tiene lugar en el catalizador durante el calentamiento en atmósfera inerte y en los instantes iniciales de la reacción. Cuando el catalizador se calienta en atmósfera inerte para alcanzar la temperatura de reacción, el Ni^0 procedente de la reducción del $Ni(NO_3)_2$ que se utiliza en la impregnación de la alúmina, interacciona con la propia alúmina dando lugar a una espinela ($NiAl_2O_4$). Al iniciarse la reacción, la atmósfera fuertemente reductora hace que esa espinela se reduzca dando lugar a cristales de Ni^0 de muy pequeño tamaño, lo que hace al catalizador más resistente a la desactivación, tanto por sinterización como por depósitos de coque. Sin embargo, tras las 50 horas de reacción se observó una cierta sinterización de los cristales de Ni^0 (su tamaño de partícula aumentó desde los 17 hasta los 24 nm tanto a 800 como a 900 ºC), lo que en sí mismo tiene un efecto desactivante y además promociona los depósitos de coque que también desactivarán el catalizador. De hecho, los análisis TOC revelaron la presencia de depósitos carbonosos inorgánicos a 800 ºC y tanto orgánicos como inorgánicos a 900 ºC. Todo esto indica que, si bien durante las 50 horas estudiadas los catalizadores no presentaron desactivación apreciable, más a la larga parece que si se desactivarían. Todo esto se encuentra con mayor detalle en Bermúdez *et al.*, 2012, Fuel 94, 197-203.

Por su parte, cuando se utilizan las mezclas de carbón activo y catalizador convencional Ni/Al_2O_3, se observa un efecto sinérgico entre ambos materiales que permite obtener mejores conversiones y selectividades, menores producciones de agua y una mayor resistencia a la desactivación.

En el caso de las conversiones, se puede observar que las obtenidas experimentalmente se encuentran bastante por encima de aquellas predichas por la Ley de las Mezclas. Incluso, en el caso del catalizador 33AC/66Ni, se observa como éste es capaz de alcanzar las mismas conversiones que en el caso del catalizador convencional Ni/Al_2O_3 por sí solo. La producción de agua, sin embargo, presenta el comportamiento contrario, ya que las producciones de agua experimentales son muy inferiores que las que predice la Ley de las Mezclas, logrando nuevamente el catalizador 33AC/66Ni valores prácticamente idénticos a los que se alcanzan con el catalizador convencional Ni/Al_2O_3.

En cuanto a la producción de depósitos carbonosos, mediante las isotermas de adsorción se pudo determinar cómo las pérdidas de área superficial, cuando los materiales se utilizaban conjuntamente, eran considerablemente inferiores a cuando éstos eran utilizados por separado, por lo que se observa que el efecto sinérgico también aumenta la resistencia a la desactivación de los catalizadores.

El efecto sinérgico se comprobó también en experimentos de larga duración con una velocidad especial intermedia y no sólo se mantuvo, sino que se observó que aumentaba a medida que la reacción progresaba, ya que la diferencia entre los valores experimentales y los predichos por la Ley de las Mezclas fueron mayores tras 50 horas que tras 6 horas. Esto es debido a que las mezclas presentan un comportamiento diferente al FY5 y el catalizador convencional Ni/Al_2O_3. Mientras que las conversiones obtenidas con el carbón activo disminuyen constantemente y las obtenidas con el catalizador convencional Ni/Al_2O_3 son estables, las conversiones obtenidas con las mezclas aumentan a lo largo del experimento. Esto hace que, tras esas 50 horas, todas las mezclas con un porcentaje de carbón activo superior o igual al 50% alcancen prácticamente la misma conversión que el catalizador convencional Ni/Al_2O_3.

Todos estos resultados sobre las mezclas, que se encuentran con mayor detalle en Bermúdez *et al.*, 2011, International Journal of Hydrogen Energy 36 (21), 13361-13368, tienen una importante consecuencia económica, y es que, a la vista de estos resultados, se podrían conseguir resultados similares (e incluso superiores) sustituyendo parcialmente un catalizador caro (el catalizador convencional Ni/Al_2O_3) por un catalizador más barato (el carbón activo FY5), reduciendo los costes asociados a dicho proceso.

La presencia del CO en la alimentación afectó de forma diferente en función del catalizador utilizado. Cundo se empleó el carbón activo la presencia de CO en el gas de alimentación dio lugar a mejores conversiones. Esto podría deberse a que el equilibrio de Boudouard (Reacción 4) se desplaza hacia el lado de los reactivos, lo que da lugar a dos efectos. Por un lado, se disminuyen los depósitos de carbono que afectan a la actividad catalítica. Por otro lado, el incremento de CO_2 que se produce promociona la reacción inversa de la *Water Gas Shift*, aumentando la producción de agua, la cual a su vez promociona el reformado con vapor de agua. Cuando se utilizó el catalizador convencional Ni/Al_2O_3, las conversiones disminuyeron ligeramente. En el caso de las mezclas, con las de alto porcentaje de catalizador convencional Ni/Al_2O_3 se alcanzaron menores conversiones que sin CO en la alimentación, mientras que las de alto porcentaje de carbón activo, dieron lugar a conversiones mayores que sin CO en la alimentación, pero en ambos casos las diferencias fueron casi inapreciables. Todo esto provocó que el efecto sinérgico perdiera fuerza. Se sigue observando dicho efecto, pero el aumento en las conversiones con carbón activo y la disminución de las mismas con el catalizador convencional Ni/Al_2O_3, hace que las diferencias entre los valores experimentales y los predichos por la Ley de las Mezclas sean menores que en el caso en el que no se introdujo el CO en la alimentación. Asimismo, cuando el CO está presente en la alimentación, las conversiones son estables por lo que la diferencia entre las experimentales y las predichas no aumenta al avanzar la reacción. Todo el este estudio sobre la influencia del CO se puede encontrar mucho más detallado en Bermúdez *et al.*, 2011, International Journal of Hydrogen Energy 36 (21), 13361-13368.

A parte de determinar las conversiones y selectividades obtenidas, es muy importante evaluar la idoneidad del gas de síntesis obtenido para la producción del metanol, para lo que se han estudiado la relación H_2/CO y el parámetro R. En el caso del gas de síntesis obtenido utilizando el carbón activo FY5 como catalizador, los resultados publicados en Bermúdez *et al.*, 2010, Fuel 89 (10), 2897-2902 muestran que los valores de estos parámetros se encuentran fuertemente afectados por las variaciones de temperatura y velocidad espacial. Debido a esto, sólo se podría utilizar este catalizador trabajando con condiciones muy extremas (1000 ºC y la menor velocidad espacial posible) ya que, de otra manera, daría lugar a un gas de síntesis con una composición que no sería la adecuada para su utilización en la producción de metanol. Por su parte, con el catalizador convencional Ni/Al_2O_3, tal y como se muestra en Bermúdez *et al.*, 2012, Fuel 94, 197-203, se puede observar que los valores del parámetro R y de la relación H_2/CO se encuentran ligeramente afectados por las variaciones de temperatura y velocidad espacial, siendo la velocidad espacial el parámetro operacional que más afecta a estos valores. Pero a pesar de ello, en todos los casos, tanto el parámetro R como la relación H_2/CO están muy próximos a los valores óptimos para la utilización de este gas de síntesis en la producción de metanol. Finalmente, tal y como se muestra en Bermúdez *et al.*, 2011, International Journal of Hydrogen Energy 36 (21), 13361-13368, en el caso de las mezclas de carbón activo FY5 y catalizador convencional Ni/Al_2O_3, dado que fueron los mejores catalizadores, el estudio del gas de síntesis ya se llevó a cabo incluyendo el CO en el gas de alimentación. Se puede observar que en todos los casos el ratio H_2/CO se sitúa ligeramente por encima de 2, mientras que el parámetro R, se sitúa en torno a 1.9, algo por debajo del valor ideal, pero esto no constituiría ningún problema ya que, como se explicó en la Sección 3.1 *Equilibrio termodinámico del reformado con CO_2 de gas de coquería*, este parámetro se puede ajustar fácilmente gracias a la recirculación del H_2 no reaccionado en la síntesis del metanol.

Artículo 3

Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis

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Dry reforming of coke oven gases over activated carbon to produce syngas for methanol synthesis

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ABSTRACT

The dry reforming of coke oven gases (COG) over an activated carbon used as catalyst has been studied in order to produce a syngas suitable for methanol synthesis. The primary aim of this work was to study the influence of the high amount of hydrogen present in the COG on the process of dry reforming, as well as the influence of other operation conditions, such us temperature and volumetric hourly space velocity (VHSV). It was found that the reverse water gas shift (RWGS) reaction takes place due to the hydrogen present in the COG, and that its influence on the process increases as the temperature decreases. This situation may give rise to the consumption of the hydrogen present in the COG, and the consequent formation of a syngas which is inappropriate for the synthesis of methanol. This reaction can be avoided by working at high temperatures (about 1000 °C) in order to produce a syngas that is suitable for methanol synthesis. It was also found that the RWGS reaction is favoured by an increase in the VHSV. In addition, the active carbon FY5 was proven to be an adequate catalyst for the production of syngas from COG.

1. Introduction

Synthesis gas, or simply syngas, is a raw material for the large-scale production of hydrogen and a wide variety of organic products, consisting mainly of hydrogen and carbon monoxide [1,2]. It is basically produced from natural gas and oil, but the limited supply of fossil fuels and the fight against climate change and greenhouse gas (GHG) emissions have intensified the search for alternative processes of production, such as biomass gasification [1] or biogas reforming [3].

Coke oven gases (COG), which can be considered a byproduct of coking plants, consist mainly of H_2 (~55–60%), CH_4 (~23–27%), CO (~5–8%) and N_2 (~3–5%), along with other hydrocarbons, H_2S and NH_3 in small proportions. Most of this gas is used as fuel in the coke ovens and other processes of the steel plant, but very often the excess of COG cannot be used in this way and so it is burnt in torches. But this gives rise to environmental problems that urgently need to be solved [4–9]. An alternative option for the excess COG is for it to be valorized by means of hydrogen separation [8,10,11] or syngas production through partial oxidation [12,13], steam reforming [7,12,14,15] or dry reforming [4,5,16]. The syngas thus produced can in turn be used for the synthesis of different other organic products, mainly methanol. Although most authors have concentrated their attention on the steam reforming of COG [7,12,14,15], in the last few years the dry reforming of COG has also been investigated [4,5,16], due to the numerous advantages that it offers compared to steam reforming, such as the saving of energy or CO_2 consumption. Another important advantage of the dry reforming of COG is the possibility of obtaining a syngas with a H_2/CO ratio of about 2, which is the ideal proportion for methanol synthesis [17,18], in only one step provided the process is carried out under stoichiometric conditions of CH_4 and CO_2. As can be seen in Fig. 1, the process can be considered as a way of "*partial recycling*" of CO_2 since it consumes, at least theoretically, half of the CO_2 produced when methanol is burnt. The prospects for this technology are far-reaching, since the demand for methanol for vehicle fuel, as a source of hydrogen for fuel cells or biodiesel production is rapidly increasing [19].

The main objective of this work is to investigate the dry reforming of COG in order to produce a syngas with a ratio of H_2/CO suitable for methanol production. The dry reforming of COG is carried out over an activated carbon, which has been proven to be an effective catalyst for the dry reforming of methane [20]. The influence of the large hydrogen amount which is present in the COG on the process of dry reforming and other operating conditions, such as temperature or space velocity, are studied.

2. Experimental

The dry reforming of COG was carried out in a fixed-bed quartz reactor under atmospheric pressure and heated in an electric furnace. The reaction temperature in the middle of the catalyst bed was monitored and controlled by means of a type K thermocouple.

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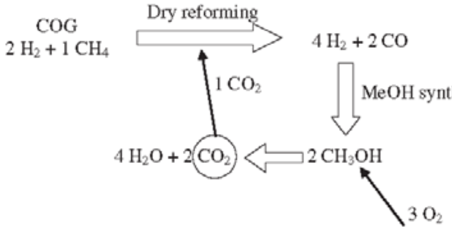

Fig. 1. Scheme of "*partial recycling*" of CO_2 in the process of dry reforming of COG for methanol production.

A commercial activated carbon with a high surface area (Filtracarb FY5), whose main characteristics are shown in Table 1, was used as catalyst.

In the first test, CH_4 and CO_2 were fed in at a ratio of 1:1. In the rest of the experiments, H_2 was added in order to study the effect of the presence of H_2 in the feed stream on the process of dry reforming of methane. The addition of H_2 gave rise to a gaseous ternary mixture (GTM) composed of 54% H_2, 23% CH_4 and 23% CO_2 (vol.%), in order that the H_2/CH_4 ratio was within the range characteristic of COG (2–2.7). The CH_4 and CO_2 were kept under stoichiometric conditions for the dry reforming of the methane. The influence of the CO present in the COG is beyond the scope of this work and will be studied in due course. In order to assess the influence of temperature on the dry reforming of the COG, tests were performed at atmospheric pressure and at three different temperatures (800, 900, and 1000 °C). In addition, tests at three different total volumetric hourly space velocities, VHSV (0.75, 1, and 1.5 $L\,g^{-1}\,h^{-1}$, which represent 0.16, 0.22, and 0.32 $L\,g^{-1}\,h^{-1}$ for the methane respectively, $VHSV_{CH_4}$) were carried out with the aim of studying the effect of this variable upon the process and the composition of the products. The VHSV was increased by reducing the mass of the catalyst bed.

Dry reforming reactions were performed in a quartz reactor charged with the carbon catalyst, which had previously been dried over night at 110 °C. Before starting the reaction, the system was flushed with N_2 (flow rate of 60 $mL\,min^{-1}$ for 15 min) and then, heated up to a pre-set operating temperature. The gas product was collected in Tedlar® sample bags periodically during the experiment. Due to the formation of steam in some of the experiments, a condenser was placed after the reactor in order to prevent water from reaching the bags. The samples were analyzed in a Varian CP-3800 gas-chromatograph equipped with a thermal conductivity detector TCD and two columns (an 80/100 Hayesep Q and an 80/100 Molesieve 13X) connected in series. The second column was bypassed by a six-port valve for the analysis of CO_2 and hydrocarbons ($\geqslant C_2$).

The CH_4 and CO_2 conversions and the selectivity to H_2 were calculated after determining the amount of water produced and the composition of the outlet stream by means of an iterative procedure based on the Newton method for non-lineal equations and using the Solver Microsoft Excel® tool, and closing mass balances within $a \pm 5\%$ error margin. Selectivity to hydrogen gives an approximate idea of the amount of methane transformed into H_2 or into other species (such as light hydrocarbons, $\geqslant$C2, or water). The parameters were calculated according to Eqs. (1)–(3):

$$CH_4\ \text{conversion}\ (\%) = 100 \times \frac{CH_{4\ \text{in}} - CH_{4\ \text{out}}}{CH_{4\ \text{in}}}, \tag{1}$$

$$CO_2\ \text{conversion}\ (\%) = 100 \times \frac{CO_{2\ \text{in}} - CO_{2\ \text{out}}}{CO_{2\ \text{in}}}, \tag{2}$$

$$H_2\ \text{selectivity},\ S\ (\%) = 100 \times \frac{H_{2\ \text{out}} - H_{2\ \text{in}}}{2 \cdot (CH_{4\ \text{in}} - CH_{4\ \text{out}})}, \tag{3}$$

where $CH_{4\ \text{in}}$, $CO_{2\ \text{in}}$ and $H_{2\ \text{in}}$, are moles of each gas at the inlet of the reactor and $CH_{4\ \text{out}}$, $CO_{2\ \text{out}}$ and $H_{2\ \text{out}}$ are moles of each gas at the outlet.

3. Results and discussion

In a previous work by our group [20], the reforming of CH_4 with CO_2 (Reaction 1) carried out over the activated carbon FY5 was studied (see Fig. 2). A possible mechanism for the dry reforming reaction and the role of CO_2 introduced were discussed. The experiments were conducted over a period of 6 h, at 800 °C and atmospheric pressure, under stoichiometric conditions of the methane and carbon dioxide and at a $VHSV_{CH_4}$ of 0.16 $L\,g^{-1}\,h^{-1}$ (total VSHV of 0.32 $L\,g^{-1}\,h^{-1}$) and conversions of more than 40% were achieved.

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO, \quad \Delta H = 247.3\ \text{kJ/mol} \tag{Reaction1}$$

If the process is carried out introducing the GTM, i.e., in the presence of hydrogen in the feed, two different phenomena may take place: (i) the equilibrium is shifted to the reactants (see Reaction 1), which results in lower CH_4 and CO_2 conversions, and (ii) the reverse water gas shift reaction (RWGS) occurs (Reaction 2), giving rise to an increase in CO_2 conversion and the formation of water [16,21,22]. Both effects result in a decrease in hydrogen production.

$$H_2 + CO_2 \leftrightarrow H_2O + CO, \quad \Delta H = 41.2\ \text{kJ/mol} \tag{Reaction2}$$

Table 1
Main chemical characteristics and textural properties of the activated carbon FY5.

Proximate analysis (wt.%)				Ultimate analysis (wt.%)[a]						
Moisture	Ash[a]	Volatile matter[a]		C	H	N	S	O[b]	H/C	
6.7	2.8	3.0		95.7	0.5	0.5	0.2	0.3	0.068	
Inorganic composition of the ashes (expressed as wt.% of metal oxides[a])										
SiO_2	K_2O	Al_2O_3	Fe_2O_3	CaO	Na_2O	SO_3	MgO	TiO_2	Ni	Co
39.79	25.40	9.06	9.04	6.4	3.01	2.77	2.71	1.18	n.d.[c]	n.d.[c]
Textural properties										
S_{BET} (m^2/g)	V_t (cm^3/g)[d]	V_m (cm^3/g)[e]	V_s (cm^3/g)[f]							
825	0.34	0.32	0.25							

[a] Dry basis.
[b] Calculated by difference.
[c] Not detected.
[d] Total specific pore volume.
[e] Specific volume of micropores (pores of internal width < 2 nm).
[f] Specific volume of small micropores (pores with an internal width < 0.7 nm).

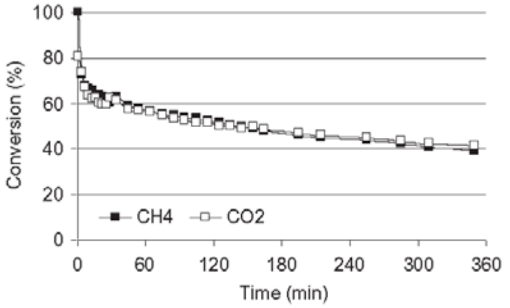

Fig. 2. CH_4 and CO_2 conversions for the dry reforming of CH_4 at 800 °C, $CH_4/CO_2 = 1$, $VHSV_{CH_4} = 0.16\ L\ g^{-1}\ h^{-1}$, $VHSV = 0.32\ L\ g^{-1}\ h^{-1}$ and 1 atm (adapted from [20]).

Both phenomena occurred in the case of the dry reforming of the GTM at 800 °C, and led to changes in the CH_4 and CO_2 conversions resulting from the dry reforming of CH_4. As can be seen in Fig. 3, methane conversion fell to below 40% from the very beginning of the reaction, reaching values of about 20% after 6 h of reaction. The sharp decreasing observed during the first minutes may be due to initial instabilities. In addition, carbon dioxide conversion was higher than in the case of the dry reforming of methane (Fig. 2), which suggests that RWGS had more influence on the process than the effect of the shift of the equilibrium. The large amount of water collected in the condenser, representing about 8 vol.% of the products of the reaction, reinforces this suggestion, which has also been reported by other authors [16]. Besides reducing H_2 production and changing the H_2/CO ratio, water could also obstruct the synthesis of methanol, since it has a deactivating effect on the Cu catalyst [23].

3.1. Effect of the temperature

Fig. 4 shows the dry reforming of the GTM at 900 °C. As can be seen, CH_4 conversion is higher than 50% throughout the experiment, a level of conversion never reached in tests carried out at 800 °C. CO_2 conversion is also higher than it is at 800 °C. Since the RWGS reaction (Reaction 2) is less endothermic than the dry reforming of methane (Reaction 1), an increase in the operating temperature enhances dry reforming, giving rise to a higher methane conversion and, therefore, greater hydrogen production, whereas the production of water is reduced. In actual fact, the increase in CO_2 conversion may have been due to an enhancement of the dry reforming reaction, and not to the RWGS reaction, since the amount of water collected was nearly three times lower than that in the experiment at 800 °C. Other possible explanation to these results is that at higher temperatures the steam reforming of methane (Reaction 3) can occur, i.e. the water produced in the RWGS could react with the methane.

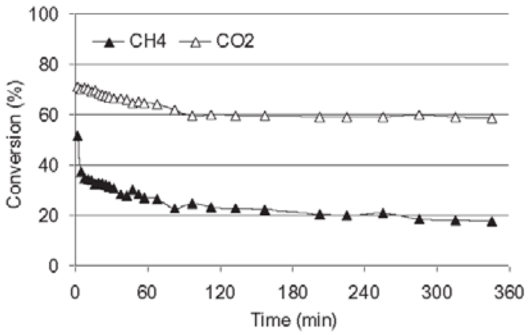

Fig. 3. CH_4 and CO_2 conversions for the dry reforming of the GTM at 800 °C, $CH_4/CO_2 = 1$, $VHSV_{CH_4} = 0.16\ L\ g^{-1}\ h^{-1}$, $VHSV = 0.75\ L\ g^{-1}\ h^{-1}$ and 1 atm.

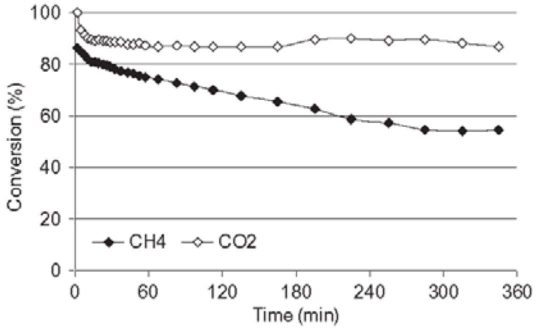

Fig. 4. CH_4 and CO_2 conversions for the dry reforming of the GTM at 900 °C, $CH_4/CO_2 = 1$, $VHSV_{CH_4} = 0.16\ L\ g^{-1}\ h^{-1}$, $VHSV = 0.75\ L\ g^{-1}\ h^{-1}$ and 1 atm.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO, \quad \Delta H = 206.1\ kJ/mol \qquad (Reaction3)$$

However, this mechanism seems less probable since it would lead to similar increments in both CH_4 and CO_2 conversions which did not take place, as can be seen in Fig. 4. Nevertheless, the sum of RWGS reaction (Reaction 2) and steam reforming reaction (Reaction 3) gives rise to the dry reforming reaction (Reaction 1), which makes difficult to distinguish the path followed by the reaction.

Fig. 5 shows the conversion results corresponding to the test carried out at 1000 °C. This increment in temperature results in an increase in the conversions, up to 80% for CH_4 and 95% for CO_2 after 6 h of experimentation. Moreover, no production of water was detected at 1000 °C. Therefore, by working at this temperature, it is possible to avoid the occurrence of RWGS, and so maximize the production of hydrogen.

3.2. Effect of the volumetric hourly space velocity (VHSV)

The effect of the VHSV on the process was studied at 900 °C and 1000 °C. The temperature of 800 °C was discarded since an increase in VHSV would lead to a further decrease in conversions [20] and to the formation of more water, which would make it difficult to study the effect of the variation of VHSV and its influence on the process.

The results of the dry reforming of the GTM at 900 °C employing three different VHSV (0.75, 1, and 1.5 $L\ g^{-1}\ h^{-1}$, respectively) are shown in Fig. 6. As can be seen, both CH_4 and CO_2 conversions

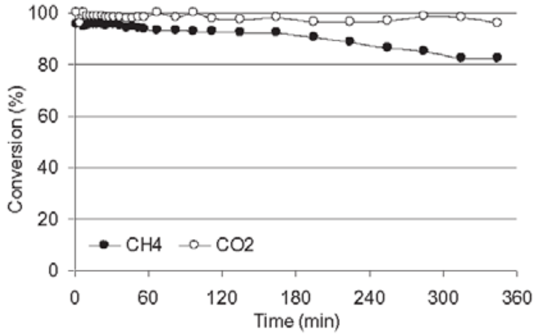

Fig. 5. CH_4 and CO_2 conversions for the dry reforming of the GTM at 1000 °C, $CH_4/CO_2 = 1$, $VHSV_{CH_4} = 0.16\ L\ g^{-1}\ h^{-1}$, $VHSV = 0.75\ L\ g^{-1}\ h^{-1}$ and 1 atm.

are affected by changes in VHSV. Thus, the levels of conversions diminish as the VHSV increases. However, the decrease in the CH_4 conversion is greater than in the case of CO_2. The loss of conversion due to dry reforming reaction and to the increase in VHSV is similar both for CH_4 and CO_2 [20]. Whereas, the consumption of CO_2 due to the RWGS reaction, which seems to be higher at elevated VHSVs, led to a smaller decrease in CO_2 conversion. Thus, high amounts of water were collected when the VHSV increased (50% higher in the experiment at 1 L g^{-1} h^{-1} and twice the amount in the experiment carried out at 1.5 L g^{-1} h^{-1}, compared to the experiment at 0.75 L g^{-1} h^{-1}), owing to the more vigorous RWGS reaction as VHSV increased. This may be due to an increase in the CO_2 concentration throughout the reactor. Since there is a high amount of H_2 present, CO_2 could be the species which limits the RWGS reaction. Consequently, high conversions of CO_2 should be avoided in order to prevent the side reaction of RWGS.

Fig. 7 shows the results of two tests carried out at 1000 °C and 0.75 L g^{-1} h^{-1} and 1.50 L g^{-1} h^{-1}, respectively. As was explained above, no water production was observed at 1000 °C and 0.75 L g^{-1} h^{-1}. When the VSHV was increased to 1.50 L g^{-1} h^{-1}, some water was produced due to the increase in the concentration of CO_2 resulting from the decrease in the conversion caused by the dry reforming reaction. However, the water collected was less than 1 vol.% of the total products, since CO_2 conversion was sufficiently high at 1000 °C, despite the increase in VSHV.

3.3. Analysis of the syngas

In order to specify how much of the hydrogen present in the CH_4 is converted into H_2 or into other species, it is necessary to evaluate the selectivity (Eq. (3)). Selectivity to H_2 for each of the experiments is shown in Table 2. Low values of selectivity were obtained at 800 °C, mainly due to the large amount of hydrogen that reacts with CO_2 to produce water. The negative values for selectivity, observed at this temperature, were caused not only by the low production of hydrogen, but also by the consumption of part of the hydrogen in the feed. When water production was lower, at 900 °C or 1000 °C, selectivity reached higher values, exceeding 90% when no water was produced (1000 °C and 0.75 L g^{-1} h^{-1}), since only light hydrocarbons, which are produced in negligible proportions (less than 1%), could have consumed part of this hydrogen. It is clear that an increase in VHSV must have affected selectivity, due to the increase in the water produced. Thus, at a given temperature, selectivity decreases as VHSV increases, this decrease being more marked at 900 °C than at 1000 °C.

To determine whether a syngas is suitable for methanol production, the H_2/CO ratio after the process of reforming must be taken into account. The appropriate H_2/CO ratio for the synthesis of methanol (Reaction 4) is 2 [17,18]. Both steam and dry reforming of methane give rise to ratios much higher or much lower than this value (i.e., 3 in the case of steam reforming and 1 in the case of dry reforming). It is therefore necessary to include other conditioning stages in the process in order to produce an appropriate syngas

Table 2
H_2/CO ratio, *R* parameter and selectivity to H_2 (*S*) for the dry reforming of the GTM at different temperatures and VHSV.

Temperature (°C)	VHSV (L g^{-1} h^{-1})	H_2/CO	*R*	*S*[a] (%)
800	0.75	3.09 ± 0.05	1.76 ± 0.04	40 to −10
900	0.75	2.26 ± 0.09	2.09 ± 0.07	85–70
900	1.00	2.35 ± 0.07	2.01 ± 0.05	85–65
900	1.50	2.69 ± 0.07	1.78 ± 0.06	75–45
1000	0.75	2.17 ± 0.02	2.13 ± 0.03	100–90
1000	1.50	2.25 ± 0.04	2.01 ± 0.04	95–85

[a] Range of variation of the selectivity to H_2 from *t* = 0 to 6 h.

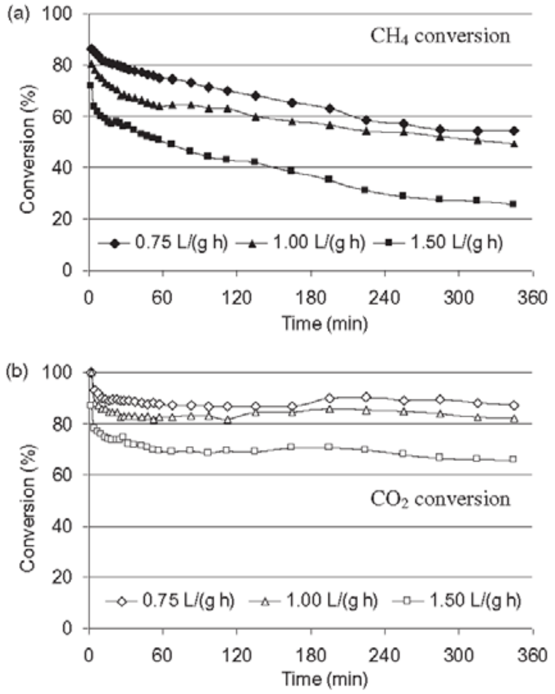

Fig. 6. Influence of the VHSV on (a) CH_4 conversion and (b) CO_2 conversion, for the dry reforming of the GTM at 900 °C, CH_4/CO_2 = 1 and 1 atm.

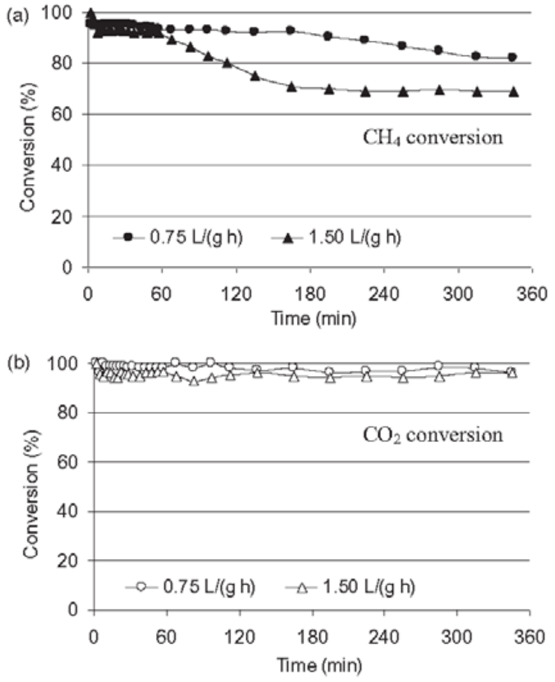

Fig. 7. Influence of the VHSV on (a) CH_4 conversion and (b) CO_2 conversion, for the dry reforming of the GTM at 1000 °C, CH_4/CO_2 = 1 and 1 atm.

for methanol synthesis [17]. Nevertheless, the presence of hydrogen in COG makes it possible to reach values near to the appropriate H_2/CO ratio by dry reforming in just one step. Although the H_2/CO ratio is the most commonly used factor to evaluate the composition of a syngas, some authors have suggested that the influence of the CO_2 in the feed should also be taken into account on the methanol synthesis stage [6,17,24,25]. CO_2 acts as a promoter of the methanol synthesis reaction (Reaction 4), it can react with hydrogen to produce methanol and water (Reaction 5) and it helps to maintain the activity of the catalyst.

$$2H_2 + CO \leftrightarrow CH_3OH, \quad \Delta H = -90.9 \text{ kJ/mol} \qquad \text{(Reaction4)}$$

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O, \quad \Delta H = -41.1 \text{ kJ/mol} \qquad \text{(Reaction5)}$$

The relation between the proportions of H_2, CO, and CO_2 in the feed in methanol synthesis is evaluated by means of the R parameter, which is defined as follows [17,24,25]:

$$R = \frac{H_2 - CO_2}{CO + CO_2}, \qquad (4)$$

where H_2, CO_2, and CO are moles of each gas fed in at the methanol synthesis stage.

In order to optimize the process, this parameter needs to be equal to or slightly higher than 2 [17,24,25]. If R takes values lower than 2, it leads to an increase in the formation of the byproducts during the methanol synthesis stage, whereas when values are higher than 2, it is necessary to increase the recycling rate in the methanol synthesis stage due to the excess of hydrogen, which makes the process less efficient and more expensive [25].

Table 2 shows the H_2/CO ratio and R parameter for the different tests of dry reforming of GTM carried out at different temperatures and VHSV.

As can be seen, at 800 °C, although the conversion of CO_2 was considerably higher than the conversion of CH_4, the H_2/CO ratio is higher than 3. This is due to the strong influence that the hydrogen in the feed has on this parameter when the conversions are low. This influence decreases as the conversions increase (900 °C and 1000 °C). Besides, even when the CH_4 and CO_2 conversions are quite different (900 °C), the H_2/CO ratios are close to 2, which is the most suitable value for methanol synthesis.

As for the R parameter, the experiment carried out at 800 °C produces a syngas with a value unsuitable for methanol synthesis. This may be due to the low conversions achieved, which lead to high amounts of CO_2 in the resulting stream. The R values of the syngas produced at 900 °C and 1000 °C are slightly higher than 2, which may be considered as acceptable for the production of methanol.

The variation in the VHSV influences both the H_2/CO ratio and R parameter. The H_2/CO ratio increases as the VHSV increases, due to the decrease in the conversions. This situation might have been expected to lead to a lower H_2/CO ratio, since the loss of conversion in the case of CH_4 is higher than for CO_2, i.e., the reduction in hydrogen production is greater than in the production of CO. However, as a consequence of the decrease in both conversions, the influence of the hydrogen present in the feed increases, which gives rise to higher values of H_2/CO. In the case of the R parameter, the opposite trend can be observed for the H_2/CO ratio, since the R parameter decreases as the VHSV increases, due to greater amount of CO_2 present in the resulting syngas.

4. Conclusions

The main objective of this work was to study the dry reforming of coke oven gases over an activated carbon in order to produce a synthesis gas suitable for the production of methanol. The influence of the high amount of hydrogen present in the COG on the process of dry reforming was studied, the most noticeable effect observed being the reverse water gas shift reaction. At 800 °C, this situation, together with the low conversions achieved, leads to the consumption of part of the hydrogen in the COG and to the production of water. As a consequence the resulting syngas has a high H_2/CO ratio and a low R parameter, which are inappropriate for methanol synthesis. As the temperature increases, the conversions become greater, reaching values of over 80% for methane and 95% for the carbon dioxide. Consequently water production decreases, until it completely disappears at 1000 °C, when the process proceeds at a low VHSV. This situation gives rise to a decrease in the H_2/CO ratio and an increase in the R parameter, making it possible to produce a syngas with values suitable for methanol production, i.e. a H_2/CO ratio of 2.2, an R parameter of 2.13 and high selectivity to H_2 (up to 90%). The influence of VHSV on the process is the reverse, since the conversions decrease and water production increases as VHSV rises. In this case, the H_2/CO ratio increases and the R parameter decreases, and as a result the values are too high and too low respectively for methanol production. Thus, it can be concluded that, at high temperatures (1000 °C) and with VHSVs no higher than 1.5 L g^{-1} h^{-1}, the activated carbon FY5 is a good catalyst for the dry reforming of COG as means of producing syngas for the production of methanol.

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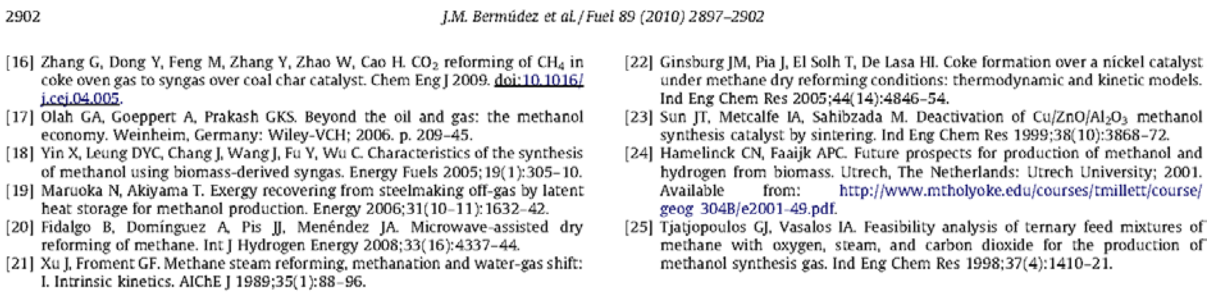

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Artículo 4

CO_2 reforming of coke oven gas over a Ni/γAl_2O_3 catalyst to produce syngas for methanol synthesis

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CO_2 reforming of coke oven gas over a Ni/γAl_2O_3 catalyst to produce syngas for methanol synthesis

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ABSTRACT

The CO_2 reforming of coke oven gases (COG) was carried out over a Ni/γAl_2O_3 catalyst in order to obtain a suitable syngas for methanol synthesis. The influence of different operating conditions, such as temperature and volumetric hourly space velocity (VHSV), was studied. It was found that the H_2 present in the feed gas promotes the Reverse Water Gas Shift reaction (RWGS), which produces water. Nevertheless, the Ni/γAl_2O_3 catalyst showed a high selectivity to the CO_2 reforming reaction and it was possible to avoid the RWGS under certain operating conditions. Moreover, a part of the reaction could take place via a different path (RWGS followed by the steam reforming of methane instead of the direct dry reforming of methane). The deactivation of the Ni/γAl_2O_3 catalyst was also studied. Both the methane and the carbon dioxide conversions remained steady for 50 h without showing any sign of deactivation. However, the sinterization of the nickel particles and the presence of carbon deposits seemed to indicate that the catalyst would eventually loose catalytic activity.

1. Introduction

Methanol is a raw material of primary importance for the chemical industry, for which there is a growing demand due mainly to its use in the production of biodiesel and as an alternative fuel [1–5]. Methanol is an excellent fuel in its own right or it can be blended with gasoline, although it has half the volumetric energy density of gasoline or diesel [1,3–5]. In addition, one of the most important attractions of methanol is that it can be used as a good hydrogen carrier, since it can be handled more easily and safely than raw hydrogen, as a direct fuel in some kinds of fuel cells (DMFC) or in internal combustion engines [1,3–6]. This gives methanol an important role to play in the emerging 'Hydrogen Economy'.

Nowadays, methanol is almost exclusively produced from synthesis gas [4,5], a raw material, consisting mainly of hydrogen and carbon monoxide, that is used in the large-scale production of hydrogen and a wide variety of organic products in industry [7,8]. Syngas is mainly produced from natural gas and oil, but increasing awareness about climate change and the emissions of greenhouse gases is promoting research into alternative processes for syngas production [7,9–11].

One of these alternative technologies is the CO_2 reforming of coke oven gas (COG). COG can be considered as a by-product from coking plants, consisting mainly of H_2 (~55–60%), CH_4 (~23–27%), CO (~5–8%) and N_2 (~3–5%) along with other hydrocarbons, H_2S and NH_3 in small proportions [12,13]. This gas is used as fuel in the coke ovens, but usually there is a surplus of gas which is used in other processes of the plant, or is simply burnt away in torches, giving rise to environmental problems, e.g. CO_2 emissions [13,14]. Only a few studies have focused on the production of syngas from COG by partial oxidation [12], steam reforming [15,16] or CO_2 reforming [13]. Dry reforming, or CO_2 reforming, offers certain advantages over the other methods, such us energy saving and CO_2 consumption. However, the most interesting characteristic of this alternative is the possibility of producing, in just one step and without the need for a conditioning stage, a syngas with a H_2/CO ratio close to 2, which is the most suitable ratio for methanol synthesis [9,17], provided that the process is carried out under stoichiometric conditions of CH_4 and CO_2 [13]. Furthermore, this method can be considered as a way of partially recycling CO_2 since it consumes, at least theoretically, half of the CO_2 produced when methanol is consumed (see Fig. 1). Another interesting aspect of the CO_2 reforming of COG is that the energy consumed by the endothermic reactions can be obtained from some of the exothermic processes that take place in the steelmaking plant. For instance, the blast furnace, which high temperature exhaust gases (1600 °C) could be used as heat source [18].

The dry reforming of methane is a catalytic process, and so a critical factor for its performance is the development of appropriate catalysts. A great deal of research has been focused in this direction over recent years. Nickel is commonly used in this reaction as active metal for the catalyst, due to its low cost and wide availability that make it a more preferable choice than other metals which have shown higher conversions and better resistance to

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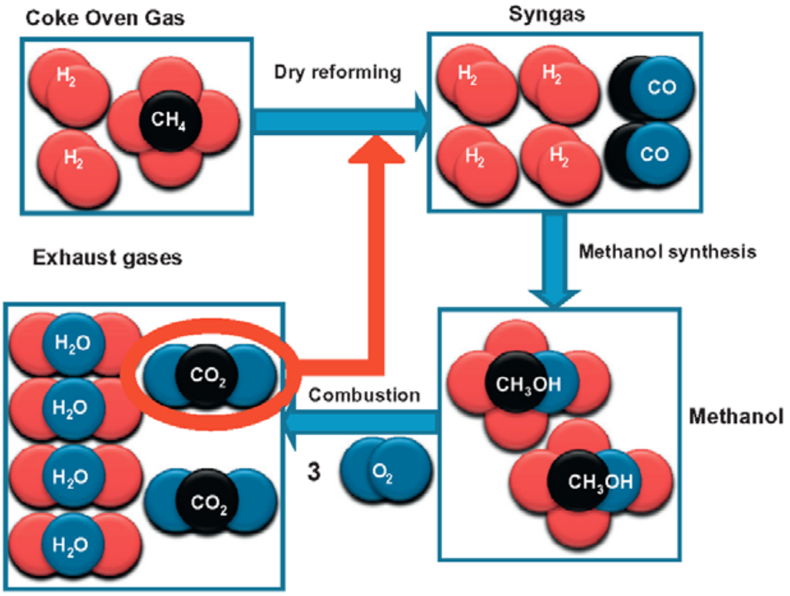

Fig. 1. CO_2 partial recycling scheme by means of the CO_2 reforming of COG for methanol production.

coke formation (like Rh, Pt, Ru or Ir) [19–24]. The choice of the support is also important in the preparation of a catalyst, because it can have a strong influence on the activity and deactivation of a catalyst [19–22,25]. A variety of materials have been tested as Ni supports in the reaction of dry reforming of CH_4, e.g. inorganic oxides [19,22] and carbon materials [20–22,25]. One of the most commonly used materials as support is Al_2O_3 (mainly α and γ species), due to its chemical and physical stability and high mechanical resistance [19,23,24].

The objective of this work is to gain further insight into the CO_2 reforming of COG over Ni/γAl_2O_3 in order to produce a syngas suitable for methanol production and to study the influence of different parameters (such us temperature, volumetric hourly space velocity and H_2 present in the feed) on the process, conversions and selectivity.

2. Experimental

2.1. Preparation and characterization of the Catalyst

Ni supported on a γAl_2O_3 catalyst (Ni/γAl_2O_3), containing 5 wt.% Ni, was prepared by the direct impregnation method using $Ni(NO_3)_2 \cdot 6H_2O$ as metal precursor. The characteristics of the γAl_2O_3 used as support have been described in previous works [26]. A weighed amount of nickel nitrate was dissolved in a beaker with distilled water. Once the salt was completely dissolved, the appropriate amount of support (γAl_2O_3) was added and then sonicated in an ultrasonic bath for 7 h. After that, the mixture was dried overnight at 100 °C. Finally, it was reduced at 400 °C in a flow of 100 mL/min of H_2 for 2 h.

The Ni content of the catalyst was analyzed using an AA-6300 Shimadzu spectrometer, in order to check the amount of Ni deposited on the catalyst. The analysis showed that the amount of Ni loaded was 4.20 wt.%.

The Ni/γAl_2O_3 species were determined by means of X-ray diffraction and the Ni particle size was evaluated by X-ray diffraction and Scherrer's equation.

The presence of carbonaceous deposits was determined by total organic carbon analysis, consisting in the IR measuring of the CO_2 formed in a catalytic oxidation at 900 °C, using a TOC V-CPH E200V instrument.

2.2. CO_2 reforming experiments

The CO_2 reforming of COG was carried out under atmospheric pressure in a fixed-bed quartz tube reactor which was heated up inside an electric furnace. The reaction temperature was monitored and controlled by means of a thermocouple located in the middle of the catalyst bed.

For comparative purposes, a test was carried out using a gaseous stream of CH_4 and CO_2 at a ratio of 1:1. For the rest of the experiments, H_2 was added in order to study its effect on the process of the CO_2 reforming of methane. This gas mixture gives way to a stream composed of 54% H_2, 23% CH_4 and 23% CO_2 (which will be referred to as gas ternary mixture, GTM), which keeps the H_2/CH_4 ratio of the COG (2–2.7) and the stoichiometric conditions of CH_4 and CO_2 for the dry reforming of the methane. The effect of the carbon monoxide present in the coke oven gas is outside the scope of this work and will be studied in due course.

Tests were performed at atmospheric pressure, at three different temperatures (800, 900 and 1000 °C) and at different volumetric hourly space velocities, VHSV (0.75–9.30 $L\,g^{-1}\,h^{-1}$) [13]. The gas product was collected in Tedlar® sample bags in the course of the experiment at different times. A condenser was used to collect water that had formed before it reached the bags. Before starting the reaction, the system was flushed with N_2 for 15 min at a flow rate of 60 mL/min under room temperature. Then, using the same N_2 flow rate, the reactor was heated up until the catalyst bed reached reaction temperature. At that point the N_2 flow was cut off and the reactant gases were introduced into the reactor to start the reaction. Samples of the outlet gases were analyzed in a Varian CP-3800 gas chromatograph.

In order to study the deactivation of the catalysts, two additional tests were carried out at 800 and 900 °C and 3.75 $L\,g^{-1}\,h^{-1}$

Table 1
Operating conditions of the experiments.

Temperature (°C)	$VHSV_{CH4}$ ($L g^{-1} h^{-1}$)	$VHSV_{total}$ ($L g^{-1} h^{-1}$)	Time (min)
800	0.16	0.75	360
800	0.51	2.25	360
800	0.84	3.75	360
800	0.84	3.75	3000[a]
800	1.38	6.15	360
800	1.80	8.00	360
800	2.09	9.30	360
900	0.16	0.75	360
900	0.84	3.75	3000[a]
900	2.09	9.30	360
1000	0.16	0.75	360

[a] Experiments carried out in the micro-reactor.

in a micro-reactor, consisting of a catalyst bed of diameter 10 mm and length 35 mm over a period of 50 h. Samples of the outlet gases were analyzed in an Agilent Technologies 3000A micro-gas chromatograph.

Table 1 summarizes the results of the experiments and the operating conditions.

The CH_4 and CO_2 conversions and selectivity to H_2 were calculated from the amount of water recovered and the product gaseous stream compositions, by means of an iterative method, based on the Newton method for nonlinear equations using Solver Microsoft Excel® tool and closing the mass balances to within a ±5% error margin. Selectivity to hydrogen gives an approximate idea of the amount of methane transformed into H_2 or into other species (such as light hydrocarbons, ⩾C2, or water). These parameters were calculated as follows:

$$CH_4 \text{ conversion, } \% = 100 \cdot (CH_{4\ in} - CH_{4\ out})/CH_{4\ in} \quad (Eq.1)$$

$$CO_2 \text{ conversion, } \% = 100 \cdot (CO_{2\ in} - CO_{2\ out})/CO_{2\ in} \quad (Eq.2)$$

$$H_2 \text{ selectivity, } \% = 100 \cdot (H_{2\ out} - H_{2\ in})/[2 \cdot (CH_{4\ in} - CH_{4\ out})] \quad (Eq.3)$$

where $CH_{4\ in}$, $CO_{2\ in}$ and $H_{2\ in}$, are moles of each gas at the inlet of the reactor and $CH_{4\ out}$, $CO_{2\ out}$ and $H_{2\ out}$ are moles of each gas at the outlet.

3. Results and discussion

3.1. Effect of the presence of H_2 in the feed gases

The results of the CO_2 reforming of methane (reaction 1) over the Ni catalyst are shown in Fig. 2. As can be seen, at 800 °C, working at atmospheric pressure, under stoichiometric conditions of methane and carbon dioxide and with a $VHSV_{CH4}$ of 0.16 L g^{-1} h^{-1} (0.32 L g^{-1} h^{-1} for the global feed) it is possible to achieve conversions of more than 90% over a period of 6 h for both gases.

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H = 247.3 \text{ kJ/mol} \quad (\text{reaction1})$$

When the process is carried out with COG, the high amount of hydrogen present in the feed can give rise to two different phenomena: (i) the equilibrium may be shifted to the side of the reactants (see reaction 1), resulting in lower CH_4 and CO_2 conversions, and (ii) the Reverse Water Gas Shift reaction (RWGS) (reaction 2) may have more influence on the process, leading to the increase in the conversion of CO_2, the production of water, the consumption of hydrogen and a decrease in the H_2/CO ratio and selectivity [27,28].

$$H_2 + CO_2 \leftrightarrow H_2O + CO \quad \Delta H = 41.2 \text{ kJ/mol} \quad (\text{reaction2})$$

The most important consequence of these two effects is the decrease in hydrogen production. Thus, as can be seen in Fig. 3, at 800 °C both phenomena take place when the GTM is used instead of methane, as a result of which changes in the conversions occur. The conversion of methane initially reaches 100%, but after a few minutes this drops to 87%, a value which is maintained throughout the experiment. This initial change in conversion is due to the amount of time necessary to reach the stationary state and to the reduction experienced by the catalyst in the presence of hydrogen, which will be discussed in Section 3.5. Compared with the dry reforming of methane, in the CO_2 reforming of GTM there is a decrease of approximately 6% in the conversion of methane. In the case of carbon dioxide, conversion is about 86% at the beginning but this gradually increases to 93%, a value which is maintained throughout the experiment and is practically the same as in the dry reforming of methane (Fig. 2). This suggests that the RWGS has the same influence on the process as the shift in the equilibrium. This is supported by the amount of water collected in the condenser. The water represents approximately 1 vol.% of the reaction products which indicates that about the 6% of the carbon dioxide has reacted through the RWGS. Also significant is the fact that the amount of water produced is very low, as water could be a problem in the synthesis of methanol, due to the deactivating effect which it has on the $Cu/ZnO/Al_2O_3$ catalyst used in this reaction [29]. The tiny amount of water produced in this experiment might be low enough to avoid this problem.

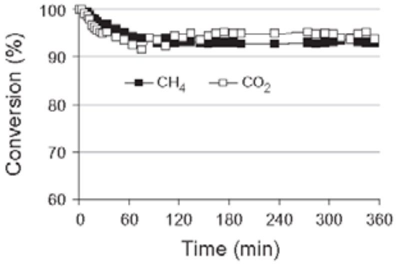

Fig. 2. CH_4 and CO_2 conversions in the CO_2 reforming of CH_4 (800 °C, CH_4/CO_2 = 1, $VHSV_{CH4}$ = 0.16 L g^{-1} h^{-1}, VHSV = 0.32 L g^{-1} h^{-1}, 1 atm).

3.2. Effect of temperature

Fig. 4 shows the results of the CO_2 reforming of GTM at 900 °C. As can be seen, both conversions increased with respect to the CO_2 reforming experiment of GTM at 800 °C (Fig. 3), a value of over 90% being retained throughout the experiment. Especially marked were the increase in methane conversion and the decrease in the production of water, to a value 3.5 times lower than in the experiment at 800 °C. These results suggest that the dry reforming reaction has been enhanced versus the RWGS reaction. This idea is

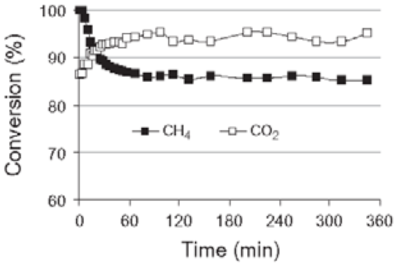

Fig. 3. CH_4 and CO_2 conversions in the CO_2 reforming of GTM (800 °C, CH_4/CO_2 = 1, $VHSV_{CH4}$ = 0.16 L g^{-1} h^{-1}, VHSV = 0.75 L g^{-1} h^{-1}, 1 atm).

thermodynamically consistent, since the dry reforming of methane reaction is more endothermic than RWGS and so any increase in temperature should enhance the former and will give rise to a higher degree of methane conversion, a greater production of hydrogen and a reduction in the amount of water produced. It is also possible that the water produced via the RWGS reaction reacts through the steam methane reaction (reaction 3) with the unreacted methane. However, this path is essentially the same as the one proposed for the dry reforming reaction because the sum of reactions 2 and 3 results in reaction 1.

$$H_2 + CO_2 \leftrightarrow H_2O + CO \quad \Delta H = 41.2\ \mathrm{kJ/mol} \qquad \text{(reaction2)}$$

$$H_2O + CH_4 \leftrightarrow 3H_2 + CO \quad \Delta H = 206.1\ \mathrm{kJ/mol} \qquad \text{(reaction3)}$$

$$CH_4 + CO_2 \leftrightarrow H_2 + CO \quad \Delta H = 247.3\ \mathrm{kJ/mol} \qquad \text{(reaction1)}$$

Fig. 5 shows the results of the test carried out at 1000 °C. If these results are compared with those shown in Figs. 3 and 4, it can be seen that, as the temperature increases, the conversions of methane and carbon dioxide also increase, achieving values of 100%. Interestingly after the experiment no water was found in the condenser. Therefore, by working at this temperature it is possible to avoid the RWGS and so maximize hydrogen production and selectivity. Similar results have also been achieved with other catalysts, such us activated carbon [13].

3.3. *Effect of the volumetric hourly space velocity (VHSV)*

The effect of the VHSV on the process was also studied at 800 °C and 900 °C. The procedure selected was to increase the VHSV at 800 °C until the conversion of methane (which was always lower than the conversion of carbon dioxide) reached values below 70%. The same VHSV was then used at 900 °C, in order to see if the influence of this parameter is affected by the change in temperature. The results of these series of experiments are presented in Figs. 6–8.

As can be seen, the CH_4 and CO_2 conversions were affected by the VHSV, but the conversion of methane decreased sharply. A possible explanation for this could be the overlapping of two different effects: the decrease in CH_4 and CO_2 reacted via the dry reforming reaction and the increase in CO_2 reacted via the RWGS reaction. The decreases in conversion in both compounds due to a worsening of the dry reforming reaction are similar, but the increase in the amount of carbon dioxide reacted via the RWGS reaction, leads to the divergence in the decreasing conversions. This result, presented in Fig. 7, suggests that the RWGS is enhanced as the VHSV is increased. This could be due to the rise in CO_2 concentration inside the reactor, since, due to the high amount of H_2 present, the CO_2 could be the species which limits the RWGS reaction. High conversions of CO_2 are therefore necessary to avoid this side reaction. Another possible explanation is that the RWGS could be a quicker reaction than dry reforming, so it is more far-reaching. Some of the water produced then reacts with the methane through the steam reforming reaction. As the VHSV increases, the RWGS reaction proceeds whereas the steam reforming reaction does not have sufficient time to react in the same extent. This supports the idea that the second path (sum of reactions 2 and 3 to give rise to reaction 1) is the principal one.

The results obtained by increasing the VHSV at 900 °C are shown in Fig. 8. As can be seen, at this temperature the variation in conversions is much lower than at 800 °C. The conversion of carbon dioxide shows the same value while the decrease in the conversion of methane is about 4%. Also worthy of note is the fact that the increase in the water production is really low. This is due either to an improvement of the first path (direct dry reforming of the methane present in the feed) over the second path (sum of reactions 2 and 3 to give rise to reaction 1) or to an improvement of the reaction rate of the steam reforming, resulting in higher conversions in shorter periods of time. Thus, it can be concluded that temperature has a greater effect on the process than the VHSV.

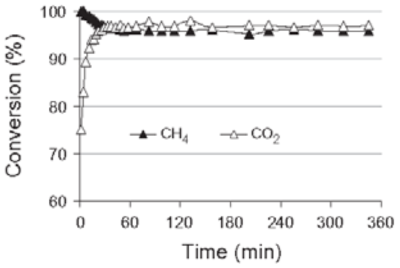

Fig. 4. CH_4 and CO_2 conversions in the CO_2 reforming of GTM (900 °C, $CH_4/CO_2 = 1$, $VHSV_{CH4} = 0.16\ L\,g^{-1}\,h^{-1}$, $VHSV = 0.75\ L\,g^{-1}\,h^{-1}$, 1 atm).

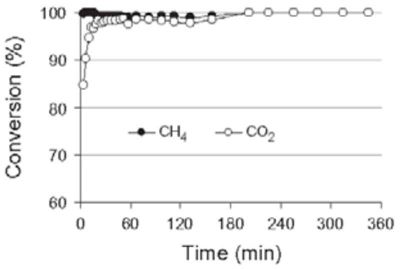

Fig. 5. CH_4 and CO_2 conversions in the CO_2 reforming of GTM (1000 °C, $CH_4/CO_2 = 1$, $VHSV_{CH4} = 0.16\ L\,g^{-1}\,h^{-1}$, $VHSV = 0.75\ L\,g^{-1}\,h^{-1}$, 1 atm).

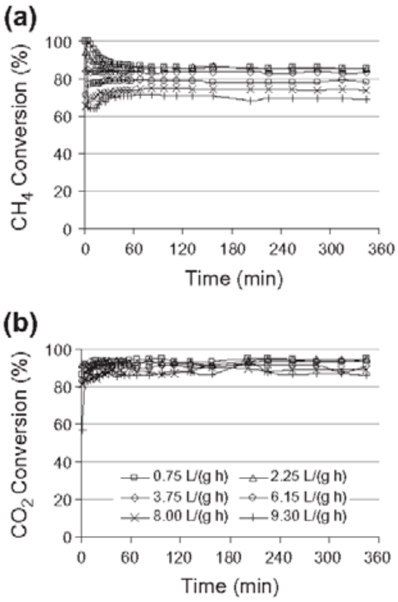

Fig. 6. Influence of the VHSV on the (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM (800 °C, $CH_4/CO_2 = 1$, 1 atm).

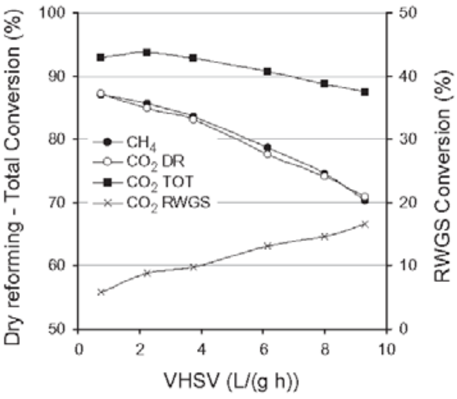

Fig. 7. Influence of the VHSV on the conversions of methane and carbon dioxide through the Reverse Water Gas Shift reaction (RWGS), the Dry Reforming reaction (DR) and total conversion (TOT) (800 °C, $CH_4/CO_2 = 1$, 1 atm).

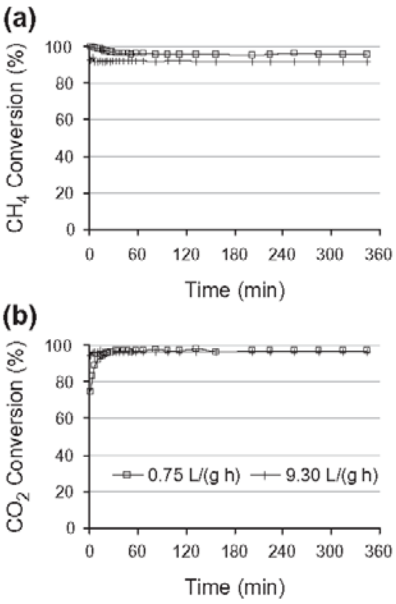

Fig. 8. Influence of the VHSV on the (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM (900 °C, $CH_4/CO_2 = 1$, 1 atm).

3.4. Analysis of the syngas

The application for which the synthesis gas is intended will determine the different proportions of hydrogen and carbon monoxide needed. To produce methanol, it is necessary to have a H_2/CO ratio of 2. However, the parameter most commonly used to study the suitability of the syngas for this purpose is the *R* parameter (Eq. (4)), which expresses the relation between the concentrations of hydrogen, carbon monoxide and carbon dioxide [17,30].

$$R = (H_2 - CO_2)/(CO + CO_2) \qquad \text{(Eq.4)}$$

In this case, it is necessary to take into account carbon dioxide, because the synthesis of methanol takes place through two different reactions (reactions 4 and 5) and, as can be seen, carbon dioxide appears in reaction 5 as one of the reactants. Moreover, carbon dioxide acts as a promoter of reaction 4 and helps to maintain the activity of the catalyst [17].

$$2H_2 + CO \leftrightarrow CH_3OH \quad \Delta H = -90.9\ \text{kJ/mol} \qquad \text{(reaction4)}$$

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H = -41.1\ \text{kJ/mol} \qquad \text{(reaction5)}$$

In order to optimize the process, the *R* parameter must have a value equal to or slightly higher than 2 [17,30]. If *R* takes on values lower than 2, there is an increase in the by-products formed during the synthesis of methanol. On the other hand, if *R* takes on values much higher than 2, it is necessary to increase the recycling rate due to the excess of hydrogen, which leads to a less efficient and more expensive process [30].

Table 2 summarizes both the H_2/CO ratio and *R* parameter for the different tests carried out for GTM reforming at different temperatures and VHSV.

As can be seen, in all the experiments the H_2/CO ratio takes on values over 2. It is noticeable that the temperature has a very slight influence on this parameter (less than 0.5% of variation from 800 °C to 1000 °C) while the VHSV has a grater influence (about 5% of variation from 0.75 to 9.3 $L\,g^{-1}\,h^{-1}$). This suggests that, in order to obtain a suitable synthesis gas, VHSV is a more critical factor than temperature. As the VHSV increases, the H_2/CO ratio increases because the conversions of methane and carbon dioxide decrease. This reinforces the influence of the high amount of H_2 present in the feed upon this parameter.

Temperature and VHSV affect the *R* parameter in different ways. When the temperature increases, the *R* parameter also increases whereas when the VHSV increases, the *R* parameter falls. This behavior can be explained in terms of variations of both conversions. When the temperature increases, the rise in methane conversion is greater than the rise in carbon dioxide conversion. This results in a greater increase in hydrogen concentration versus the increase in the carbon monoxide concentration. In the case of VHSV, the decrease in methane conversion is greater than the decrease in carbon dioxide conversion. This leads to a greater drop in the concentration of hydrogen versus the drop in carbon monoxide concentration. In all of the experiments, the *R* parameter takes on values higher than 2, and in some cases higher than 2.2. This problem could probably be corrected if carbon monoxide were added to the feed (since in COG there is 5–8% of CO which has not been added to the GTM).

As explained above, selectivity can be used to determine how much of the hydrogen present in the CH_4 is transformed into H_2 or other species. Table 2 also shows the selectivity to H_2 in the different experiments. The results lower than 100% are due to the production of water, since no hydrocarbons other than CH_4 (e.g. C_2H_2 and C_2H_6) were detected. The best results were obtained when the temperature was increased, a selectivity value of 100% being achieved at 1000 °C. This also shows that the RWGS reaction

Table 2
H_2/CO ratio, *R* parameter and selectivity in the CO_2 reforming of GTM at different temperatures and VHSV.

Temperature(°C)	VHSV ($L\,g^{-1}\,h^{-1}$)	H_2/CO (adim.)	*R* (adim.)	Selectivity (%)
800	0.75	2.25 ± 0.01	2.176 ± 0.004	91
800	2.25	2.29 ± 0.02	2.173 ± 0.006	83
800	3.75	2.29 ± 0.02	2.161 ± 0.006	83
800	6.15	2.31 ± 0.01	2.140 ± 0.005	80
800	8.00	2.33 ± 0.02	2.117 ± 0.007	78
800	9.30	2.35 ± 0.02	2.093 ± 0.008	75
900	0.75	2.24 ± 0.02	2.208 ± 0.007	94
900	9.30	2.27 ± 0.01	2.207 ± 0.001	90
1000	0.75	2.24 ± 0.01	2.228 ± 0.001	100

is handicapped against dry reforming reaction when the temperature is increased, since a lower percentage of hydrogen from the reacted methane is transformed into water. However, when the VHSV increases, the opposite occurs. In this case, selectivity decreases as VHSV increases, showing that the RWGS reaction is favored against the dry reforming reaction when VHSV is increased.

3.5. Deactivation of the catalyst

Figs. 9 and 10 show the results of the CO_2 reforming of GTM at 800 and 900 °C during 50 h at a medium total VHSV ($3.75\ \text{L g}^{-1}\ \text{h}^{-1}$). As can be seen, the catalyst did not show signs of deactivation in any of the experiments, since the conversions of methane and carbon dioxide were steady over the reaction time. Two main effects may lead to deactivation in the dry reforming of methane: (i) carbon deposits from the decomposition of methane may block the access of the reactants to the active centers [31]; and (ii) the sintering of nickel particles on the catalyst surface. The second effect has only a slight influence on the activity of the catalyst, compared to the carbon deposition, but it may nevertheless promote the coking effect [32,33].

The XRD patterns of the catalyst at different stages of the experiments revealed the species present in the catalyst. These XRD spectrums were obtained at the beginning of the reaction, when the conversions reached a constant value (after 60 min at 800 °C and 30 min at 900 °C) and at the end of the experiments (50 h). The diffractograms obtained for the catalyst used in the experiment at 900 °C are shown in Fig. 11. As can be seen, at the beginning of the experiment, when the catalyst has been heated in an inert atmosphere, the reduced nickel from the $Ni(NO_3)_2$ deposited on the γAl_2O_3 reacts with the latter to give rise to a spinel ($NiAl_2O_4$). After several minutes under the reaction atmosphere, which is strongly reducing, this spinel is reduced to Ni^0, and from this moment the conversions remain stable throughout the experiment.

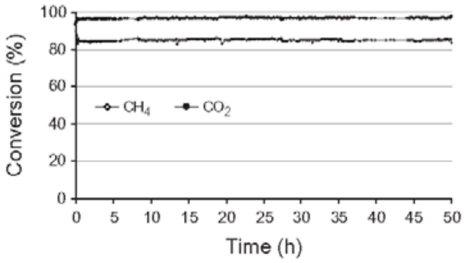

Fig. 9. CH_4 and CO_2 conversions in the CO_2 reforming of GTM for 50 h (800 °C, $CH_4/CO_2 = 1$, $VHSV_{CH4} = 0.84\ \text{L g}^{-1}\ \text{h}^{-1}$, $VHSV = 3.75\ \text{L g}^{-1}\ \text{h}^{-1}$, 1 atm).

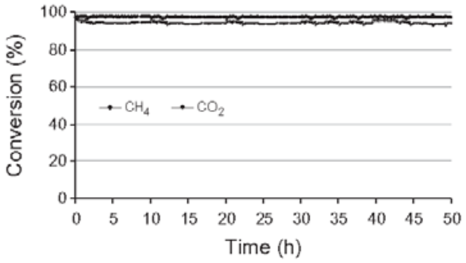

Fig. 10. CH_4 and CO_2 conversions in the CO_2 reforming of GTM for 50 h (900 °C, $CH_4/CO_2 = 1$, $VHSV_{CH4} = 0.84\ \text{L g}^{-1}\ \text{h}^{-1}$, $VHSV = 3.75\ \text{L g}^{-1}\ \text{h}^{-1}$, 1 atm).

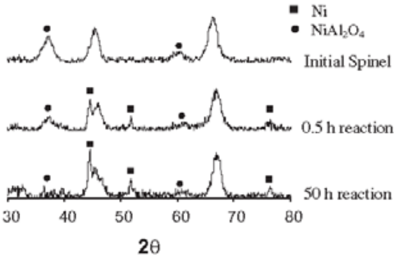

Fig. 11. XRD patterns of the catalyst at the beginning of the experiment (initial spinel), after 30 min in the reaction stream (0.5 h) and at the end of the experiment (50 h).

Table 3
TOC analysis results from the experiments carried out for 50 h.

Temperature (°C)	TC (mg C/g cat)	IC (mg C/g cat)	TOC (mg C/g cat)
800	1.0	1.0	0.0
900	4.4	1.0	3.4

After 50 h the XRD spectrum shows the same species as after 30 min, which may explain the steady conversions obtained throughout the experiment.

After the experiments, the catalysts were again subjected to XRD to compare the Ni^0 particle sizes. The Ni^0 particle size has increased from around 17 nm to around 24 nm after 50 h of reaction at both temperatures, which qualitatively indicates that the sintering process is taking place and that coke deposition is favored as time passes. In order to study the presence of these carbon deposits, the catalysts used in the experiments were subjected to total organic carbon (TOC) analysis. The results, which are summarized in Table 3, shows that the coking effect is also taking place. In the case of the experiment carried out at 800 °C, 1 mg of carbon/g of catalyst was found compared to 4.4 mg of carbon/g of catalyst at 900 °C. This shows that not only is the coking effect taking place but also that temperature has a critical influence on the process, since at 900 °C the amount of carbon is four times higher than at 800 °C. It is also noticeable that, at 800 °C all the carbon deposited on the catalyst is inorganic (IC), probably nickel carbide, since it has been previously reported that this species may appear in such processes [34]. Nevertheless, when the reaction was carried out at 900 °C, the same amount of IC was found, while the rest of the carbon deposited (3.4 mg C/g catalyst) was organic carbon (TOC), probably deposited as amorphous or graphitic carbon [34].

To conclude, although after 50 h of reaction the conversions of methane and carbon dioxide still show high and stable values, if the reaction goes on for a longer period of time, the catalyst may eventually lose its catalytic activity.

4. Conclusions

Upgrading coke oven gases via CO_2 reforming followed by methanol synthesis, could be an effective way to partially recycle the CO_2 produced when methanol is burnt.

The hydrogen present in the COG shifts the equilibrium to the reactants (reducing the conversions of methane and carbon dioxide) and promotes the reverse water gas shift reaction, with part of the hydrogen being consumed to produce water. Nevertheless the $Ni/\gamma Al_2O_3$ catalyst shows a high selectivity to the CO_2 reforming, which minimizes this problem. However, as the reaction temperature increases, it is possible to increase the conversions of methane and carbon dioxide and so reduce the amount of water produced, it being possible to achieve conversions of 100% for both gases.

When the volumetric hourly space velocity is increased, the conversions of both gases decrease. In this case the decrease in the conversion of methane is greater than that of the carbon dioxide. This could be due to a worsening of the dry reforming reaction accompanied by an enhancement of the RWGS reaction. Another possible explanation is that part of the process takes place through a different path, composed of the RWGS reaction followed by the steam reforming of the methane. Via this path, the RWGS takes place completely, while the steam reforming does not has sufficient time to react in the same extent as the VHSV is increased.

Whereas the H_2/CO ratio of the syngas is almost unaffected by the variation in temperature, it is affected by VHSV, giving rise to an increase in its values. In the case of the *R* parameter, a rise in temperature leads to an increase in the *R* parameter values whereas an increase in the VHSV causes the *R* values to fall. Another important parameter of the process is selectivity, which has also been shown to be affected by temperature and VHSV. The selectivity values increase with temperature (to values of 100% at 1000 °C) while selectivity falls as VHSV is increased.

After 50 h there were no signs of deactivation in the catalyst. Nevertheless, analysis of the used catalyst revealed that both sintering and coke deposition had taken place. Therefore, deactivation may eventually take place if the reaction proceeds beyond 50 h.

Acknowledgments

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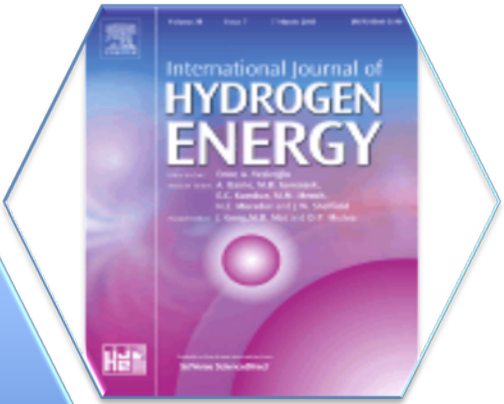

Artículo 5

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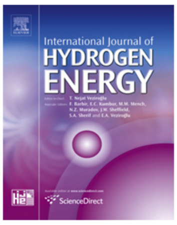

Syngas from CO_2 reforming of coke oven gas: Synergetic effect of activated carbon/Ni–γAl_2O_3 catalyst

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A B S T R A C T

The CO_2 reforming of coke oven gas for the production of synthesis gas has been studied over an activated carbon, an in-lab prepared Ni/Al_2O_3 catalyst and physical mixtures of both materials in different proportions (AC + Ni) at 800 °C. It was found that there are two possible coexisting reaction pathways: the direct dry reforming of methane (decomposition of methane followed by gasification of the carbon deposits) and the reverse water gas shift reaction followed by the steam reforming of methane. If the process is carried out with the physical mixtures AC + Ni, there is a synergetic effect between both materials. The experimental conversions are higher than the conversions predicted by the law of mixtures, whereas the production of water is lower, resulting in a higher selectivity. The mixtures also showed a lower loss of porosity than when the activated carbon and the in-lab prepared Ni/Al_2O_3 were used individually. Therefore, the combination of these materials may produce catalysts that are more resistant to deactivation. The synthesis gas obtained was analyzed and it was found suitable for the production of methanol.

1. Introduction

The CO_2 reforming of methane (reaction 1), or dry reforming, has been shown to be a promising alternative to steam reforming in recent years [1–4]. This is mainly due to environmental factors, since in the CO_2 reforming two greenhouse gases (methane and carbon dioxide) are consumed, giving rise to synthesis gas, a raw material consisting mainly of H_2 and CO, which is widely used in the chemical industry [3,5]. This process is also attractive because it produces a synthesis gas with a low H_2/CO ratio, suitable for the production of higher hydrocarbons and oxygenated derivatives [4].

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H = 247 kJ/mol \qquad \text{(reaction 1)}$$

The vast majority of the studies in this area have focused on the dry reforming of just methane alone, since it is the main component of natural gas, but there are other methane sources which could be adapted for this reaction. An interesting example is that of coke oven gas (COG) [6–9]. COG can be considered as a byproduct of coking plants, which mainly consists of H_2 (~55–60%), CH_4 (~23–27%), CO (~5–8%) and N_2 (~3–5%) along with other hydrocarbons, H_2S and NH_3 in small proportions [6,10]. COG is mostly used as fuel in the coking plant or in the associated steel industry, but sometimes it is produced in excess. This situation gives rise to environmental problems, in the form of greenhouse gases emissions [6,11]. When this gas is upgraded via CO_2 reforming under stoichiometric conditions of methane and carbon dioxide, it is possible to obtain a syngas with a H_2/CO ratio close to 2, which is the ratio suitable for methanol synthesis [12]. This process can be considered as a partial recycling of carbon dioxide, since half of the carbon dioxide produced in the combustion of the methanol is consumed [6].

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Research efforts have so far been focused on the development of catalysts suitable for the process, since the most important drawback of the dry reforming of methane is that there are no commercial catalysts able to resist deactivation caused by carbon deposition [1,3,13–15]. Almost all of the metals in Group VIII have been tested over different supports, resulting in catalysts with a good catalytic activity, although nickel has captured most attention on this matter [13,14,16,17]. Nickel is more susceptible to deactivation by carbon deposits than noble metals, but its low cost and high availability compensate for this drawback [13,14]. The support used also exerts great influence on the catalytic activity and deactivation of the catalyst, so different materials have been tested as Ni supports for the CO_2 reforming of methane, e.g. inorganic oxides or carbon materials [13–15]. Moreover, carbon materials, especially activated carbons, have been successfully used as catalysts in their own right in methane reforming, offering advantages such as low cost, a high mechanical resistance, a high surface area, the possibility of modifying pore size distribution, good reductive properties and the possibility of easily modifying surface chemistry [18,19]. In addition, some carbon materials can be heated by microwave energy, giving rise to hot spots (or microplasmas) which improve their catalytic activity [20,21]. Furthermore, it has been reported that mixtures of activated carbon with nickel-based catalysts can give rise to a synergetic effect in the dry reforming of methane [22]. In the case of COG, there are a few works which have studied the process using carbons or Ni/Al_2O_3 as catalyst [6,7,9,23].

The aim of the present work is to study the catalytic performance of different mixtures of an activated carbon and an in-lab prepared Ni/Al_2O_3 catalyst in the CO_2 reforming of coke oven gas, in an effort to determine whether the synergetic effect observed between both fractions in the CO_2 reforming of CH_4 also takes place when coke oven gas is used. Although this synergetic effect has been proved in the case of the dry reforming of methane [22], it has never been studied with COG. In this case, the presence in the feeding gases of two reaction products (H_2 and CO) may promote other reactions or change the conversions, having an effect on this synergetic effect. Thus, the influence of composition of COG has been studied. The possibility of using the resulting synthesis gas for the production of methanol has also been considered.

2. Experimental

2.1. Preparation and characterization of the catalyst

A series of physical mixtures of grains (0.5–2 mm) of a commercial activated carbon FY5 (supplied by CPL Carbon Link) and cylindrical pellets (2 mm in diameter and 3 mm in height) of an in-lab prepared Ni/Al_2O_3 were used as catalyst. The catalysts composed exclusively of FY5 or exclusively of Ni/Al_2O_3 were labeled 100AC and 100Ni respectively, while the mixtures of both these materials were labeled as XXAC/YYNi, where XX and YY are the weight percentages of the activated carbon and Ni/Al_2O_3 respectively.

The main chemical characteristics of the activated carbon FY5 can be found elsewhere [15]. Proximate analysis (moisture, ash and volatile matter content) and elemental analysis (C, H, O, N, S) were carried out in a LECO TGA-601 thermo-balance and in a LECO CNHS-932 apparatus, respectively. The oxygen content was calculated by difference. Textural characterization was carried out by means of N_2 adsorption–desorption isotherms at −196 °C in the pressure range of $2\cdot10^{-6}$–1 bar in a Micromeritics Tristar 3000. The Dubinin–Raduskevich method and BET equation were applied to the N_2 adsorption isotherms in order to determine the volume of micropores (V_{mic}) and BET surface area (S_{BET}), respectively. The total pore volume (V_t), i.e., the contribution of mesopores and micropores, was calculated from the quantity adsorbed at the saturation point of the N_2 adsorption–desorption isotherms, in accordance with the Gurvistsh rule.

The Ni/Al_2O_3 pellets were prepared in the lab as follows: a weighed amount of nickel nitrate was dissolved in distilled water and then the appropriate amount of γAl_2O_3 (commercial pellets provided by Alfa Aesar GmbH & Co) was added and sonicated for 7 h in an ultrasonic bath. The mixture was then dried overnight at 100 °C. Finally, it was reduced at 400 °C in a flow of H_2 for 2 h. The Ni content of the catalyst was analyzed using an AA-6300 Shimadzu spectrometer, which showed the amount of Ni loaded to be 4.20 wt. %. The characterization of the Ni/Al_2O_3 has been described in detail in previous works of this group [22].

2.2. CO_2 reforming experiments

The CO_2 reforming experiments were conducted in a fixed-bed quartz tube reactor heated up by an electric furnace. The reaction temperature was monitored and controlled in the middle of the catalyst bed using a thermocouple.

The experiments were carried out in a gaseous stream composed of 54% H_2, 23% CH_4 and 23% CO_2 (which will be referred to as gas ternary mixture, GTM). This mixture maintains the H_2/CH_4 ratio of the COG and ensures the stoichiometric conditions of CH_4 and CO_2 for the dry reforming of the methane. The effect of the carbon monoxide present in the coke oven gas was also studied by adding it to the gas feed. This results in a mixture (which will be referred to as gas quaternary mixture, GQM) composed of 52% H_2, 21% CH_4, 21% CO_2 and 6% CO, which also maintains the $H_2/CH_4/CO$ ratio of the coke oven gas and the stoichiometric conditions of CH_4 and CO_2 for the dry reforming of methane.

Tests were performed at atmospheric pressure, 800 °C and at two different volumetric hourly space velocities, VHSV (1.00 and 3.75 L g^{-1} h^{-1}). Before the reaction, the system was drained with N_2 for 15 min at a flow rate of 60 mL/min under room temperature. Then it was heated up to the reaction temperature. Once at 800 °C, the N_2 flow was cut off and the reactant gases were introduced to start the reaction. A condenser was placed at the outlet of reactor in order to collect the water produced in the experiments. The gaseous products were analyzed in an Agilent Technologies 3000A micro gas chromatograph.

With the water recovered and the product gaseous stream compositions, the CH_4 and CO_2 conversions were calculated using an iterative method and closing the mass balances to within a ±5% margin of error. These parameters were calculated as follows:

$$CH_4\text{conversion}, \% = 100 \cdot \frac{(CH_{4_{in}} - CH_{4_{out}})}{CH_{4_{in}}} \tag{1}$$

$$CO_2\text{conversion}, \% = 100 \cdot \frac{(CO_{2_{in}} - CO_{2_{out}})}{CO_{2_{in}}} \tag{2}$$

$$H_2\text{selectivity}, \% = 100 \cdot \frac{(H_{2_{out}} - H_{2_{in}})}{(2 \cdot (CH_{4_{in}} - CH_{4_{out}}))} \tag{3}$$

where $CH_{4\ in}$, $CO_{2\ in}$ and $H_{2\ in}$, are moles of each gas at the inlet of the reactor and $CH_{4\ out}$, $CO_{2\ out}$ and $H_{2\ out}$ are moles of each gas at the outlet.

3. Results and discussion

The results of the CO_2 reforming of GTM experiments conducted at 800 °C and a total VHSV of 1 L g^{-1} h^{-1} at 800 °C are shown in Fig. 1.

In all of the experiments, the conversion of methane initially achieved its highest values. Then, when the catalyst contained Ni/Al_2O_3, it quickly decreased for a period of approximately 60 min. This behavior is the consequence the Ni/Al_2O_3 undergoing a reduction process. When the catalyst is heated up under a N_2 atmosphere, the Ni and the Al_2O_3 interact to give a spinel ($NiAl_2O_4$). Once the reaction begins, the spinel is reduced to Ni^0 under the strongly reducing atmosphere of the reaction. This process, which yields very small Ni^0 particles, has been described in detail in previous works [22].

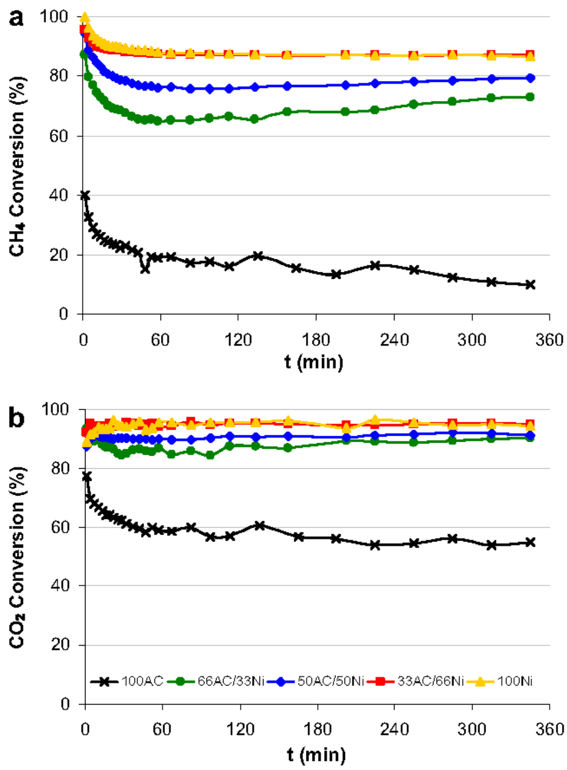

Fig. 1 – (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM with different mixtures used as catalysts (800 °C, CH_4/CO_2 = 1:1, 1 atm).

After this, the 100Ni catalyst shows stable conversions (about 87% for methane and 93% for carbon dioxide) throughout the experiment while the conversions with the 100AC catalyst continuously decrease (from 25% to 10% in the case of methane and from 65% to 55% in the case of carbon dioxide). What is more, when the 100Ni catalyst is used, a small amount of water is produced (approximately 1% vol. of the products) while with the 100AC catalyst a much higher amount of water remains in the condenser (approximately 10% vol. of the products). The mechanism proposed to describe the dry reforming of methane is the decomposition of methane (reaction 2) to produce hydrogen and carbon deposits followed by the gasification of these deposits with carbon dioxide due to the Boudouard equilibrium (reaction 3).

$$CH_4 \leftrightarrow 2H_2 + C \quad \Delta H = 75 kJ/mol \tag{reaction 2}$$

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H = 172 kJ/mol \tag{reaction 3}$$

However in the case of the CO_2 reforming of the coke oven gas, the presence of water after the experiments, suggests that a different mechanism is accompanying that of the dry reforming. This second probable mechanism is the reverse water gas shift reaction (RWGS, reaction 4) followed by steam reforming (reaction 5).

$$H_2 + CO_2 \leftrightarrow H_2O + CO \quad \Delta H = 41 kJ/mol \tag{reaction 4}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad \Delta H = 206 kJ/mol \tag{reaction 5}$$

Finding the preferential mechanism is not straightforward, since the combination of so many different reactions makes this very difficult. Nevertheless, the smaller amount of water obtained when the 100Ni catalyst is used suggests that this catalyst is able to transform, via steam reforming, almost all the water that is produced through the RWG, whereas the 100AC catalyst is unable to do this.

The mixtures show a different behavior. When the mixtures are used, the conversions seem to rise during the experiment, especially that of methane. This phenomenon appears to be more pronounced as the percentage of activated carbon present in the catalyst increases. This situation could be a consequence of the synergetic effect that these mixtures show in the dry reforming of methane [22]. This effect can be observed in the closeness of the conversions achieved by the mixtures to those of 100Ni. Even when the highest proportion of activated carbon is present in the catalyst, the conversions are closer to the conversions achieved with 100Ni than with 100AC. This phenomenon is especially accentuated in the case of the 33AC/67Ni catalyst. This catalyst reaches almost the same values as 100Ni for both methane and carbon dioxide conversions. The synergetic effect can be clearly observed in Fig. 2. Here, the theoretical conversions predicted by the law of mixtures (continuous line) are plotted against the experimental conversions (squares) after 6 h of reaction. As can be seen, the experimental conversions achieved with the mixtures are much better than the theoretically predicted ones. This means that the loss of catalytic activity due to the replacement of the Ni

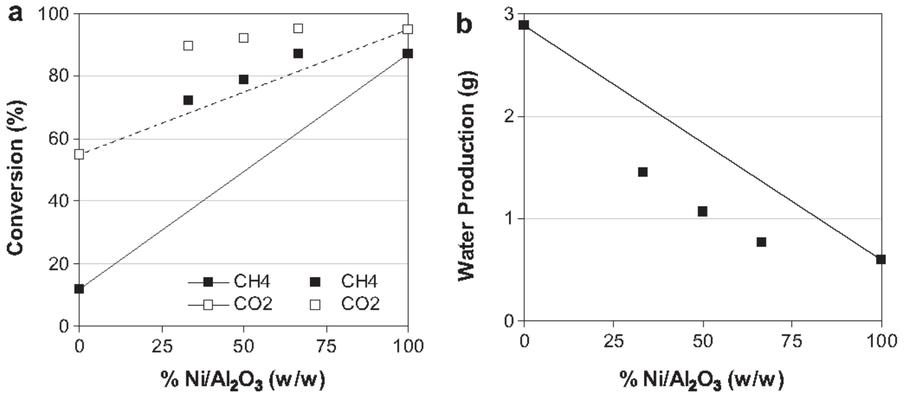

Fig. 2 – Comparison of the results predicted by the law of mixtures (continuous line) with those achieved in the experiments (squares) for the: (a) conversions of CH_4 and CO_2; and (b) water production, after 6 h of reaction in the CO_2 reforming of GTM.

catalyst (much more active than the activated carbon) by the activated carbon is not as great as one would have expected. This synergetic effect has interesting economic implications in this kind of processes, since the replacement of part of the expensive catalyst (Ni/Al_2O_3) by a cheaper material (activated carbon or other carbon materials) while at the same time achieving almost the same conversions could lead to lower process costs.

If the same analysis is applied to the production of water, it can be seen that the synergetic effect not only affects the direct dry reforming mechanism [22], but also the alternative mechanism, i.e., the RWGS followed by steam reforming. Fig. 2 shows the amount of water collected in the condenser after 6 h of reaction with the different catalysts. The continuous line represents the predicted amount of water by the law of mixtures and the squares the experimental results. As can be seen, when the mixtures are used, the amount of water produced is less than the theoretically predicted amount. This could mean either that less water is produced through the RWGS or that more water reacts through the steam reforming reaction. Either way, the most important conclusion from this is that the mixtures are able to increase the conversions and decrease the formation of byproducts such as water.

In order to study the presence of this synergetic effect with higher flows and its long term persistence, a series of experiments was carried out at 800 °C and at 3.75 L g^{-1} h^{-1} of VHSV for 50 h with the same catalysts. The results are shown in Fig. 3.

These results confirm the presence of the synergetic effect. Working at a VHSV of 3.75 L g^{-1} h^{-1}, the activated carbon appears to be inactive in the dry reforming or the steam reforming reactions. Almost none of the methane is transformed and all of the carbon dioxide reacts through the RWGS, as the amount of water collected in the condenser indicates. In the case of the Ni catalyst, the conversion of methane drops slightly compared to the experiments carried out at 1.00 L g^{-1} h^{-1}. However, it is important to point out that, at the end of the 50 h, the catalysts with 50% or more of Ni/Al_2O_3 achieved practically the same conversion of methane (approximately 4% difference between the highest value and the lowest value). In the case of the conversion of carbon dioxide the results were similar to the ones achieved working at a 1.00 L g^{1} h^{-1}. In addition, the conversion of CO_2 was practically the same for all the mixtures and for the 100Ni catalyst (about 5% difference between the highest value and the lowest value). When the mixtures are used as catalyst, again it is possible to appreciate that the conversions of both

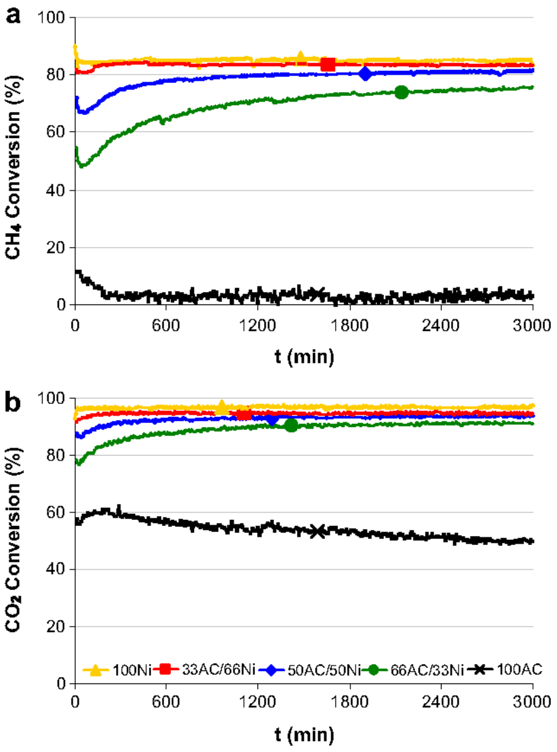

Fig. 3 – (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM with the different mixtures used as catalysts during 50 h of reaction (800 °C, CH_4/CO_2 = 1:1, $VHSV_{tot}$ = 3.75 L g^{-1} h^{-1}, 1 atm).

gases are nearer to the conversions achieved with the 100Ni catalyst than to the conversions achieved with the 100AC catalyst. From Fig. 3 it can also be seen that when the mixtures are used as catalysts, the conversions, and therefore the synergetic effect, continuously improve throughout the entire experiment. This phenomenon is specially marked in the case of the 67AC/33Ni catalyst, with conversions of just 10% and 5% lower for methane and carbon dioxide respectively than in the case of the 100Ni catalyst after 50 h Fig. 4 compares, after six and 50 h of reaction, the experimental and the theoretically predicted values by the law of mixtures for methane and carbon dioxide conversions and water production.

As can be seen, after 6 h and after 50 h the experimental conversions are above the predicted conversions, confirming the presence of the synergetic effect at a high VHSV and its long term persistence. After 6 h, the differences between the experimental and the predicted conversions are lower than in the case of the experiments carried out al 1.00 L g^{-1} h^{-1} of VHSV. But after 50 h, the differences between the experimental and predicted conversions increase, reinforcing the idea that the synergetic effect improves as the experiment proceeds.

Variation in the porous textural properties during the experiments was also studied. In previous works it was found that, in the case of activated carbons, the CO_2 reforming of CH_4 occurs mainly in the micropores [18]. Thus, a large volume of micropores is necessary to obtain good CH_4 and CO_2 conversions. During the reaction, CH_4 decomposition leads to the blockage of the micropores. This process, known as Chemical Vapor Deposition (CVD) [24], is one of the main reasons for the loss of catalytic activity in the activated carbons. The results for the porous textural properties of the activated carbon and the Ni/Al_2O_3 catalyst before and after the experiments are shown in Table 1. Analysis of these results provides further evidence of the synergetic effect that take place between both materials. When the activated carbon or the Ni/Al_2O_3 are used alone, they experience a decrease in their porous textural properties, mainly due to the carbon deposits. This decrease is especially pronounced in the case of the activated carbon, which after the experiment of 50 h and at a VHSV of 3.75 L g^{-1} h^{-1} with the 100AC catalyst, reduced its BET surface to almost a third of the initial surface area and its microporosity to less than the half. In the case of Ni/Al_2O_3 this reduction in porous textural properties was lower. These differences can be attributed to the different active centers of both materials. The activated carbon has a very high BET surface area (about 1000 m^2/g) and its active centers are mainly located in the micropores. The methane diffuses into the micropores, reacts and gives rise to the carbon deposits which block the access to the active centers. The carbon dioxide regenerates some of these deposits, but cannot regenerate them all because part of the carbon dioxide reacts with the carbon from the initial activated

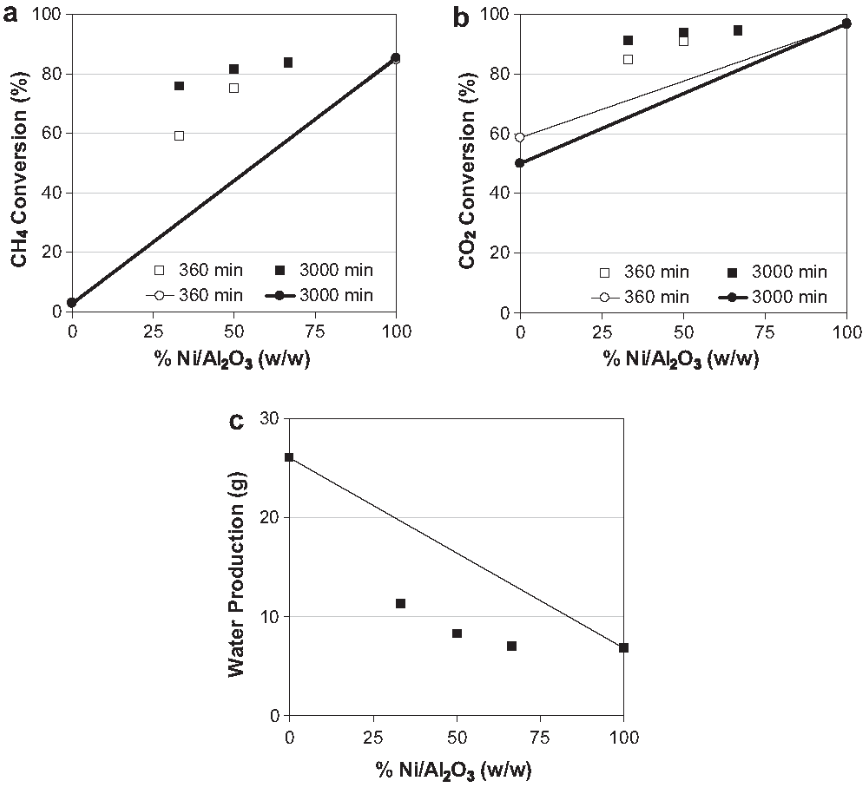

Fig. 4 – **Comparison of the results predicted by the law of mixtures (continuous lines) with those achieved in the experiments (squares) for the: (a) conversion of CH_4; (b) conversion of CO_2 after 6 h of reaction (open symbols) and 50 h of reaction (closed symbols); and (c) water production after 50 h of reaction.**

Table 1 – Porous textural properties of the activated carbon FY5 and the Ni/Al_2O_3 catalyst before and after the experiments.

		FY5			Ni/Al_2O_3		
		S_{BET}[a] (m^2/g)	V_t[b] (cm^3/g)	V_{mic}[c] (cm^3/g)	S_{BET}[a] (m^2/g)	V_t[b] (cm^3/g)	V_{mic}[c] (cm^3/g)
	Before	1153	0.51	0.44	166	0.53	0.06
1.00 L/(g h) 6 h	100AC	953	0.42	0.35	n.a	n.a	n.a
	50AC/50Ni	998	0.44	0.37	162	0.53	0.06
	100Ni	n.a	n.a	n.a	159	0.51	0.06
3.75 L/(g h) 50 h	100AC	473	0.24	0.18	n.a	n.a	n.a
	50AC/50Ni	968	0.48	0.35	149	0.51	0.06
	100Ni	n.a	n.a	n.a	138	0.50	0.05

a BET surface area obtained from the N_2 adsorption isotherms at −196 °C.
b Total specific pore volume, defined as the liquid volume adsorbed at $p/p^0 = 0.95$ from the isotherm of nitrogen at −196 °C.
c Specific volume of micropores (pores of internal width <2 nm), calculated from the isotherm of nitrogen at −196 °C.

carbon. The reaction with the carbon from the initial activated carbon is more rapid than with the carbon deposits located in the micropores, since the CO_2 does not need to diffuse into the micropores. On the other hand, the Ni/Al_2O_3 has a low BET surface area (about 100 m^2/g) but its active centers are located on the external surface, not inside the micropores. The active centers blocked by the carbon deposits are easy to regenerate since the carbon dioxide does not need to diffuse in order to reach them and there is no other carbon which can compete with them to react with the carbon dioxide. In contrast, when the mixtures/blends are used this decrease is much lower for both materials. When the 50AC/50Ni catalyst is used, although the conversions are much higher than in the case of 100AC, there is a reduction in the BET surface of about 15% and the microporosity at the end of the experiment is twice as high as that achieved with 100AC. Thus, the catalysts showed a greater resistance to the loss of BET surface area and microporosity when they were used in the mixtures/blends than when used alone. This is an interesting finding since it means that the mixtures/blends may be more resistant to the deactivation produced by carbon deposits than when the activated carbon or the Ni/Al_2O_3 are used alone.

3.1. *Effect of carbon monoxide*

Apart from hydrogen and methane, carbon monoxide is the third gas in the composition of the coke oven gas. Carbon monoxide normally appears in concentrations between 5 and 8% vol. The presence of carbon monoxide could affect the CO_2 reforming of COG in several ways. It could shift the equilibrium of the dry reforming (reaction 1) to the side of the reactants, in the same way as the presence of H_2 does [6,25]. This would have negative consequences, since it would decrease the conversion of methane and carbon monoxide. It could also shift the equilibrium of the RWGS to the side of the reactants. This would decrease the production of water, thereby increasing the selectivity of the process. However, seeing that this water could react with the methane through the steam reforming reaction, it could also have a negative effect, by partially preventing the second path of the process. The most probable situation is a combination of both effects leading to several different results. To determine the influence of the presence of CO on the process, experiments in which carbon monoxide was added to the feed were conducted, the results of which are shown in Fig. 5.

As can be seen, the results of these experiments show only minor differences in comparison to the case when no CO is added to the feed. If only the activated carbon is used as catalyst, the presence of CO clearly has a positive effect. Both the methane and carbon dioxide conversions increase and show more stable values. The increase in the conversions is 8% for the methane and 14% for the carbon monoxide. In contrast, when the Ni/Al_2O_3 is used, the conversions decrease. However, the

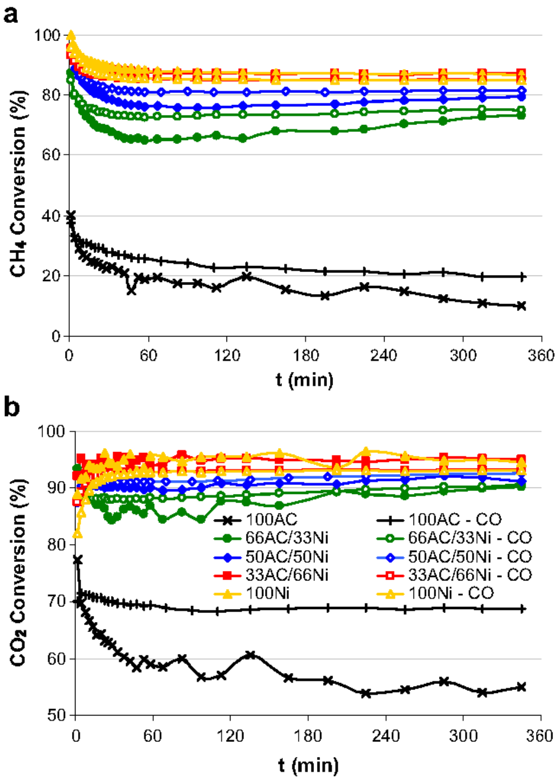

Fig. 5 – (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM and the GQM with the different mixtures used as catalysts(800 °C, $CH_4/CO_2 = 1:1$, 1 atm).

effect is much lower than in the experiment with activated carbon used as catalyst, because the conversions are only 2% lower than in the experiments without CO. When the physical mixtures are used, whether the effect is negative or positive, depends on the percentage of activated carbon used. When catalysts 67AC/33Ni and 50AC/50Ni are employed, the conversions increase, whereas in the case of 33AC/67Ni catalyst, the conversions decrease. As in the case of the experiments with no CO, the behaviors of 100Ni and 33AC/67Ni are practically the same. In any case, the differences between the experiments carried out with and without CO using the physical mixtures as catalyst are insignificant. It seems that in the case of the Ni/Al_2O_3 catalysts both effects (the shift in the equilibriums of dry reforming and RWGS) are taking place, but their influence is almost negligible. In the case of the activated carbon, a possible explanation for the rise in the conversions is a combination of both effects. The presence of carbon monoxide shifts the Boudouard equilibrium to the side of the reactants. This will give rise to an increase in the carbon dioxide concentration, the positive effect of which would outweigh the negative effect of the presence of CO over the RWGS. As a result of these shifts in equilibriums, the conversion of CO_2 and the production of water are higher than in the case of the experiments without CO. In the case of the conversion of CH_4 there is also an enhancement, but it is lower than in the case the conversion of CO_2. The presence of more water probably increases the amount of methane transformed through steam reforming, though not to the same extent as in the case of carbon dioxide. This hypothesis is supported by the higher amount of water produced when carbon monoxide is introduced into the feed (approximately 15% higher). Another possible explanation is that the higher amount of carbon deposits formed due to carbon dioxide disproportionation leads to a decrease in the catalytic activity of the catalyst for the transformation of methane [26].

With regard to the synergetic effect, the experiment carried out with the GQM show only minor differences with the experiments carried out with the GTM. First of all it should be noted that, in the experiments carried out adding CO to the feed and using the mixtures as catalysts, the conversions are stable. Therefore, there is no increase in the synergetic effect as the experiment proceeds. When CO is added to the feed, the synergetic effect is not as strong as in the experiments with no addition of CO. This is mainly due to the significant improvement in methane and carbon dioxide conversions in the case of the 100AC catalysts (+8% and +14% respectively), whereas in the other cases the improvement is not as great (+2% for methane and +1% for carbon dioxide when the 67AC/33Ni and the 50AC/50Ni catalysts are used) or there is even a worsening (−2% for the methane and-2% for the carbon dioxide when the 33AC/67Ni and the 100Ni catalysts are used).

3.2. *Analysis of the synthesis gas*

The use of the synthesis gas to produce different organics products depends on its H_2/CO ratio [5]. When the ratio is near to 1 it can be used to synthesize higher hydrocarbons and oxygenated derivatives, such us acetic acid, whereas if it takes on values of 3 or higher it may be used to produce H_2 or CH_4 [5]. Probably the most interesting application of the CO_2 reforming of COG is the production of a syngas suitable for the synthesis of methanol, which requires a H_2/CO ratio of 2 [6]. In order to be suitable for methanol production, the syngas produced must also satisfiy the R parameter (Eq. (4)). The R parameter is an expression that relates the proportions of H_2, CO and CO_2 in the syngas which must take on values slightly higher than 2 [27,28]. In the production of methanol it is necessary to bear in mind that the CO_2 takes part in the process (reactions 6 and 7). It appears in reaction 6 and acts as a promoter of reaction 7.

Table 2 – H_2/CO ratio, R parameter and selectivity in the CO_2 reforming of GQM with the different catalysts.

Catalyst	H_2/CO (dimensionless)	R (dimensionless)	Selectivity (%)
100AC	2.14 ± 0.02	1.44 ± 0.02	(−10)–(−60)[a]
67AC/33Ni	2.00 ± 0.01	1.835 ± 0.009	76
50AC/50Ni	2.008 ± 0.006	1.888 ± 0.001	80
33AC/67Ni	2.004 ± 0.002	1.905 ± 0.001	85
100Ni	2.01 ± 0.02	1.906 ± 0.001	85

a Results of the selectivity at the beginning and at the end of the experiment.

$$R = \frac{(H_2 - CO_2)}{(CO + CO_2)} \tag{4}$$

$$2H_2 + CO \leftrightarrow CH_3OH \quad \Delta H = -90.9\ \text{kJ/mol} \qquad \text{(reaction 6)}$$

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H = -41.1\text{kJ/mol} \qquad \text{(reaction 7)}$$

Given that the GQM composition is more or less the average composition of a typical COG, the H_2/CO ratio and R parameter of the different experiments carried out with the GQM are shown in Table 2.

As can be seen, in all of the experiments the H_2/CO ratio took on values of about 2, and the syngas obtained can be considered as suitable for the synthesis of methanol. However, the values of the R parameter also have to be taken into account. The results of the R parameter reveal that it is possible to use this synthesis gas for the production of methanol when the catalysts 50AC/50Ni, 33AC/67Ni and 100Ni are used. In fact, the R parameter took on values a little bit lower than two, but in the production of methanol this situation is usually corrected by adding the H_2 that has not reacted in the methanol synthesis stage, and which is recovered at the end of the process.

It is also productive to study the selectivity of the process. This parameter (Eq. (3)) gives an idea of the amount of reactants transformed into products or byproducts. Table 2 also shows the results of selectivity achieved over the different catalysts. The results for the 100CA catalyst are specially striking, since they are negative values. This means that, not only is all of the hydrogen from the methane transformed into water (this is the only byproduct detected), but part of the hydrogen present in the feed is also transformed into water. For the rest of the catalysts the results of selectivity are much higher, so they are able to transform most of the methane to produce hydrogen. Close examination of the values achieved with the different catalysts provides further evidence of the synergetic effect, since the selectivity values of the 67AC/33Ni, 50AC/50Ni and 33AC/67Ni catalysts are much nearer to the value of the 100Ni catalysts than to the value of the 100AC catalyst.

4. Conclusions

There are two different possible paths for the CO_2 reforming of COG: the direct dry reforming of methane and the reverse water gas shift reaction followed by the steam reforming of methane. As a consequence of this second path some water is produced as a byproduct.

The use of the physical mixtures of activated carbon and Ni/Al_2O_3 gives rise to a synergetic effect. Thus, the conversions achieved are significantly higher than those predicted by the law of mixtures, whereas the amount of water produced is lower. The loss of BET surface area and microporosity experienced by the materials when they are used in the mixtures is much lower than when they are used by themselves.

The presence of CO in the COG leads to a considerable increase in the conversions when the activated carbon is used as catalyst and to a slight decrease when Ni/Al_2O_3 is used. In the case of the mixtures, when the percentage of activated carbon is higher than that of Ni/Al_2O_3 there is a small increase in the conversion, while an excess of Ni/Al_2O_3 produces a decrease. Such variations undermine the strength of the synergetic effect.

In sum, the use of mixtures of activated carbon and Ni/Al_2O_3 as catalysts for the CO_2 reforming of COG is preferable that using they separately.

Acknowledgments

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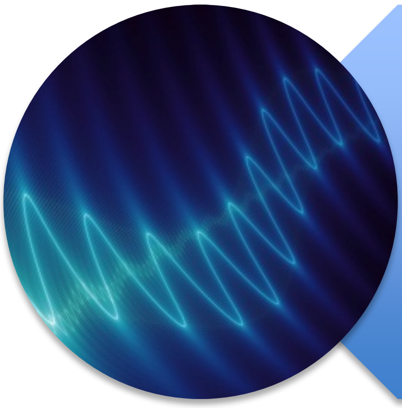

3.3. REFORMADO CON CO_2 DE GAS DE COQUERÍA ASISTIDO CON MICROONDAS

¿Qué?

En esta Sección se muestran los resultados obtenidos en el estudio del reformado seco de gas de coquería asistido mediante calentamiento con microondas. Se ha estudiado el proceso a 800 ºC para posteriormente comparar los resultados de conversiones, selectividades y resistencia a la desactivación de los catalizadores con los obtenidos utilizando el calentamiento convencional. En esta ocasión, y a la vista de los resultados (que se encuentran resumidos en las conclusiones de esta Sección), el estudio de la adecuación del gas de síntesis para su utilización en la producción de metanol no se ha llevado a cabo. Estos resultados se encuentran en el artículo *Microwave-assisted CO_2 reforming of coke oven gas: An exception to the general rule?*, publicado en Afinidad, 69-559 (2012), 185-190.

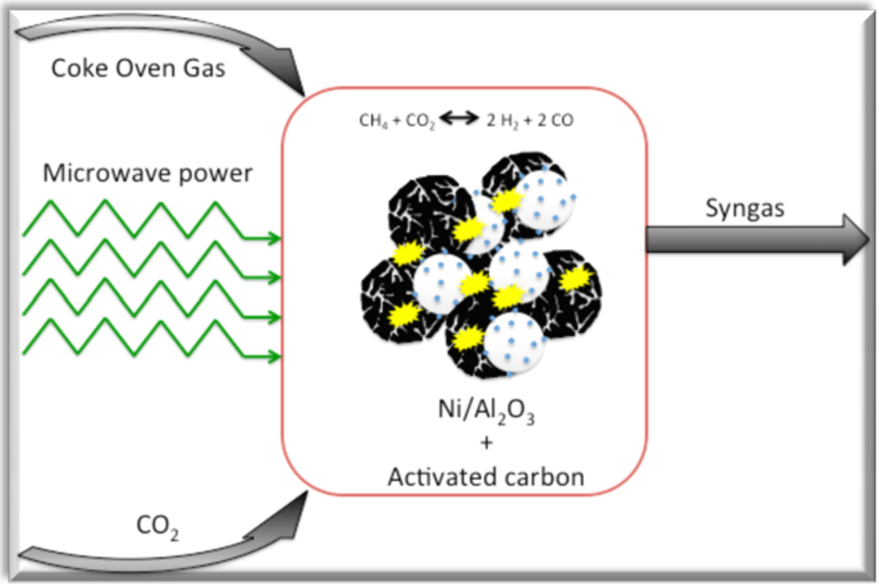

Figura 12. *Graphical abstract* del artículo *Microwave-assisted CO_2 reforming of coke oven gas: An exception to the general rule?*.

¿Por qué?

El calentamiento con microondas es una tecnología en auge que se ha mostrado tremendamente eficiente en muchos procesos, más aún cuando se encuentran implicados materiales carbonosos [56, 72, 86, 88, 95-113].

En el caso de las reacciones catalíticas heterogéneas, como es el caso del reformado de metano con CO$_2$, el microondas se ha mostrado como una tecnología capaz de dar lugar a mejores conversiones que el calentamiento convencional [56, 72, 86, 95, 105, 106, 108, 111, 114-116] . Los diferentes autores que han estudiado este fenómeno atribuyen esta mejora de las conversiones a un efecto pseudo-catalítico asociado a los microplasmas que aparecen durante el calentamiento microondas [95, 108, 116-121] . Estos microplasmas, los cuales aparecen durante el calentamiento de algunos materiales con microondas, son pequeños arcos eléctricos que ocupan una minúscula región del espacio y cuya duración se encuentra en la escala de los milisegundos [95, 108, 116-121]. En el Anexo 2 se pueden encontrar más detalles del calentamiento de materiales carbonosos con microondas así como de la naturaleza de los plasmas que se forman en dicho calentamiento.

El reformado con CO$_2$ de metano asistido con microondas es una reacción que ha sido ampliamente estudiada por el Grupo de Microondas y Carbones para Aplicaciones Tecnológicas del Instituto Nacional del Carbón [56, 72, 73, 82, 83, 87, 88, 90, 91, 122]. En estos estudios se ha podido comprobar cómo el calentamiento con microondas da lugar a conversiones considerablemente superiores a las que se derivan del calentamiento convencional con diferentes catalizadores, entre los que se encuentran el carbón activo FY5 o las mezclas de dicho carbón activo con catalizadores convencionales como el Ni/Al$_2$O$_3$. Incluso, se ha comprobado que mezclas de dicho carbón activo o de coque metalúrgico con materiales ricos en Fe (escorias de acería en este caso), que en principio no es un catalizador adecuado para este proceso por promocionar la reacción inversa de la *Water Gas Shift*, dan lugar a buenos resultados[123]. Estos resultados, discutidos con más detalle se pueden encontrar en el Anexo 1.

¿Cómo?

Dispositivos

Para este estudio se utilizaron dos dispositivos: el horno convencional detallado en la Sección 3.2 *Catalizadores para el reformado con CO$_2$ de gas de coquería*, y un dispositivo de calentamiento microondas que se muestra en la Figura 13.

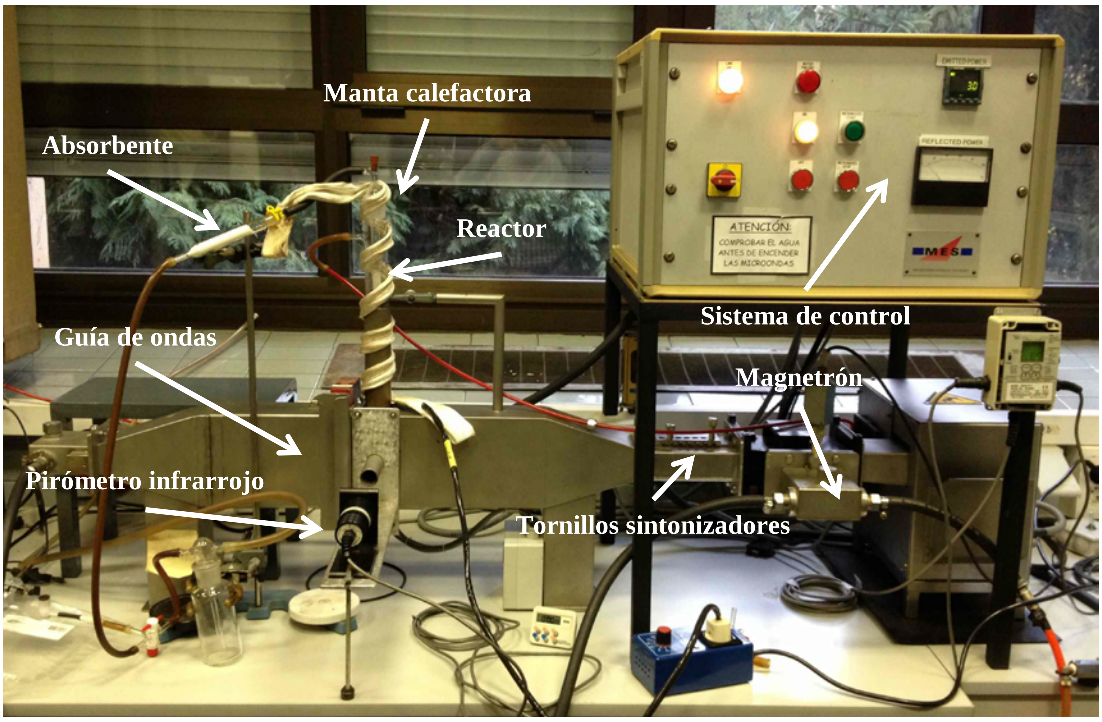

Figura 13. Dispositivo de calentamiento microondas unimodo para los ensayos de reformado con CO_2 de gas de coquería.

El dispositivo utilizado es un horno microondas unimodo (es decir, que trabaja teóricamente en un único modo de resonancia siempre que ningún elemento perturbe el campo electromagnético) que opera a una frecuencia de 2450 MHz. El equipo consiste en un magnetrón, que transforma la energía eléctrica en radiación microondas, con una potencia variable de 0 a 1860 W, que está acoplado a una guía de ondas, a través de la cual se transmite la radiación. En el interior de la guía se coloca el reactor de cuarzo con el lecho de catalizador. La guía dispone de dos orificios, uno en la parte superior por donde se introduce el reactor y otro en el lateral, a través del cual se realiza la medida de temperatura con un pirómetro óptico de infrarrojos. No toda la radiación emitida por el magnetrón es absorbida por el lecho de catalizador para su aumento de temperatura, sino que parte atraviesa la guía sin ser absorbida (potencia transmitida) y parte se refleja de vuelta hacia el magnetrón (potencia reflejada). Al final de la guía de ondas se sitúa un detector que mide la potencia transmitida, la cual va a parar a una corriente de agua que la absorbe, para posteriormente pasar a través de un circulador de agua donde se enfría. La potencia reflejada se minimiza a través de un sistema de tornillos sintonizadores, ya que puede dañar el magnetrón. Aún así es imposible evitarla por completo, por lo que se coloca otro detector entre la guía de ondas y el magnetrón, así como otra corriente de agua para absorber esa fracción reflejada.

Condiciones experimentales

Los ensayos del reformado con CO_2 del gas de coquería asistido con microondas se realizaron a presión atmosférica, a una temperatura de 800 ºC, y con una velocidad de 1.00 L g^{-1} h^{-1}. En cuanto a la composición del gas de alimentación, se utilizó la mezcla ternaria de 54% de H_2, 23% de CH_4 y 23% de CO_2. Debido a que los resultados que se obtuvieron fueron peores que los inicialmente esperados, se decidió no extender el estudio a más temperaturas y condiciones experimentales.

Catalizadores

Para este estudio se han utilizado dos de los tres catalizadores que se utilizaron en la Sección 3.2 *Catalizadores para el reformado con CO_2 de gas de coquería*: el carbón activo FY5 y las mezclas de FY5 y el catalizador convencional Ni/Al_2O_3. Esto es debido a que el catalizador convencional Ni/Al_2O_3 no es capaz de captar microondas y por tanto no puede calentarse por sí solo en presencia de ellas pero sí cuando se encuentra mezclado con el carbón activo FY5.

Conclusiones

A pesar de la demostrada capacidad del calentamiento microondas para mejorar los resultados en reacciones catalíticas heterogéneas, en este caso la mejora no fue la esperada, produciéndose incluso resultados considerablemente peores a los alcanzados en el horno convencional.

Cuando el catalizador utilizado fue el carbón activo FY5, las conversiones de CH_4 y CO_2 mejoraron al realizarse la reacción en el horno microondas, pero esa mejora fue considerablemente inferior a la que se obtuvo para el reformado seco de metano. Para el caso de las mezclas, la situación fue la contraria, ya que la utilización de calentamiento microondas no sólo no dio lugar a mejores conversiones, sino que se obtuvieron peores conversiones que en el horno eléctrico. De hecho, la diferencia entre los resultados obtenidos en horno eléctrico y horno microondas son mayores a medida que aumenta el porcentaje de Ni/Al_2O_3 en la mezcla.

Se plantearon diferentes hipótesis para tratar de explicar este comportamiento:

1. Bloqueo de los poros de los materiales debido a los depósitos de carbono procedentes de la descomposición del metano. Esta hipótesis se descartó ya que no había diferencias significativas en las variaciones de área superficial de los materiales cuando se utilizan en horno eléctrico y en microondas.

2. Aumento de las reacciones secundarias, más concretamente de la reacción inversa de la *Water Gas Shift* (Reacción 2). Efectivamente se produjo un aumento en la producción de agua, pero no es suficiente para explicar por sí sola las diferencias entre los resultados obtenidos en horno eléctrico y en horno microondas.

3. Naturaleza de los depósitos de carbono. A parte de la cantidad de depósitos, la naturaleza de los mismos también juega un papel fundamental, ya que no todos son igual de reactivos, lo que hace que pueda ser más difícil su regeneración. En el caso del carbón activo, las imágenes SEM mostraron la formación de nanofibras de carbono en el caso del horno microondas, las cuales no se formaron en el horno eléctrico. Sin embargo, este hecho también sucede en el caso del reformado de metano [87, 89], el cual va a la perfección en horno microondas, por lo que la aparición de estos depósitos no puede ser la causa de los malos resultados, más aún teniendo en cuenta que aparecen en el carbón activo, que es el que da mejores resultados en microondas. En el caso del Ni/Al_2O_3, las imágenes SEM no mostraron ningún tipo de depósito carbonoso.

4. Naturaleza de los microplasmas. Los microplamas que se forman en el interior del reactor cuando se utiliza el calentamiento con microondas dependen de los gases que haya en su interior. En este caso, la composición difiere de forma importante con respecto a la del reformado seco de metano, ya que hay una gran cantidad de H_2 en el interior en todo momento. Esto parece dar lugar a microplasmas que alcanzan mayores temperaturas, promocionando la sinterización de las partículas de níquel, y la consiguiente desactivación del catalizador Ni/Al_2O_3. Esto se ha comprobado tanto con las imágenes SEM como con difracción de rayos X.

Por todo ello, se puede concluir que la principal causa de los malos resultados obtenidos en el horno microondas para el reformado seco de gas de coquería es la naturaleza de los plasmas generados en el interior del reactor, debido a la elevada proporción de H_2 presente en el mismo.


Afinidad

SECCIONES

Artículo 6

Microwave-assisted CO_2 reforming of coke oven gas: An exception to the general rule?

Afinidad, 69 (2012), 185-191

Afinidad, 69 (2012), 185-190

Microwave-assisted CO_2 reforming of coke oven gas: An exception to the general rule?

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Reformado de gas de horno de coque con CO_2 asistido con microondas: Una excepción a la regla general?

Reformat de gas de forn de coc amb CO_2 assistit amb microones: Una excepció a la regla general?

Recibido: 19 de abril de 2012; revisado: 18 de agosto de 2012; aceptado: 5 de septiembre de 2012

RESUMEN

En publicaciones anteriores se ha demostrado que los resultados del reformado seco de metano mejoran cuando éste se lleva a cabo utilizando calentamiento con microondas. En este artículo, el calentamiento con microondas se aplica al reformado con CO_2 de gas de batería. Los resultados obtenidos difieren mucho de los que previamente se han publicado para el reformado con CO_2 de CH_4, ya que en el caso del gas de batería el calentamiento con microondas tan solo mejora las conversiones ligeramente cuando se utiliza un carbón activo como catalizador, mientras que los resultados obtenidos con mezclas de carbón activo y un catalizador de Ni/Al_2O_3 fueron incluso peores que los obtenidos con el calentamiento convencional. Se consideraron diversas hipótesis para tratar de hallar una explicación a estos pobres resultados, siendo probablemente la naturaleza de los microplasmas formados durante el proceso de calentamiento en microondas el factor más influyente. Cuando el reformado seco de gas de batería se lleva a cabo, en el interior del reactor hay una elevada proporción de H_2, lo que parece provocar microplasmas de temperaturas superiores a los que se producen en el reformado seco de metano. Esto da lugar a la sinterización de las partículas de Ni, provocando una caída de las conversiones.

Palabras clave: reformado con CO_2, gas de horno de coque, Microondas, carbón activo, catalizador de Ni/Al_2O_3

SUMMARY

It has been previously reported that the dry reforming of methane can be enhanced by means of microwave heating. In this article, this technology is applied to the CO_2 reforming of coke oven gas (COG). The results obtained were opposite to those reported in the CO_2 reforming of CH_4, since in the case of the COG, microwave heating only slightly enhanced the conversions when an activated carbon was used as catalyst, whereas the results achieved when mixtures of activated carbon and Ni/Al_2O_3 were employed as catalyst were even worse than those obtained in a conventional oven. Several hypotheses were considered in order to find an explanation for these poor results, the nature of the microplasmas formed during the process being the most likely factor. The high proportions of H_2 present in the reactor when the dry reforming of coke oven gas is carried out may give rise to microplasmas of higher temperature than in the dry reforming of CH_4. This will cause the Ni particles to sinter significantly, leading to a decrease in the conversions.

Keywords: CO_2 reforming, Coke oven gas, Microwave, Activated carbon, Ni/Al_2O_3 catalyst

RESUM

S'ha publicat que el reformat sec de metà pot ser millorat mitjançant calefacció amb microones. En aquest article, s'ha aplicat aquesta tecnologia al reformat amb CO_2 de gas de forn de coc (GFC). Els resultats obtinguts són oposats als publicats en el reformat de CH_4 amb CO2, ja que en el cas del GFC, la sola calefacció amb microones va millorar lleugerament les conversions quan es va utilitzar carboni activat com a catalitzador, mentre que els resultats aconseguits quan es van utilitzar com a catalitzador barreges de carboni activat i Ni/Al_2O_3 van ser fins i tot pitjors que els obtinguts en un forn convencional. Es van considerar diverses hipòtesis per explicar aquests pobres resultats, essent el factor més probable la naturalesa del microplasma format durant el procés. L'alta proporció d'H_2 present en el reactor quan es duu a terme el reformat sec de gas de forn de coc pot donar lloc a la formació de microplasma de temperatura més alta que en el reformat sec de CH_4. Això causarà una significativa sinterització de partícules de Ni, ocasionant una disminució en les conversions.

Paraules clau: reformat amb CO_2, gas de forn de coc, microones, carbó actiu, catalitzador de Ni/Al_2O_3.

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1. INTRODUCTION

The CO_2 reforming, or dry reforming, of methane (reaction 1) has been proposed as a promising alternative to steam reforming during recent years, since it has considerable advantages over the conventional method, especially the consumption of two important greenhouse gases, CO_2 and CH_4 [1-3].

$$CH_4 + CO_2 \leftrightarrow 2\,H_2 + 2\,CO \qquad \Delta H = 247\ kJ/mol$$

(reaction 1)

This process can be carried out with different CH_4 feedstocks, such as natural gas [4], biogas [5], landfill gas [6] or coke oven gas [7-9]. The upgrading of coke oven gas is currently the focus of much attention, since it is an important source of GHG emissions, resource wastage and energy inefficiency in the steel industry [10, 11]. In addition, the CO_2 reforming of COG yields a synthesis gas suitable for methanol production in a process which can be regarded as a partial recycling of CO_2 [7, 8, 12, 13]. Several papers have reported the use of microwave heating to favor heterogeneous catalytic reactions [14, 15]. Moreover, the CO_2 reforming of CH_4 under microwave heating has been studied with a series of different catalysts in previous tests, the results of which were consistently better than those obtained under conventional heating [16, 17]. The main reason for this improvement of heterogeneous catalytic processes seems to be the hot spots that appear when microwave heating is used [18, 19]. These hot spots are microplasmas [18], where the temperature is considerably higher than the average temperature of the catalyst bed. They are therefore able to increase the reaction rate, giving rise to higher conversions.

Although some studies have dealt with the microwave-assisted dry reforming of methane, there are no references to the topic of coke oven gases. The main objective of the present article is to study the dry reforming of coke oven gases under microwave heating, paying special attention to the effect of the presence in the feed of hydrogen, that has been demonstrated to be of critical importance when the process is carried out with conventional heating [7-9].

2. MATERIAL AND METHODS

2.1. Preparation and characterization of the Catalyst

A series of physical mixtures consisting of grains of a commercial activated carbon FY5 and cylindrical pellets of an in-lab prepared Ni/Al_2O_3 were used as catalyst. A detailed preparation of the catalyst and its characterization has been described elsewhere [8]. Samples of the FY5 and the Ni/Al_2O_3 before and after the reaction were examined using a scanning electron microscope (SEM) from Carl Zeiss SMT. The reason for choosing these mixtures was their dielectric properties. Activated carbons are easily heated by microwaves, but alumina is not a good absorber of microwave energy, so it is not possible to achieve the reaction temperatures. Whereas when the mixtures are employed, the activated carbon absorbs the microwaves and is heated up to the reaction temperature and the Ni/Al_2O_3 is heated by conduction through the heat provided by the activated carbon. Moreover, mixtures of this kind have shown a very interesting synergetic effect in the dry reforming of CH_4 [20] and COG [8]. The catalyst composed exclusively of FY5 was labeled 100AC, whereas the mixtures were labeled XXAC/YYNi, where XX and YY are the weight percentages of FY5 and Ni/Al_2O_3 respectively.

2.2. CO_2 reforming experiments

The CO_2 reforming experiments were performed in a fixed-bed quartz tube reactor heated by two different devices: a conventional oven (CH), i.e. an electric furnace, and a microwave oven (MW).

A gaseous stream composed of 54% H_2, 23% CH_4 and 23% CO_2 was used. This mixture will be referred to as gas ternary mixture (GTM). With this composition, it is possible to maintain the H_2/CH_4 ratio of the COG and to ensure the stoichiometric conditions of CH_4 and CO_2 necessary for the dry reforming of methane.

The tests were performed at atmospheric pressure, at a temperature of 800 ºC (which was monitored and controlled in the middle of the catalyst bed using a thermocouple) and at a volumetric hourly space velocity of 1.00 $L\,g^{-1}\,h^{-1}$. Before the reaction, the system was purged with N_2 for 15 min. Then it was heated up to the reaction temperature. Once the reactor reached 800 ºC, the N_2 flow was stopped and the reactant gases were introduced to start the reaction. One of the products of the reaction was water (due to the reverse water gas shift reaction, RWGS, see reaction 4 of section 3. Results and discussion). To collect the water, a condenser was placed at the outlet of reactor. The gaseous products were collected in Tedlar® sample bags and analyzed in a Varian CP-3800 gas.

The CH_4 and CO_2 conversions were calculated on the basis of the amount of water collected in the condenser and the product gaseous stream compositions using an iterative method, based on the Newton method for non-lineal equations and Solver Microsoft Excel® tool. The mass balances were closed to within a margin of error of ± 5%. These parameters were calculated as follows:

$$CH_4\ conversion,\ \% = 100 \times (CH_{4\,in} - CH_{4\,out}) / CH_{4\,in}$$

(Eq. 1)

$$CO_2\ conversion,\ \% = 100 \times (CO_{2\,in} - CO_{2\,out}) / CO_{2\,in}$$

(Eq. 2)

where $CH_{4\,in}$ and $CO_{2\,in}$ are moles of each gas at the inlet of the reactor and $CH_{4\,out}$ and $CO_{2\,out}$ are moles of each gas at the outlet.

3. RESULTS AND DISCUSSION

The results of the conversions of CH_4 and CO_2 are shown in Figure 1.

As can be seen, there are clear differences between the results of conventional heating and those of microwave heating. When the catalyst is composed exclusively of activated carbon (100AC), the conversions achieved under microwave heating are better than those of conventional heating (methane and carbon dioxide increased approximately 10% when microwave heating is used), although this improvement is considerably lower than that obtained in the dry reforming of methane (where methane conversion increases 25% and CO_2 conversions increases a 35%, approximately) [16]. When the mixtures are used, the conversions are better under conventional heating. As the Ni/Al_2O_3 content in the mixture is increased, the gap between the results of conventional heating and those of microwave heating increases. This suggests that whatever the cause of the difference in the results is, it has a greater effect on Ni/Al_2O_3 than on the activated carbon. This is the opposite to what happens in the case of the dry reforming of methane, where both, the activated carbon and the mixtures, lead to better results under microwave heating than under conventional heating [17]. Besides, the difference in the results when Ni/Al_2O_3 fraction increases is larger in the case of CH_4 conversion, may be due because the methane decomposition takes places preferably over the Ni/Al_2O_3 than over the AC [17].

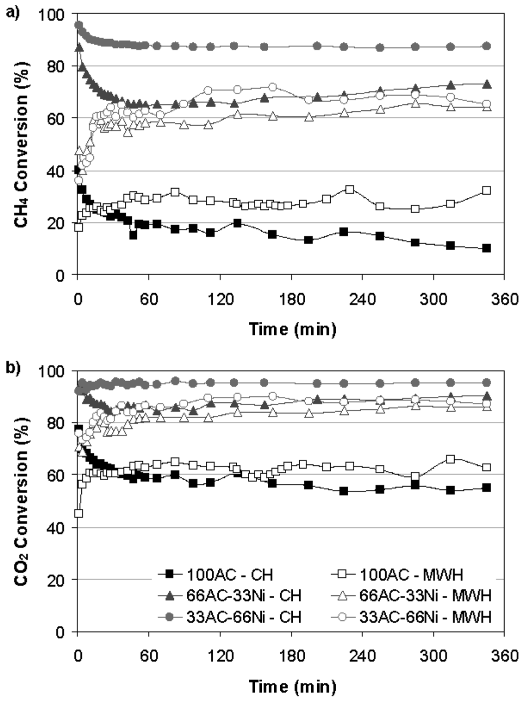

Fig. 1. *CH_4 and CO_2 conversions in the CO_2 reforming of GTM (800 °C, 1 atm, CH_4/CO_2 = 1, VHSV = 1.00 L g^{-1} h^{-1}, 1 atm) under different kinds of heating (microwave or conventional)*

Moreover these results were confirmed by repeating each test 3 times. The findings contradict all previous research, not only for the microwave-assisted dry reforming of methane [5, 16, 17] but also for other heterogeneous catalytic reactions [15, 18], like NO_x reduction studied by Kong and Cha [21, 22] or SO_2 reduction studied by Cha and Kim [23]. The only difference between the dry reforming of methane and the dry reforming of coke oven gases is the presence of hydrogen in the feed, which leads to a higher hydrogen content inside the reactor. This higher content in hydrogen may be the factor responsible for the poorer results obtained with the mixtures of activated carbon and Ni/Al_2O_3 used as catalyst.

Four different possible explanations for these poor results are presented and discussed below:

- Blockage of the porosity of the activated carbon, which is the main factor responsible for the catalytic activity of this material [24], and inability of the reactant gases to gain access to the active centers of the Ni/Al_2O_3 catalyst, due to the formation of carbon deposits [1].
- An increase in the rate of side reactions
- The different natures of the carbon deposits, which may be less reactive in the case of microwave heating
- The different nature of the microplasmas formed during the heating.

Hypothesis 1: blockage due to carbon deposits

In order to study this hypothesis, N_2 adsorption isotherms of the materials used as catalysts, before and after the reaction, were performed. The results of this textural characterization are presented in Table 1.

Table 1. *Porous textural properties of the activated carbon FY5 and the Ni/Al_2O_3 catalyst before and after the experiments.*

	FY5			Ni/Al_2O_3		
	S_{BET} [a] (m^2/g)	V_t [b] (cm^3/g)	V_{mic} [c] (cm^3/g)	S_{BET} [a] (m^2/g)	V_t [b] (cm^3/g)	V_{mic} [c] (cm^3/g)
Before	1153	0.51	0.44	166	0.53	0.06
100AC-CH	953	0.42	0.35	n.a	n.a	n.a
100AC-MW	938	0.41	0.35	n.a	n.a	n.a
66AC/33Ni-CH	1013	0.44	0.37	163	0.52	0.06
66AC/33Ni-MW	1106	0.52	0.42	166	0.55	0.06
33AC/66Ni-CH	1060	0.47	0.40	163	0.52	0.06
33AC/66Ni-MW	1074	0.51	0.39	156	0.55	0.06

[a] *BET surface area obtained from the N_2 adsorption isotherms at -196 °C.*

[b] *Total specific pore volume, defined as the liquid volume adsorbed at p/p^0 = 0.95 from the isotherm of nitrogen at -196 °C.*

[c] *Specific volume of micropores (pores of internal width <2 nm), calculated from the isotherm of nitrogen at -196 °C.*

In view of the results, the first hypothesis can be discarded, at least in so far as the blockage of the porosity of the activated carbon is concerned. It can be seen that, only when the 100AC is used, is the porosity of the activated carbon after the reaction lower under microwave heating. In any case, the differences between the final porous textures in the experiments carried out under microwave heating and under conventional heating are so small that they should not be taken into consideration.

In the case of Ni/Al_2O_3, the porosity was not affected during the reaction, so it would appear that there were no carbon deposits blocking access of the reactant gases to the active centers of the catalysts. To confirm this, several SEM images were taken, some of which are shown in Figure 2.

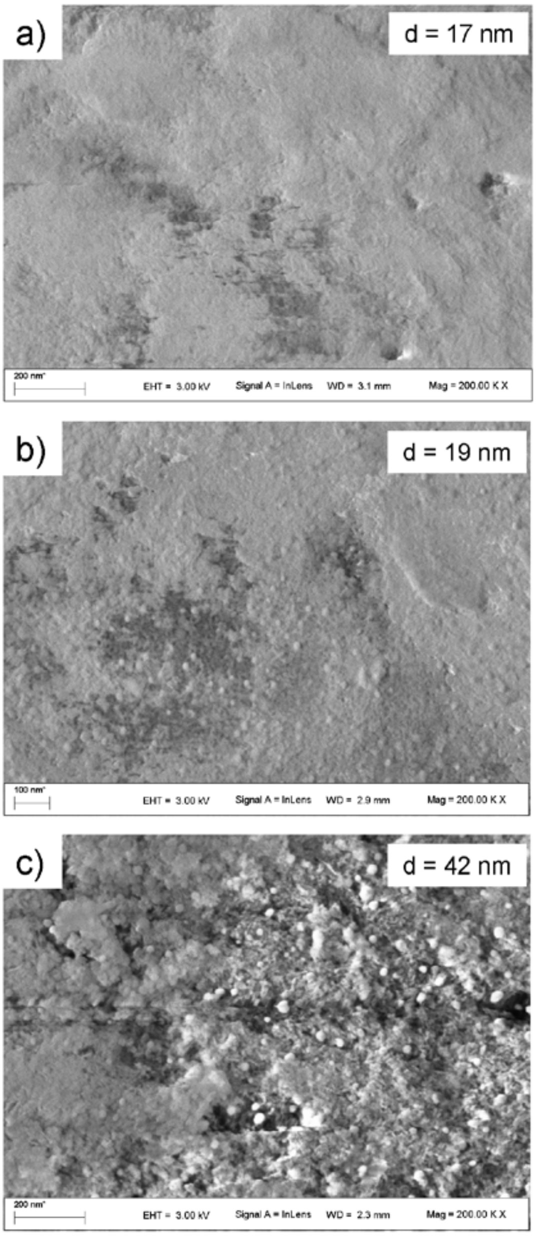

Fig. 2. *SEM images of the Ni/Al_2O_3 catalyst: (a) before the reaction; (b) after the reaction under conventional heating; and (c) after the reaction under microwave heating. The mean size of the Ni particles of each sample (determined by XRD diffraction) is indicated inside the white boxes in the right upper corner of each SEM image.*

In these photographs, there is no evidence of carbon deposits. Although there are differences in appearance between each sample, these are due to other causes, which will be discussed below.

Hypothesis 2: side reactions

To justify this hypothesis, it is necessary to consider the possible reaction mechanisms involved in the process. It has previously been reported [9] that the CO_2 reforming of coke oven gas can take place through two different reaction pathways: direct dry reforming, which is normally considered as the sum of methane decomposition (reaction 2) followed by the gasification of carbon (reaction 3), or the reverse water gas shift (reaction 4) followed by the steam reforming of methane (reaction 5) [8, 9].

Reaction path I

$$CH_4 \rightarrow 2\,H_2 + C \qquad \Delta H = 75\ \text{kJ/mol}$$

(reaction 2)

$$C + CO_2 \rightarrow 2\,CO \qquad \Delta H = 172\ \text{kJ/mol}$$

(reaction 3)

Reaction path II

$$H_2 + CO_2 \leftrightarrow H_2O + CO \qquad \Delta H = 41\ \text{kJ/mol}$$

(reaction 4)

$$CH_4 + H_2O \leftrightarrow 3\,H_2 + CO \qquad \Delta H = 206\ \text{kJ/mol}$$

(reaction 5)

The problem with reaction path II (RWGS followed by steam reforming) is that the RWGS reaction can act as a side reaction. If all the water produced through RWGS does not react with the methane it will give rise to large amounts of water [25, 26].

Table 2. *Water production obtained in the different experiments expressed as volume percentage of the products.*

	Conventional Heating	Microwave Heating
100AC	10.5 %	8.0 %
66AC/33Ni	4.3 %	5.1 %
33AC/66Ni	2.1 %	5.0 %

The water produced in the experiments is reported in Table 2. As can be seen, in the case of 100AC, water production is higher when conventional heating is used, whereas when the catalysts are the mixtures, water production is higher under microwave heating. Again the differences between the results of both heating mechanisms are only slight and the conversion of CO_2 follows the same pattern as that of CH_4, i.e. in both cases conversions are higher in the microwave oven when the 100 AC is used as catalyst but lower in the microwave oven when the mixtures are used as catalyst. Consequently, the different behaviors observed in the dry reforming of COG and in the dry reforming of methane cannot be fully explained by this hypothesis alone.

Hypothesis 3: carbon deposits nature

When methane decomposition takes place, it gives rise to different kinds of carbon deposits. Not only is the amount of these carbon deposits important for the catalytic activity of the materials used as catalyst, but also their reactivity. In the case of Ni/Al_2O_3 (see SEM images in Figure 2) the formation of carbon deposits can be discarded. In the case of the activated carbon, its BET surface is reduced during the process, suggesting that its pores must have been blocked. The amount of carbon deposits is probably similar irrespective of the heating device used, since no significant differences in the BET surface area of the activated carbon at the end of the experiment in the two heating devices can be seen. However, this does not rule out the possibility that the nature of the deposits may be different. Figure 3 shows SEM images of the activated carbon before and after the reaction in the different heating mechanisms.

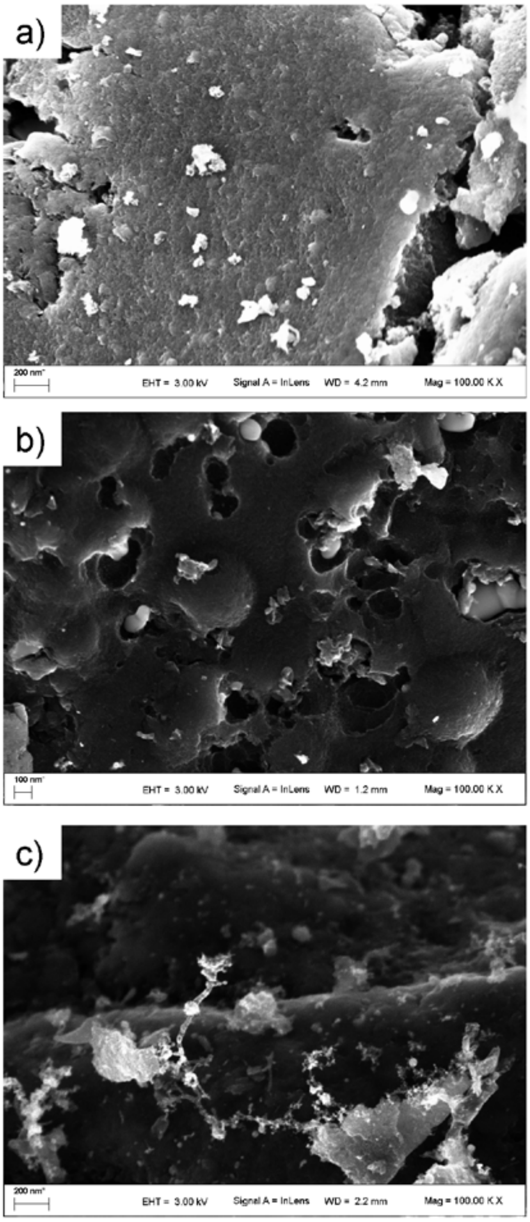

Fig. 3. *SEM images of FY5: (a) before the reaction; (b) after the reaction under conventional heating; and (c) after the reaction under microwave heating.*

The most important difference is that, in the case of microwave heating, nanofibers were formed on the carbon surface in all cases, but not under conventional heating. However this also occurred in the case of the dry reforming of methane, so the presence of such deposits does not explain the differences in conversion [5]. Also worth noting is that these fibers did not appear on Ni/Al_2O_3, even though Ni is a typical catalyst used for the production of this kind of fibers [27, 28]. However, they appeared on the surface of the activated carbon (which only has a small percentage of inorganic ashes) in every mixture (i.e., 66A/33Ni and 33AC/66Ni). However this issue will not be discussed further since it lies outside the scope of this paper.

Hypothesis 4: nature of the microplasmas

During the microwave heating of carbon materials microplasmas are produced [19]. The improvement in catalytic activity produced by microwave heating in the heterogeneous process has been attributed to these microplasmas, since at these points the temperature is able to reach values considerably higher than the mean temperature of the catalyst bed [15, 29]. Moreover, Zhang *et al.* [15] have suggested that these microplasmas may result in apparent shifts of the equilibrium constant. It is therefore possible to talk about a “pseudo-catalytic” effect produced by these microplasmas in microwave heating.

In this work, the microplasmas were observed during the process as in the case of the dry reforming of methane. However, as mentioned before, the gases present in the reactor exhibit one very important difference: a much higher proportion of H_2 in the case of coke oven gas. It is therefore possible to state that the nature of the microplasmas is different. A possible consequence of this difference in the microplasmas can be seen in the SEM images of Ni/Al_2O_3 (Figure 2). The appearance of the surface of the Ni/Al_2O_3 catalyst under conventional heating is completely different to that of the Ni/Al_2O_3 catalyst after reaction under microwave heating. In the catalyst used in the microwave oven, tiny granules can be seen on the surface of the material. At first sight, it seems that the Ni particles have experienced sintering during the reaction. Indeed, this was confirmed by DRX analysis performed in order to determine the Ni particle size employing Scherrer’s equation. The results of the Ni particle size (d) are included in Figure 2. As can be seen, the Ni particle size of the catalyst after reaction in the microwave oven is considerably greater than that of the catalyst after reaction in the conventional oven (it is even higher than when the reaction was carried out in a conventional oven over a 50-hour period [9]). Considering that the mean temperature in the microwave is the same as in the conventional oven, a possible explanation or the difference may be that the microplasmas have created hot spots with temperatures high enough to promote the sintering of the Ni particles. Since microplasmas were also formed in the microwave-assisted dry reforming of methane, it seems that the presence of such high proportions of hydrogen gives rise to microplasmas with higher temperatures. The sintering of the Ni particles alone will lead to deactivation, but sintering will also ultimately promote the formation of carbon deposits, thereby increasing the deactivation rate of the catalysts even further [30, 31].

To sum up, the nature of the microplasmas is the main cause of the bad behavior of the microwave assisted dry reforming of coke oven gas, although the other three hypotheses will also have contributed to the final results.

4. CONCLUSIONS

The use of microwave energy in the dry reforming of coke oven gas yields better results than those obtained under conventional electric heating if the process is carried out with an activated carbon as catalyst. However, when the process is carried out with mixtures of activated carbon and Ni/Al_2O_3 as catalyst, the results obtained in the microwave oven are worse than those obtained in a conventional oven. These results differ significantly from those achieved in the dry reforming of CH_4, which are considerably higher in the case of the microwave oven, independently of the kind of catalyst, with conversions of 100 % being achieved for both gases.

Several hypotheses have been proposed in order to explain the differences, which must be due to the presence of H_2 in the reactant gases, since this is the only difference between the two processes. These hypotheses were: (i) blockage of the carbon porosity by carbon deposits; (ii) increase in the gases reacting through side reactions; (iii) the nature of the carbon deposits; (iv) the nature of the microplasmas formed during the heating. All of these causes contribute to the poor results achieved in the microwave-assisted dry reforming of coke oven gas, although the last hypothesis, the nature of microplasmas, is the most influential, since it causes a very important sintering of the Ni particles. Furthermore the microplasmas formed in the presence of such high proportions of H_2 can reach higher temperatures than in the case of the microwave-assisted dry reforming of methane. This promotes the sintering process which in turn leads to a decrease in the conversions.

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3.4. COMPARACIÓN CON PROCESOS CONVENCIONALES DE PRODUCCIÓN DE METANOL

¿Qué?

En este capítulo se lleva a cabo una comparación entre un proceso convencional de producción de metanol (es decir, utilizando reformado con vapor de agua y oxidación parcial para la generación del gas de síntesis) y el proceso de producción de metanol a partir de gas de coquería utilizando el reformado con CO_2 para la producción de gas de síntesis, estudiado en esta Tesis. Para este análisis comparativo se ha utilizado el programa de simulación de procesos Aspen Plus ®, y se han evaluado:

- Las necesidades energéticas de ambos procesos.
- La producción de CO_2 por kg de metanol producido para ambos procesos.
- El grado de reciclado real de CO_2 obtenido con el proceso que utiliza gas de coquería como materia prima.
- Los rendimientos en carbono e hidrógeno de cada uno de los procesos.
- La calidad del metanol obtenido previamente a la etapa de purificación con torres de destilación.

Los resultados de este estudio se recogen en artículo *New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process*, enviado para su publicación a Applied Energy.

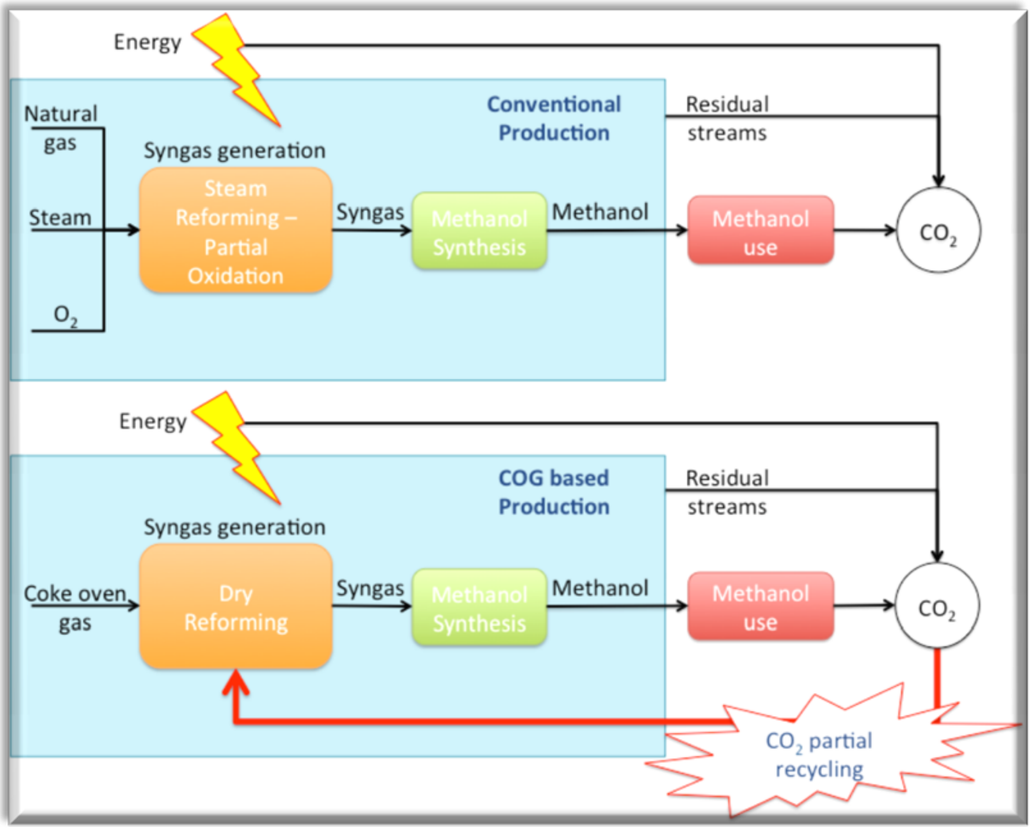


Figura 14. *Graphical abstract* del artículo *New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process.*

¿Por qué?

Es importante comprobar que, además de ser técnicamente posible, el proceso propuesto tiene beneficios reales sobre los procesos convencionales de producción de metanol, que puedan impulsar su futura implantación a nivel industrial.

Como se ha repetido a lo largo de toda esta Memoria, la producción de metanol a partir de gas de coquería mediante reformado seco presenta una ventaja muy importante como es el reciclado parcial de CO_2, que permite una disminución de las emisiones de CO_2 con respecto a los procesos convencionales de un 50%, al menos, teóricamente. Sin embargo, esta ventaja teórica debe ser corroborada, es decir, se debe evaluar qué nivel de CO_2 se puede reciclar realmente en el proceso. También es importante tener en cuenta que este reciclado parcial es el resultado de un balance en el que sólo se han considerado las materias primas y los productos del proceso, pero los consumos energéticos pueden tener un peso muy importante en la generación de emisiones de CO_2, y por lo tanto es necesario evaluar ese consumo, así como sus emisiones de CO_2, e incluirlas en dicho balance. Así mismo, como en cualquier proceso industrial, puede haber corrientes residuales que contribuyan a las emisiones de CO_2 que también deben ser consideradas.

Por otro lado, es importante también conocer los rendimientos del proceso, que permitirán evaluar el aprovechamiento de las materias primas, ya sea gas natural o gas de coquería, ya que cuanto mayor sea el aprovechamiento de la materia prima, más eficiente técnica y económicamente será el proceso.

Por último, también resulta muy interesante evaluar la calidad del metanol obtenido antes de la etapa de purificación, es decir, su grado de pureza (expresado normalmente como porcentaje en masa). Esta pureza alcanzada tras la síntesis del metanol condicionará el coste de la etapa de purificación posterior: a peor calidad, mayor coste.

¿Cómo?

Para realizar este estudio, se han modelizado (usando Aspen Plus®) dos procesos: uno convencional de producción de metanol a partir de gas natural y otro de producción de metanol a partir de gas de coquería mediante reformado con CO_2. Para comparar ambos procesos se ha establecido una base de cálculo de 1 kmol/h del gas utilizado como materia prima (gas natural o gas de coquería). En las Figuras 15 y 16 se muestran los diagramas de bloques de estos procesos.

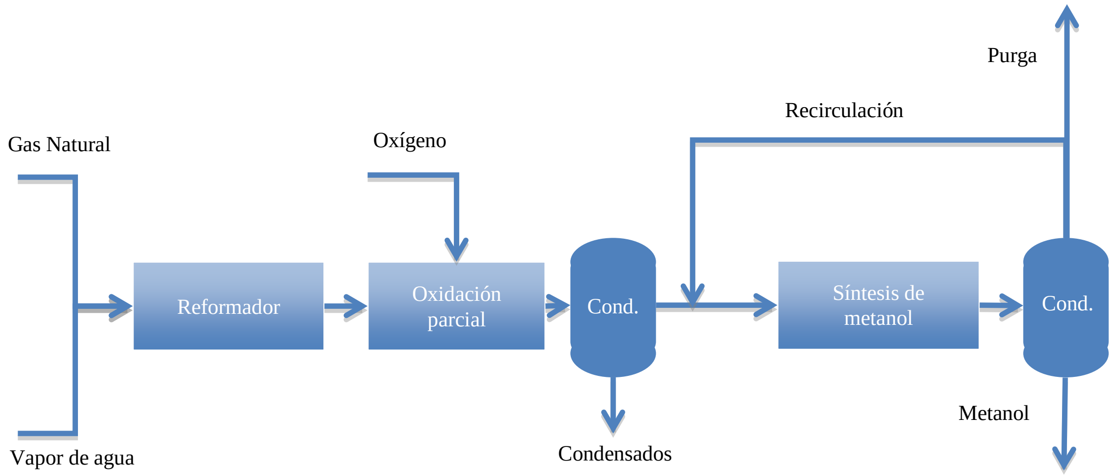


Figura 15. Diagrama de bloques del proceso convencional de síntesis de metanol.

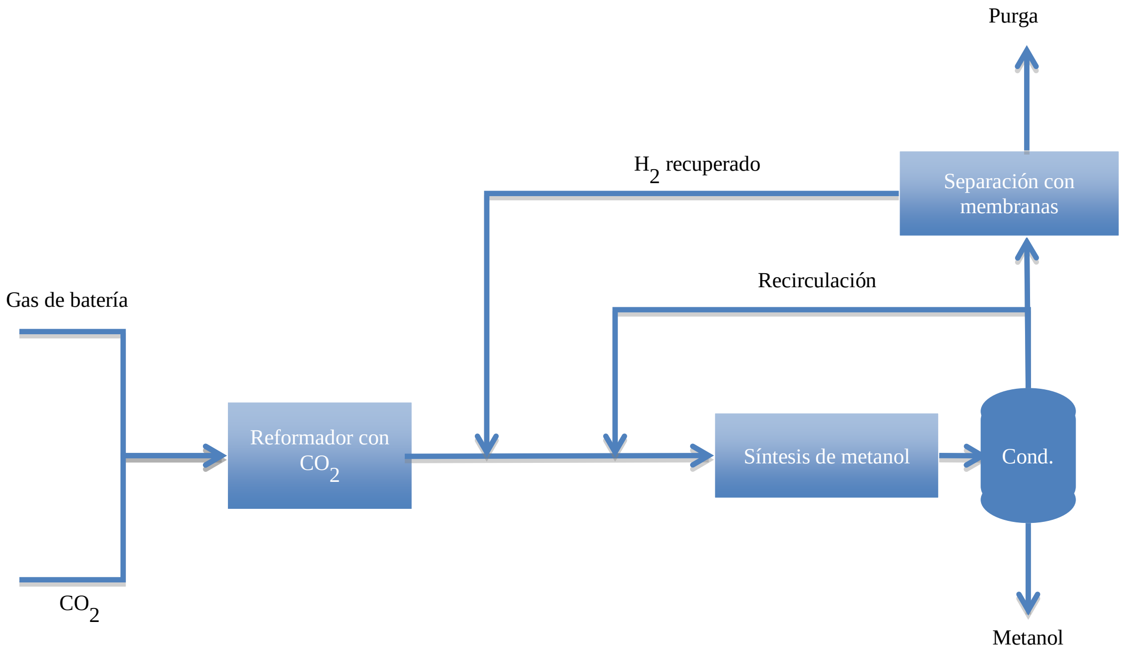


Figura 16. Diagrama de bloques del proceso de síntesis de metanol a partir de gas de coquería mediante reformado con CO_2.

En el proceso convencional de producción de metanol (para referirse a él, de ahora en adelante, se utilizará el acrónimo CP, que proviene del inglés *Conventional Production*, y es el que se ha utilizado en el artículo *New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process*, en el que se resumen los resultados de esta Sección), el gas natural entra en un reformador, donde tiene lugar el reformado con vapor de agua (Reacción 5). Dado que el valor de la relación H_2/CO y el parámetro R del gas de síntesis así obtenido no son los adecuados, este gas de síntesis entra en un segundo reactor donde tiene lugar una oxidación parcial del metano que previamente no ha reaccionado. Tras esta reacción, se condensa el exceso de H_2O que no ha reaccionado y el gas de síntesis, ya con los valores de H_2/CO y R adecuados, entra en el reactor de síntesis de metanol. Debido a que las conversiones por paso son bajas, se trabaja con recirculación, incluyendo una purga para evitar la acumulación de inertes.

El proceso que utiliza gas de coquería como materia prima (de ahora en adelante se utilizará el acrónimo DR-COG para referirse a él, el cual proviene de *Dry Reforming of Coke Oven Gas*, y es el utilizado en el artículo anteriormente mencionado), parte de este gas que se hace reaccionar con CO_2 en un reformador. El gas de síntesis obtenido aquí tiene una relación H_2/CO y un parámetro R muy próximo a los ideales (es decir, 2 para la relación H_2/CO y entre 2.03 y 2.05 para el parámetro R), pero necesita ser ajustado, para lo que se utiliza H_2 recuperado del final del proceso. Una vez ajustada la composición del gas de síntesis, éste entra en el bloque de síntesis de metanol. En este caso, la purga de la recirculación se introduce en un bloque de separación con membranas para recuperar el H_2, con el cual se ajusta la composición del gas de síntesis. Este bloque de separación tuvo que ser modelizado, ya que Aspen Plus® no tiene un bloque de simulación para este tipo de operaciones. Para ello se programó la operación en Fortran y el programa se introdujo en la simulación a través de un bloque de separación estándar.

La comparación se ha realizado desde cuatro puntos de vista: consumo energético, balance de CO_2, rendimientos de carbono e hidrógeno y calidad del metanol obtenido. En el caso del consumo energético, se calcularon las necesidades energéticas de todos los equipos utilizados en cada proceso. Dado que en algunas operaciones tiene lugar un desprendimiento de energía en vez de consumirse y que la corriente de purga contiene especies con un elevado calor de combustión (como el CH_4), se establecieron tres casos para el estudio:

1. Considerando tan sólo los equipos que consumen energía.

2. Considerando los equipos que consumen energía además de la energía obtenida de la corriente de purga.

3. Considerando los equipos que consumen energía, la energía de la corriente de purga y la energía desprendida en los reactores.

En esta última opción no se han considerado todos los equipos que permiten la recuperación de energía debido a que esta recuperación es imposible que sea completa, ya que está afectada por las eficacias y por factores como la temperatura a la que se recupera (por ejemplo, si recuperamos energía a una temperatura baja no podemos utilizarla para calentar una corriente que se encuentra a una temperatura superior). Para el balance al CO_2 se han tenido en cuenta:

- Las emisiones que se generarían tras la utilización del metanol, es decir, un mol de CO_2 por cada mol de metanol producido.

- Las emisiones de CO_2 producidas en la combustión de la purga.

- Las emisiones de CO_2 producidas en la generación de la energía necesaria para llevar a cabo el proceso que, como se verá más adelante, tienen un peso muy importante en el balance global.

Dado que las emisiones de CO_2 por kWh producido dependen notablemente de la zona geográfica en que se encuentre situada la planta de generación energética (ya que cada país tiene su propio mix energético), se han tomado cuatro referencias geográficas para el estudio: China y Estados Unidos como los mayores productores de gas de coquería (y en el caso de China también de metanol) y la Unión Europea y España que es donde se ha desarrollado esta Tesis. Estos datos fueron tomados de informes de la Agencia Mundial de la Energía[124]. Los rendimientos en carbono e hidrógeno, que sirven para dar una idea del aprovechamiento que se consigue de las materias primas, se han calculado teniendo en cuenta el metanol producido y todas las especies que contienen estos elementos presentes en la corrientes de alimentación. Por último, la calidad del metanol obtenido se ha valorado en función de la pureza del mismo.

Conclusiones

Desde el punto de vista energético, los resultados fueron muy diferentes dependiendo del caso estudiado:

- Cuando sólo se tuvo en cuenta los equipos que consumían energía, se determinó que el proceso DR-COG consumía menos energía que el proceso CP, 4.92 kWh/kg de metanol producido para el caso del proceso CP frente a los 4.08 kWh/kg de metanol necesarios en el caso del proceso DR-COG.

- En el caso de considerar también la energía proveniente de la combustión de la corriente de purga, los resultados fueron mucho más parejos. En el proceso CP se necesitarían 2.63 kWh/kg de metanol producido y en el caso del proceso DR-COG 2.59 kWh/kg de metanol producido.

- Finalmente, si consideramos también la recuperación energética de los reactores, es el proceso CP el que da lugar a un menor consumo energético, ya que sólo necesitaría 1.07 kWh/kg de metanol producido, sin embargo para el proceso DR-COG sería necesario consumir 1.74 kWh/kg de metanol producido.

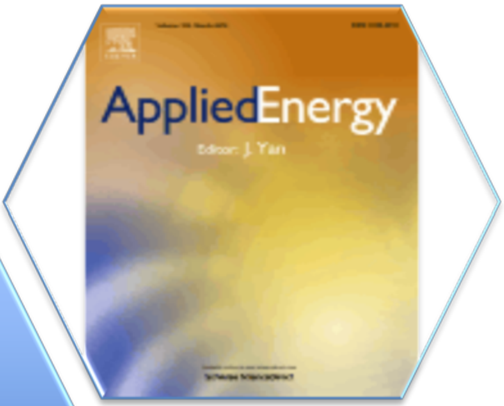
De esta primera parte del estudio comparativo se puede concluir que el proceso basado en el gas de coquería, DR-COG, es el que tiene menores consumos energéticos. Sin embargo, el proceso convencional, CP, permite mayores recuperaciones energéticas, por lo que el diseño del proceso, así como los rendimientos obtenidos en la recuperación energética, juegan un papel fundamental para que el proceso DR-COG pueda ser superior desde el punto de vista energético al proceso convencional CP.

En lo que al balance de CO_2 se refiere, antes de considerar las emisiones producidas por el consumo de energía, se comprobó que, aunque no es posible alcanzar el máximo teórico correspondiente a un reciclado del 50% con el proceso DR-COG, sí que se consigue un reciclado importante de alrededor del 40%. Una vez consideradas las emisiones procedentes de la generación de la energía necesaria para llevar a cabo cada uno de los procesos (estudiando de nuevo los tres casos planteados para el estudio del consumo energético), se pudo comprobar que, en todos los casos estudiados, el proceso DR-COG daba lugar a menores emisiones de CO_2 que el proceso CP. Estas diferencias varían desde una disminución del 6% en el caso más desfavorable (aquel en cuyo balance energético se consideran los equipos que consumen energía, la energía de la corriente de purga y la energía desprendida en los reactores y la planta se situaría en China) hasta 31% en el más favorable (en el que en el balance energético sólo se consideran los equipos que consumen energía y la planta estaría situada en España). Asimismo, se comprobó que la capacidad que tiene para disminuir las emisiones de CO_2 el proceso DR-COG depende en gran medida de la situación geográfica de la planta debido al gran peso que tienen las emisiones procedentes de la generación de energía en el balance de CO_2.

Los rendimientos en carbono e hidrógeno de ambos procesos son muy elevados (75.8% en C y 73.2% en H para el proceso CP y 79.7% en C y 83.9% en H para el proceso DR-COG). En el caso del proceso DR-COG son ambos superiores, pero especialmente destacable es la diferencia en los rendimientos en hidrógeno, siendo más de un 10% superior el obtenido en el DR-COG. Dado que se espera que el metanol juegue un papel fundamental en la denominada “Economía del Hidrógeno”, esta diferencia de rendimientos puede resultar fundamental en la futura implantación industrial de este proceso, ya que el proceso DR-COG alcanza un grado de utilización del hidrógeno mucho mayor que el proceso CP.

Finalmente, la pureza del metanol obtenido es del 96.8% en masa para el proceso CP y del 98.4% para el proceso DR-COG, lo que implicaría que la etapa de posterior purificación tendría un coste más elevado en el caso del proceso CP. De hecho, el metanol producido mediante el proceso DR-COG puede ser utilizado como combustible (mezclado con gasolina) sin necesidad de ninguna purificación adicional.

En resumen, el proceso DR-COG se muestra superior al proceso CP desde el punto de vista medioambiental, de utilización de las materias primas y de los costes de purificación. Desde el punto de vista energético, la integración energética de la planta juega un papel fundamental, ya que el proceso DR-COG necesita menores consumos energéticos, pero el proceso CP permite mayores recuperaciones energéticas lo que podría hacer que las necesidades energéticas de este proceso terminen siendo inferiores.



Artículo 7

New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process

Enviado a Applied Energy

New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process.

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Abstract

A novel method of producing methanol from coke oven gas (COG), involving the CO_2 reforming of COG to obtain an appropriate syngas for the synthesis of methanol is proposed. This method is compared with a conventional process of methanol synthesis from natural gas, in terms of energy consumption, CO_2 emissions, raw materials exploitation and methanol purity. Whereas this new process requires the consumption of less energy, the conventional process allows a higher energy recovery. CO_2 emissions are considerably lower with the new process, but the geographic situation of the plant plays a determinant role. From the point of view of raw materials exploitation and methanol purity, the process proposed yields better results. These results suggest that methanol production from coke oven gas would be a more attractive alternative to conventional processes.

Keywords

Methanol; CO_2 Reforming; Coke oven gas; CO_2 emissions; Energy

1. Introduction

Methanol is one of the most important chemical materials produced today due to the wide variety of processes in which it is used [1,6]. Its applications range from chemical uses (as solvent or in the production of organic products such as formaldehyde) to energy uses (e.g., the production of biodiesel or as a fuel itself) [1, 4-6]. Nowadays, methanol is manufactured using a technology based mainly on natural gas as feedstock, although some processes use oil [4,7]. A block diagram of the conventional process is shown in Fig. 1.

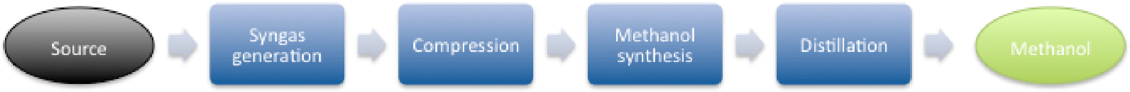


Fig. 1. Process of the production of methanol from natural gas.

This process involves four steps: syngas generation, compression, the synthesis of methanol and distillation [4]. Syngas generation and methanol synthesis are areas of increasing scientific development. In a conventional methanol plant, syngas generation accounts for 55 % of the financial outlay required for the process units [4]. Different syngas production processes are available depending on the characteristics of the natural gas and the economics restraints imposed on the plant [2, 4, 7-13]. These processes are steam reforming, autothermal reforming, and combined reforming. However, in the last few years an alternative source of syngas production has emerged: coke oven gas [14-23]. COG is a by-product from coking plants, consisting mainly of H_2 (55–60 %), CH_4 (23–27 %), CO (5–8 %) and N_2 (3–5 %) along with other hydrocarbons, H_2S and NH_3 in small proportions. Most of this gas up is used as fuel in the coke ovens, but usually there is a surplus of gas which is used in other processes of the plant, or is simply burnt away in torches [16, 23-27], giving rise to environmental problems, in the form of greenhouse gases emissions. The thermal upgrading of COG would provide an ideal solution to these environmental problems. However, none of the previously mentioned processes for syngas production from natural gas can be used if the final product is methanol. This is due to the high H_2/CO ratios and R parameters (Eq. 1) resulting from these processes if the coke oven gas is used as source of methanol production [15, 18, 20, 21, 23].

$$R\text{, dimensionless} = (H_2 - CO_2) / (CO + CO_2) \qquad \text{(Eq. 1)}$$

In order for the syngas to be used for the production of methanol the H_2/CO ratio needs to be around 2 whereas the optimum value for the R parameter lies within the range of 2.03-2.05 [1, 2, 28]. A possible solution to this problem could be to generate the syngas by means of CO_2 reforming (or dry reforming). CO_2 reforming is a reaction between CO_2 and CH_4 that gives rise to H_2 and CO (Reaction 1).

$$CH_4 + CO_2 \leftrightarrow 2\ H_2 + 2\ CO \qquad \text{(Reaction 1)}$$

By applying CO_2 reforming to the coke oven gas, under stoichiometric conditions of methane and carbon dioxide, it is possible to obtain a syngas with a H_2/CO ratio and a R parameter slightly lower than the optimum values. Only minor adjustments of these values would then be required, and this can be done using the H_2 recovered at the end of the process of methanol production [18]. Moreover, the production of methanol from coke oven gas via CO_2 reforming could be considered as a “partial recycling” of carbon dioxide, since half of the carbon dioxide produced, when methanol is used, is consumed [15, 18, 20, 21, 23]. This balance is illustrated in Fig. 2.

However, this advantage has yet to be demonstrated, as it is possible that the yields and the energy needs of the process will affect the abovementioned balance. Moreover, no references can be found in the literature to any previous comparison of this technology with that of conventional methanol production. Hence, the aim of the present work is to carry out a comparative simulation analysis of methanol production from coke oven gas via dry reforming and the conventional process of methanol production from natural gas, using Aspen Plus® software.

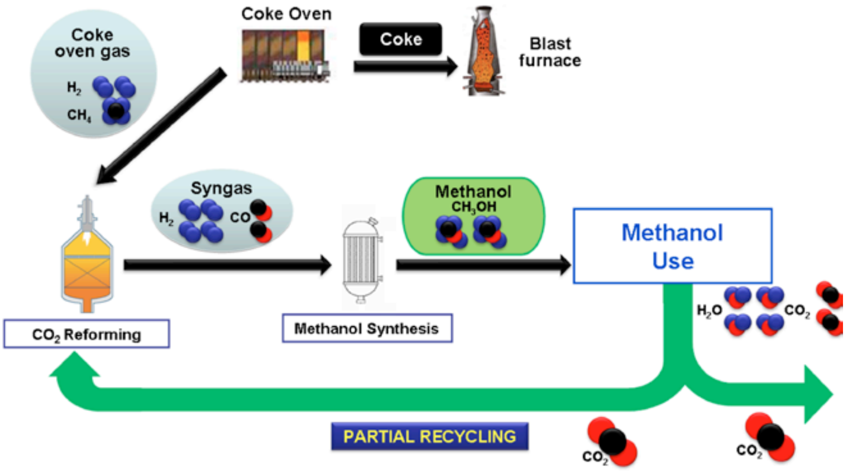


Fig. 2. Partial recycling of CO_2 in the synthesis of methanol from COG via dry reforming.

2. Simulation Methodology

Two different processes were studied: the conventional production process (CP) and the novel technology proposed for the dry reforming of coke oven gas (DR-COG). These processes were modelled using Aspen Plus® software. In each process a flow rate basis of 1 kmol/h of feed gas, natural gas or coke oven gas, was employed. The compositions of these gases are shown in Table 1.

Table 1. Natural gas and coke oven gas compositions used in the simulation.

Component	Natural Gas (vol. %)	Coke oven gas (vol. %)
CH_4	91.2	26.0
H_2	0	62.0
CO_2	1.0	1.5
CO	0	7.0
N_2	0.5	2.2
C_2H_6	6.4	0.5
C_3H_8	0.8	0
C_4H_{10}	0.1	0
C_2H_4	0	0.8

2.1. CP process model

Figure 3 shows a block diagram of the CP process, which is the most widespread methanol production process in use.

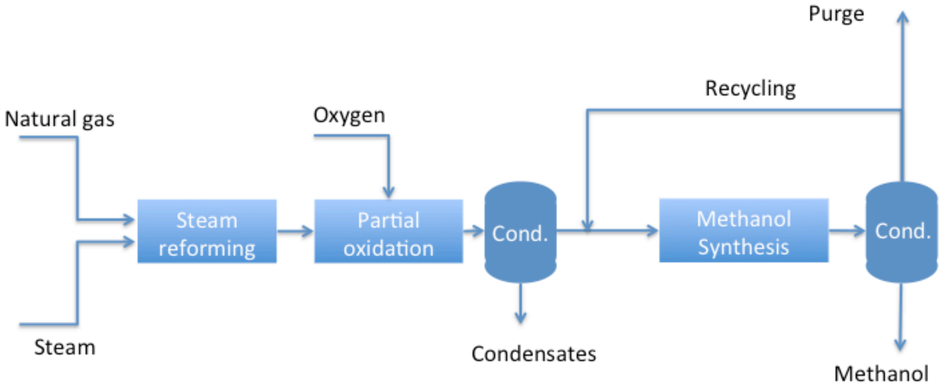


Fig. 3. Block diagram of the CP process of synthesis of methanol from natural gas.

In this process, the natural gas is fed into a reformer where the methane reacts with excess steam through a steam reforming reaction. Since the H_2/CO ratio and the R parameter of the syngas obtained are higher than that desired, the syngas is fed into a second reactor where it reacts with O_2 through partial oxidation. In this way, the H_2/CO ratio and the R parameter are adjusted to the desired values. Since there is a surplus of H_2O that has not reacted in the first reactor, a condensation stage is required to separate the excess water. The syngas is then introduced into the methanol synthesis loop. Recirculation is required because the conversion in each cycle is very low. A purge is included in the loop to prevent the accumulation of inerts.

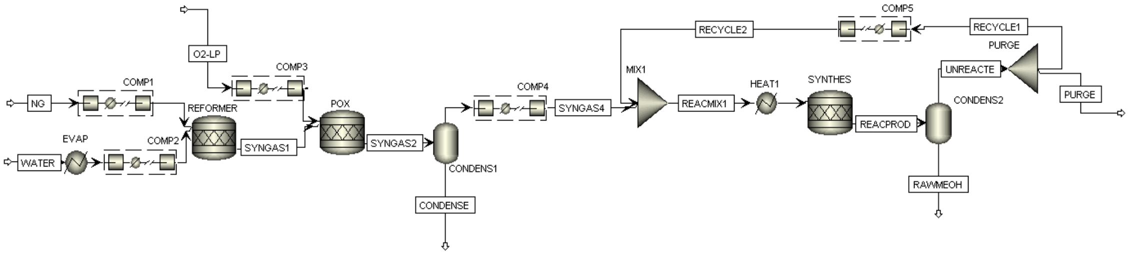


Fig. 4. Aspen Plus® flowsheet of the CP process.

The model developed for this study (Fig. 4) is composed of:

1. A line of compressed natural gas (NG), the composition of which is shown in Table 1.
2. A line of steam production (WATER).
3. A steam reformer (REFORMER) where the NG and WATER react to give rise to the initial syngas (SYNGAS1), the composition of which is still far from that required for methanol production.
4. A line of compressed O_2 (O2-LP).
5. A partial oxidation reactor (POX) where the SYNGAS1 and O2-LP react to give rise to a second syngas. After the excess of water has been separated this syngas is compressed (SYNGAS2) and introduced into the recycling loop.
6. Inside the recycling loop there is a methanol synthesis reactor (SYNTHES) and next a condenser where the products are separated from the unreacted gases (CONDENS2). The unreacted gas stream is split by means of a purge (PURGE) into two streams, the purge stream (PURGE) and a stream of recycled products (RECYCLE1) which are compressed (RECYCLE1) before being mixed with SYNGAS2

Table 2 shows the operation conditions corresponding to the main units of the process. These conditions have been set from bibliographic data process available [1, 2, 4, 7].

2.2. DR-COG process model

Fig. 5 shows a block diagram of the DR-COG process. In this case there is only one reactor, since it is possible to obtain a suitable syngas in one step. There is then a double loop: one for the recirculation and the other for recovering unreacted H_2 so that the values of the R parameter and the H_2/CO ratio can be adjusted.

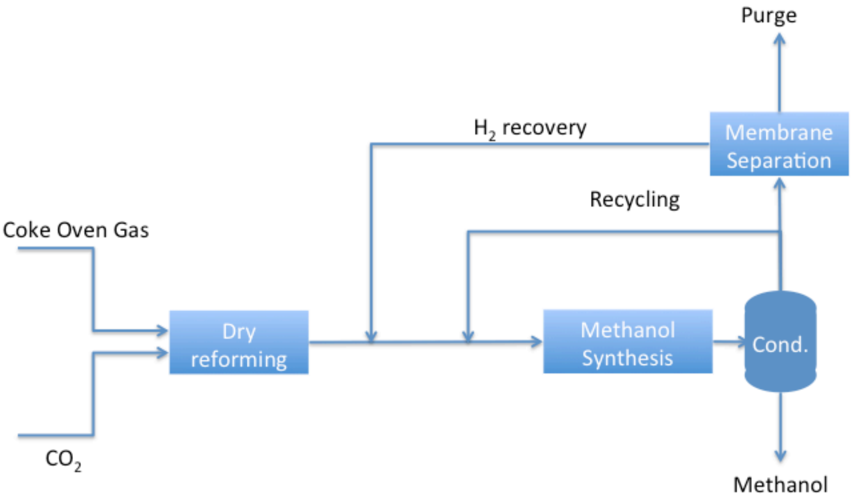


Fig. 5. Block diagram of the proposed new process of methanol synthesis from coke oven gas via dry reforming.

Fig. 6 shows the model developed using Aspen Plus®.

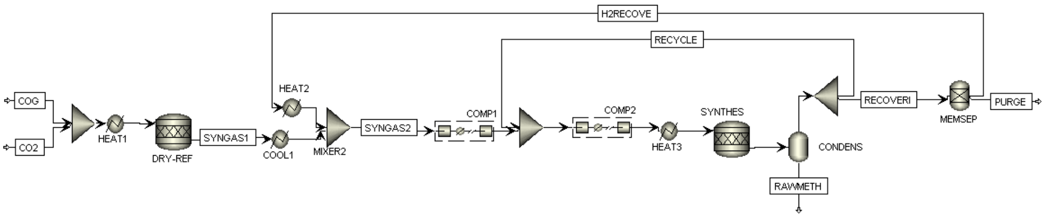


Fig. 6. Aspen Plus® flowsheet of the DR-COG process.

This model is composed of:

1. Two initial streams of CO_2 (CO2) and coke oven gas (COG), the composition of which is shown in Table 1.
2. A dry reformer where CO2 and COG react to give rise to the synthesis gas (SYNGAS1), the composition of which is adjusted using the H_2 recovered at the end of the process. The synthesis gas obtained is then introduced into the recycling loop (SYNGAS2).
3. The recycling loop is analogous to that of the CP process with the difference that in this case the stream purged in the CP process (RECOVERI in this case) enters a membrane separation unit (MEMSEP) to allow the recovery of the H_2 needed to adjust the composition of the syngas. Since membrane separation process is not included in the Aspen Plus® software, it was programmed using Fortran and included in the model as a custom-defined split component unit [29]. The modelling of this unit and the Fortran programme are explained in the Supplementary Material. From this unit, two streams are obtained: one rich in H_2 (H2RECOVE) and the other rich in the rest of the purged gases (PURGE).

Table 2 shows the operation conditions of each of the main units in the process. These conditions have been set from experimental results [15, 18, 20, 21, 23] previously obtained bibliographic data process available [1, 2, 4, 7].

Table 2. Simulation conditions of the main equipment [1, 2, 4, 7, 15, 18, 20, 21, 23].

Conventional (CP)		**Process proposed (DR-COG)**	
Equipment	**Conditions**	**Equipment**	**Conditions**
Steam reformer	800 ºC 30 bar	Dry reformer	900 ºC 1 bar
POX reactor	1000 ºC 30 bar	MeOH Synthesis reactor	230 ºC 75 bar
MeOH Synthesis reactor	230 ºC 75 bar	Splitter	97 % recycled 3 % purged
Purge	97 % recycled 3 % purged		

2.3. Model evaluation

In order to study and compare the processes, four parameters were chosen:

- Energy consumption: the total amount of energy consumed in the process was obtained from the model in order to determine how much energy is consumed per kg of methanol produced.

- CO_2 balance: a CO_2 balance was set up, that included the emissions of the products and the purged stream, and the CO_2 consumed in the dry reforming in the case of the DR-COG. The emissions of CO_2 resulting from the consumption of energy by the process were also taken into consideration.

- Carbon and hydrogen yields: in addition to energy and CO_2 emissions, the efficiency of the process in terms of the exploitation of raw materials is also important. Since different raw materials are employed, efficiency was evaluated on the basis of the use of carbon and hydrogen fed in. The carbon and hydrogen yields were calculated as follows (Equations 2 to 5):

CP

$$C_{yield} = MeOH_{prod}/(CH_{4fed} + CO_{2fed} + 2\cdot C_2H_{6fed} + 3\cdot C_3H_{8fed} + 4\cdot C_4H_{10fed}) \qquad \text{(Eq. 2)}$$

$$H_{yield} = 4\cdot MeOH_{prod}/(4\cdot CH_{4fed} + 6\cdot C_2H_{6fed} + 8\cdot C_3H_{8fed} + 10\cdot C_4H_{10fed} + 2\cdot(H_2O_{fed}-H_2O_{rec})) \qquad \text{(Eq. 3)}$$

where $MeOH_{prod}$ are the moles of methanol produced; $CH_{4fed,}$ CO_{2fed}, C_2H_{6fed}, C_3H_{8fed} and C_4H_{10fed} are the moles of CH_4, CO_2, C_2H_6, C_3H_8 and C_4H_{10} present in the natural gas fed into the process; H_2O_{fed} are the moles of water fed into the reformer; and H_2O_{rec} are the moles of water recovered from the condenser after partial oxidation.

DR-COG

$$C_{yield} = MeOH_{prod}/(CH_{4fed} + 2\cdot C_2H_{6fed} + 2\cdot C_2H_{4fed} + CO_{2fed}) \qquad \text{(Eq. 4)}$$

$$H_{yield} = 4 \cdot MeOH_{prod}/(2 \cdot H_{2fed} + 4 \cdot CH_{4fed} + 6 \cdot C_2H_{6fed} + 4 \cdot C_2H_{4fed}) \qquad \text{(Eq. 5)}$$

where $MeOH_{prod}$ are the moles of methanol produced; H_{2fed}, CH_{4fed}, C_2H_{6fed} and C_2H_{4fed} are the moles of H_2, CH_4, C_2H_6 and C_2H_4 present in the coke oven gas fed into the process; and CO_{2fed} are the moles of CO_2 fed into the reformer.

- Quality of raw methanol: at the end of the process of methanol synthesis, it is necessary to include a purification stage to obtain the required level of purity depending on the end use of the methanol [1]. Since the end use of the methanol lies outside the scope of this work, the final purification stage has not been included. Nevertheless, the methanol purity prior to this stage was evaluated given that the lower the level of purity the higher the cost (in energetic and economic terms) of the purification stage.

3. Results and discussion

3.1. Energy consumption

The energy consumption comparison is based on the amount of methanol produced. In the case of the conventional CP process, with 1 kmol/h of natural gas it is possible to produce 0.86 kmol/h of methanol, whereas in the DR-COG process 1 kmol/h of coke oven gas gives rise to 0.50 kmol/h of methanol.

Table 3 shows the energy consumption of the units in each process. This table also includes the energy that can be obtained from the combustion of the purged gases, which could contribute to a reduction of the overall consumption of energy in the process. Since the entire study has been performed on a flow basis, the data in the table are expressed in units of power instead of units of energy. As can be seen, not all of the units consume energy. Some of them, such us condensers, coolers, methanol synthesis reactors and partial oxidation reactor generate energy. This energy can be recovered in order to reduce the overall energy consumption of the process. However, the recovery will not be total, since it is affected by the yields, which are normally quite low. For this reason, three different possibilities have been considered for evaluating the energy consumption of each process:

Table 3. Power of the different units and purge streams of each process.

CP process		DR-COG process	
Unit	**Power (kW)**	**Unit**	**Power (kW)**
COMP1	5.01	HEATER1	10.66
EVAP	26.29	DRY-REF	19.01
COMP2	13.64	COOLER1	-11.31
REFORMER	39.56	COMP1	13.40
COMP3	3.52	COMP2	18.24
POX	-19.64	SYNTHES	-13.54
CONDENS1	-63.92	CONDENSE	-31.85
COMP4	3.86	HEATER2	0.14
HEAT1	14.45	HEATER3	3.55
SYNTHES	-22.50		
CONDENS2	-51.04		
COMP5	26.22		
PURGE	-61.61	PURGE	-23.77

1. Case 1: where only the units which consume energy are taken into account. It is clear that, since the simulation has been performed without considering efficiencies, at least this amount of energy will be consumed, whereas it is not possible to establish how much energy can be recovered from the units which generate energy. In this case, the energy consumption of the CP process is 4.92 kW·h/kg of methanol and the consumption of the DR-COG process is 4.08 kW·h/kg of methanol.

2. Case 2: where the units which consume energy and the energy generated by the combustion of the purge are taken into account. The purged gases give rise to a highly energetic by-product stream which can be burnt to obtain energy, something that is common practice in this kind of plants. In this case the energy consumption in both processes is very similar: 2.63 kW·h/kg of methanol in the CP process and 2.59 kW·h/kg of methanol in the DR-COG process.

3. Case 3: where the units which consume energy, the energy generated by the combustion of the purge and the energy recovered from the reactors are taken into account. In

this case, the energy recovered from the reactors has been included, since the recovery of energy from the condenser may be affected by lower yields than the reactors. In this case, the CP process energy consumption is 1.07 kW·h/kg of methanol compared to a DR-COG energy consumption of 1.74 kW·h/kg of methanol.

Although the results of the energy consumption differ depending on the assumptions used in the evaluation, two main conclusions can be drawn: (i) the DR-COG process consumes less energy per kg of methanol produced, (ii) the CP process allows a higher energy recovery. Thus the design of the process and the yields achieved will play a key role in determining whether the DR-COG is able to compete with the CP process from the point of view of energy consumption.

3.2. CO_2 balance

Table 4 shows the direct CO_2 emissions (i.e., those associated with the different streams involved in the carbon dioxide balance of each process).

Table 4. CO_2 emissions in the different processes.

CP		**DR-COG**	
Source	**Emission (kmol/h)**	**Source**	**Emission (kmol/h)**
Methanol	0.817	Methanol	0.491
Purge	0.243	Purge	0.121
		CO_2 feed	- 0.245
Total (mol CO_2/mol CH_3OH)	**1.23**	**Total (mol CO_2/mol CH_3OH)**	**0.74**

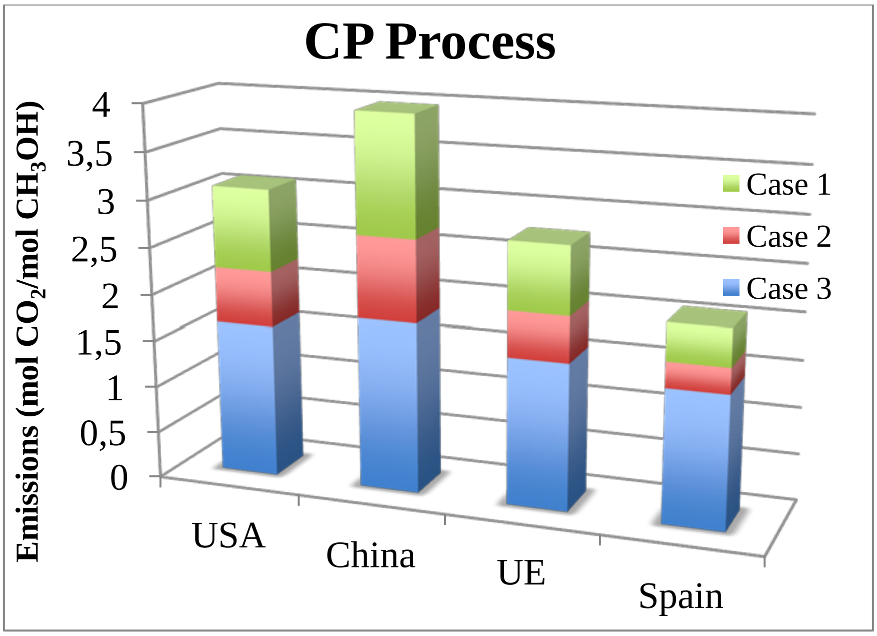
Leaving aside the CO_2 emissions resulting from the energy used in the processes, it can be seen from the table that, although partial recycling is not able to recover 50 % of the CO_2 emitted, the DR-COG process is able to prevent 40 % of the CO_2 emitted per mol of methanol produced. However, energy consumption also produces CO_2 emissions that need to be considered in this balance. In order to cover as many different scenarios as possible, all three cases contemplated in the evaluation of energetic consumption were considered. Given that the CO_2 emissions per kW·h produced vary according to the country in which the plant is located, 4 different references have been used: USA, People's Republic of China, European Union and Spain. Table 5 shows the kg CO2 emitted/kW·h produced in these countries during the period 2007-2010 [30].

Table 5. CO_2 emissions per kW·h (in kg CO_2/kW·h) produced in USA, the People's Republic of China, the European Union and Spain [30].

	2007	**2008**	**2009**	**2010**
USA	0.560	0.545	0.517	0.522
China	0.822	0.803	0.800	0.766
EU	0.480	0.458	0.439	0.429
Spain	0.387	0.327	0.297	0.238

To perform these calculations only the most recent data available (from 2010) have been employed. Figure 7 shows the final emissions of CO_2 per mol of methanol produced in each process for the different scenarios previously defined.

As can be seen, DR-COG gives rise to considerably lower CO_2 emissions, even when the emissions due to energy consumption are included. The differences vary from 6 % in the least favourable case (Case 3 in China) to 31 % in the most favourable case (Case 1 in Spain). Thus, the environmental benefit obtained with DR-COG depends to a large extent on the location of the plant.



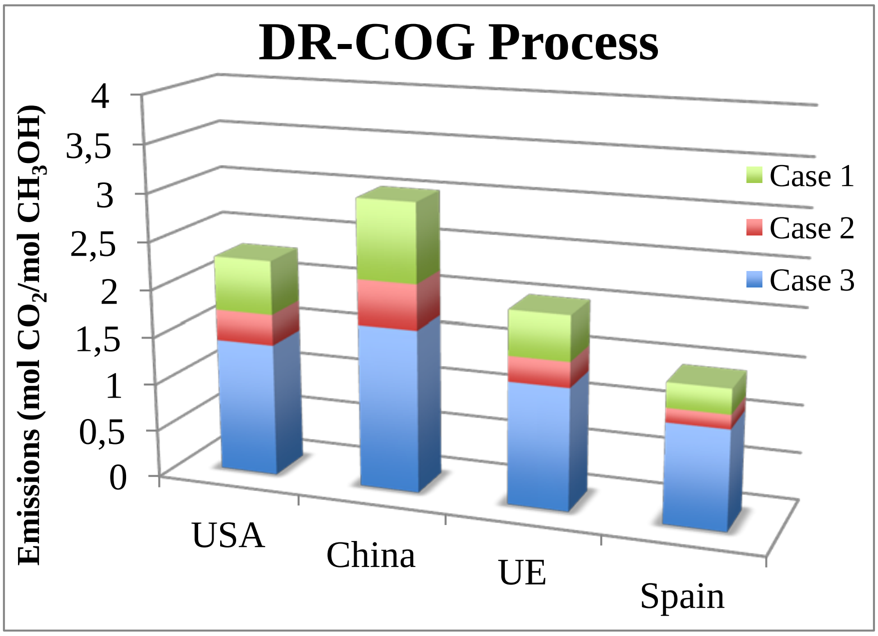


Fig. 7. CO_2 emissions of the CP and DR-COG processes from the streams and energy consumption.

3.3. Carbon and hydrogen yields

Besides energy consumption and CO_2 emissions, another key issue in any industrial process is the need to ensure an efficient exploitation of the raw materials employed. Since in the processes we are comparing the raw materials are different, the most practical way to compare them from the point of view of the raw materials exploitation is to evaluate the carbon and hydrogen yields (Equations 2 to 5), which will provide an idea of the efficiency with which the raw materials are being exploited. Table 6 shows the carbon and hydrogen yields achieved in each process.

Table 6. Carbon and hydrogen yields of the CP and DR-COG processes

	CP	DR-COG
Carbon yield (%)	75.8	79.7
Hydrogen yield (%)	73.2	83.9

Although both processes show high levels of exploitation of the raw materials, the DR-COG process is more efficient than the CP process. Both, the carbon and hydrogen yields are higher in the case of the DR-COG process. Especially noteworthy is the H_2 yield, which is more than 10 % higher in the case of DR-COG. Given that methanol is expected to play an important role as H_2 carrier in the future, this higher yield may be crucial in deciding in favour of the industrial implantation of methanol production from COG using CO_2 reforming to generate the syngas.

3.4. Methanol quality

Finally, the purity of the methanol obtained at the end of the process might necessitate the inclusion of additional purification units (e.g., distillation columns) [1-4]. Depending on its subsequent use, methanol must be able to satisfy different purity requirements, e.g. 99.85 wt % if it is to be used in chemical synthesis or 97-98 wt % if it is to be blended with gasoline as fuel [1].

In the case of the CP process, raw methanol purity is 96.8 wt %, whereas in the case of the DR-COG, the raw methanol purity is 98.4 wt %. Therefore, methanol produced by means of the DR-COG process can be directly used as fuel in blends with gasoline, whereas additional purification is required for other uses. In the case of the CP process, additional purification stages are necessary, which will entail additional energetic and economic costs.

4. Conclusions

A new process for producing methanol from coke oven gas, using CO_2 reforming to produce syngas, has been proposed and compared with the conventional process from different points of view: that of energetic performance, CO_2 emissions, raw materials exploitation and methanol quality.

In the analysis of energy consumption, it was found that the CP process has higher energy requirements than the DR-COG process. However, the CP process allows a higher energy recovery, which might result in lower energy consumption per kg of methanol produced than in the case of DR-COG.

The CO_2 balance revealed that the DR-COG process is more sustainable than the CP process. With respect to direct emissions, although DR-COG is not able to achieve the 50 % of CO_2 recycling, it avoids 40 % of the CO_2 emitted in the conventional CP process. However, the energy consumed produces substantial emissions that significantly affect the global balance of CO_2, which depends to a large extent on the geographic location of the plant.

From the viewpoint of raw materials exploitation, both processes show a high level of exploitation, though DR-COG is the more efficient. Especially interesting are the results of the H_2 yield, which is more than 10 % higher in the case of DR-COG (83.9 % as against 73.2 % with the CP process).

The raw methanol obtained with the DR-COG process also fulfils the purity requirements for use as a fuel without the need for additional purification stages though a higher level of purification will be required for other uses. In the case of the CP process, the level of purity achieved is lower, and further purification will be required in all cases, which will entail higher costs.

To sum up, the novel DR-COG process has been shown to be superior to the conventional CP process from the perspective of environment, raw materials exploitation and purification costs. From the energy point of view, an appropriate energy integration strategy will play a decisive role in turning the scales in favour of one process or the other. DR-COG requires lower energy inputs, but the possibility of recovering energy is considerably higher in the CP process, which could result in a reduction in energy consumption to a level below that achieved by DR-COG.

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New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process.

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Supplementary material

Glossary

Symbol	Description	Units
A	Membrane area	m^2
A_{tot}	Overall membrane area	m^2
F	Feed molar flowrate	mol/s
i	Stage i	dimensionless
J	Permeate flux	$mol(m^{-2}\cdot s^{-1})$
k	Component k	dimensionless
l	Membrane thickness	m
P_k	Permeability of k component	$(mol\cdot m)/(m^2\cdot s\cdot Pa)$
P_F	Feed pressure	Pa
P_P	Permeate pressure	Pa
P_r	Reduced pressure	dimensionless
R	Retentate molar flow rate	mol/s
X	H_2 recovery in each stage	dimensionless
X_{tot}	Total H_2 recovery	dimensionless
y_{Fk}	Mole fraction of the k component in the feed	dimensionless
y_{Rk}	Mole fraction of the k component in the retentate	dimensionless
y_{Pk}	Mole fraction of the k component in the permeate	dimensionless
$\alpha_{H2/k}$	Membrane selectivity of k component- respect to H_2	dimensionless
Θ	Stage-cut	dimensionless

The Aspen Plus® software does not contain a simulation block for membrane separation. To include a membrane separation unit in the simulation, it is necessary to program it with Fortran. Here it is shown how the modelling of the unit was done and the Fortran program that was used in the simulation of the DR-COG process.

1. Modelling of the membrane separation unit

Fig. 1 shows a scheme of the membrane gas separation unit. The feed is the stream RECOVERI which comes from the condenser at 30 ºC and 30 bar. The products are the retentate (the stream PURGE), under the same conditions of temperature and pressure as the feed, and the permeate (the stream H2RECOVE) which leaves the unit at 30 ºC and 1 bar. The objective of the unit was to achieve a H_2 recovery of 40%, which would make it possible to obtain an optimum value for the R parameter in the synthesis gas.

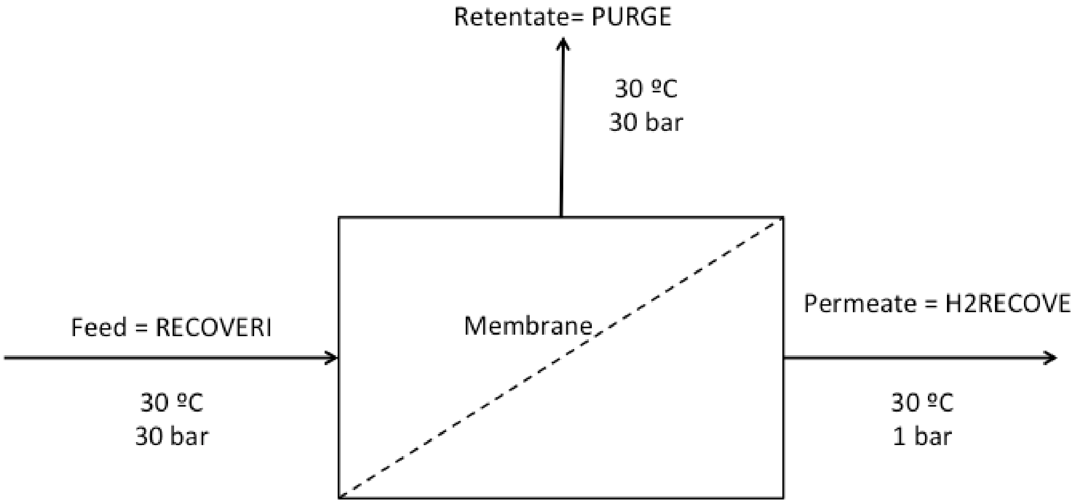

Fig. 1. Scheme of the membrane separation unit

For modelling purposes, the unit was split into several stages and it was assumed that the exiting streams were always perfectly mixed. Each stage was computed so that it would result in a H_2 recovery of 5% (based on the H_2 fed into each stage). The overall calculation involved an iterative loop in which the number of stages was increased until the targeted overall recovery of the unit was 40 %. This model is shown in Fig. 2.

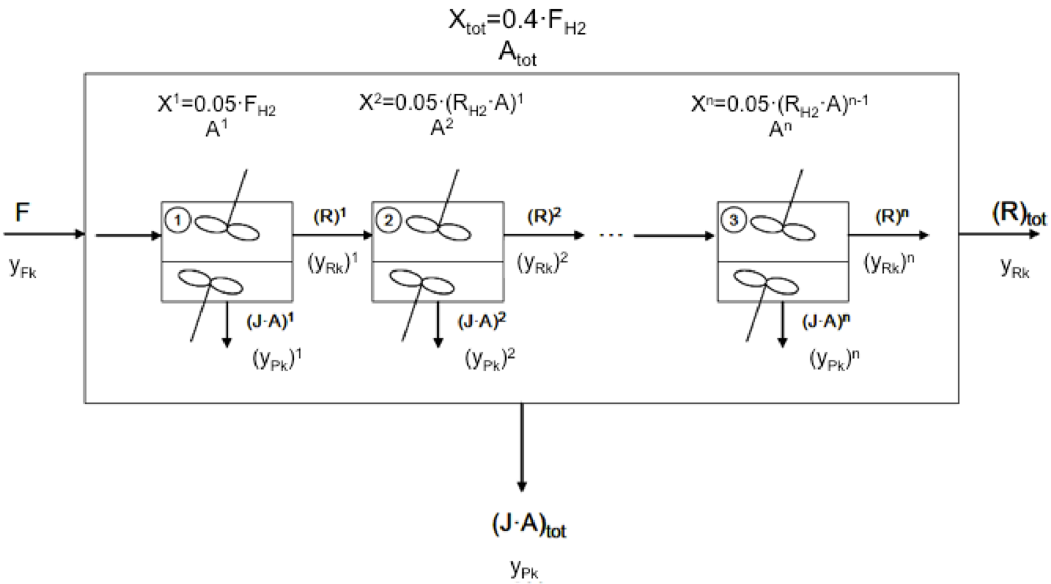

Fig. 2. Model consisting of a series of perfectly mixed stages for the membrane separation unit

In order to solve each of the perfectly mixed stages (Fig. 3), another iterative procedure (an inner loop) was set up, starting with the transport equation and the mass balances for each stage (Equations 1, 2 and 3)

$$J\cdot y_{Pk} = \frac{P_k}{l}\cdot\left(P_F\cdot y_{Rk} - P_P\cdot y_{Pk}\right) \rightarrow \frac{y_{PH_2}}{y_{Pk}} = \alpha_{H_2/k}\cdot\left(\frac{y_{RH_2}-P_r\cdot y_{PH_2}}{y_{Rk}-P_r\cdot y_{Pk}}\right) \qquad \text{(Equation 1)}$$

$$F = J\cdot A + R \qquad \text{(Equation 2)}$$

$$F\cdot y_{Fk} = J\cdot A\cdot y_{Pk} + R\cdot y_{Rk} \qquad \text{(Equation 3)}$$

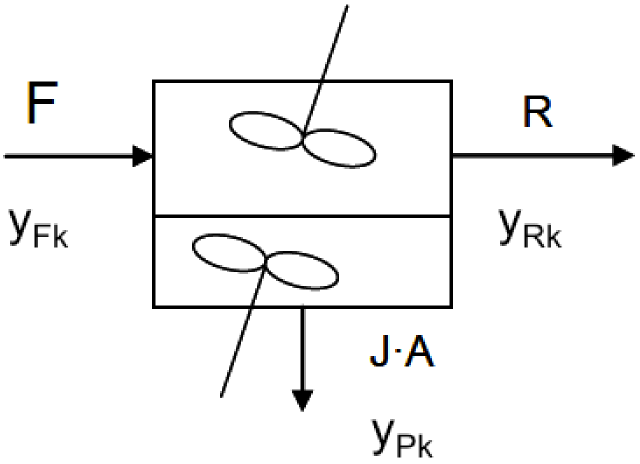

Fig. 3. Scheme of a perfectly mixed stage

The permeated fraction of the feed is then defined, the so-called stage-cut (θ, Equation 4), and the mass balance for the component j is rewritten as follows (Equation 5).

$$\theta = \frac{J \cdot A}{F} \qquad \text{(Equation 4)}$$

$$y_{Fk} = \theta \cdot y_{Pk} + (1-\theta) \cdot y_{Rk} \qquad \text{(Equation 5)}$$

Next, the recovery of the reference component, H_2 (represented by X), is defined and related to the stage-cut. This allows the mass balances of the rest of the compounds to be rewritten on the basis of the reference substance. By rearranging the balances Equation 8 is obtained. This equation is used in the iterative calculation to relate the mole fraction of the i component in the retentate to its molar fraction, those of H_2 in the feed and in the permeate and the H_2 recovery.

$$X = \frac{J \cdot A \cdot y_{PH_2}}{F \cdot y_{FH_2}} = \theta \cdot \frac{y_{PH_2}}{y_{FH_2}} \qquad \text{(Equation 6)}$$

$$y_{Fk} = X \cdot \frac{y_{PH_2}}{y_{FH_2}} \cdot y_{Pk} + \left(1 - X \cdot \frac{y_{PH_2}}{y_{FH_2}}\right) \cdot y_{Rk} \qquad \text{(Equation 7)}$$

$$y_{Rk} = \frac{y_{Fk} \cdot y_{PH_2} - X \cdot y_{FH_2} \cdot y_{Pk}}{y_{PH_2} - X \cdot y_{FH_2}} \qquad \text{(Equation 8)}$$

By substituting Equation 8 into Equation 1 and rearranging, the second equation needed for the iterative procedure (Equation 9) is obtained.

$$y_{Pk} = \frac{y_{Fk} \cdot y_{PH_2}^2}{\alpha_{H_2/k} \cdot \left(y_{PH_2} - X \cdot y_{FH_2}\right) \cdot \left(y_{RH_2} - P_r \cdot y_{PH_2}\right) + y_{PH_2} \cdot \left[P_r \cdot y_{PH_2} + X \cdot y_{FH_2} \cdot \left(1 - P_r\right)\right]}$$

(Equation 9)

The iterative procedure was as follows:

1. The calculation is initialized by estimating a value for $(y_{PH2})^i$. This initial value is obtained from Equation 1 by assuming a maximum transport gradient, e.g., permeate

pressure equal to 0 bar. For the subsequent iterations, this value is updated with the outcome of the previous iteration.

2. $(y_{RH2})^i$ is obtained from Equation 8.
3. $(y_{Pk})^i$ is computed from Equation 9.
4. $(y_{Rk})^i$ is calculated from Equation 8.
5. Convergence is checked by $\sum_{k=1}^{n} (y_{Pk})^i = 1$ and $\sum_{k=1}^{n} (y_{Rk})^i = 1$.
    a. If this condition is not achieved, the value of y_{PH2} is updated as follows:

$$(y_{PH_2})^{i+1} = (y_{PH_2})^i + \left[1 - \sum_{k=1}^{n} (y_{Pk})^i\right] \qquad \text{(Equation 10)}$$

    b. If the condition is achieved, then the stage cut (θ) is calculated by means of Equation 6, the molar flow rates of each component in the permeate and retentate are computed from Equations 11 and 12, and the membrane area from Equation 13.

$$(J \cdot A)_k = \theta \cdot F \cdot y_{Pk} \qquad \text{(Equation 11)}$$

$$(R)_k = F \cdot y_{Fk} - (J \cdot A)_k \qquad \text{(Equation 12)}$$

$$A = \frac{(J \cdot A)}{J} \qquad \text{(Equation 13)}$$

This procedure is repeated for as many stages as are needed in order to achieve the H_2 recovery initially set as a target.

The Fortran programme was then embedded in a custom block within the Aspen Plus simulation package.

2. Implementation of the Fortran programme in Aspen Plus ®

In Aspen Plus ®, before the Fortran programme is introduced, it is necessary to establish which variables need to be imported from the flowsheet to the custom block for the calculation to be performed and those that need to be exported from the Fortran programme to the flowsheet. These variables are shown in Table 1.

Table 1. Imported and exported variables for the Fortran Programme

Imported variables		**Exported variables**	
Fortran Acronym	**Definition**	**Fortran Acronym**	**Definition**
PF	Pressure of RECOVERI stream	XTOT	H_2 recovery. H_2 split of MEMSEP
PP	Pressure of H2RECOVE stream	COREC	CO recovery. CO split of MEMSEP
FEED	Mole flow of RECOVERI stream	CH4REC	CH_4 recovery. CH_4 split of MEMSEP
YFH2	Molar fraction of H_2 in RECOVERI stream	CO2REC	CO_2 recovery. CO_2 split of MEMSEP
YFCO	Molar fraction of CO in RECOVERI stream	N2REC	N_2 recovery. N_2 split of MEMSEP
YFCH4	Molar fraction of CH_4 in RECOVERI stream	METREC	CH_3OH recovery. CH_3OH split of MEMSEP
YFCO2	Molar fraction of CO_2 in RECOVERI stream	H2OREC	H_2O recovery. H_2O split of MEMSEP
YFN2	Molar fraction of N_2 in RECOVERI stream	AREA	Membrane area
YFMET	Molar fraction of CH_3OH in RECOVERI stream		
YFH2O	Molar fraction of H_2O in RECOVERI stream		

2. Fortran programme

```
C    Program GS multicomponent
C    Model of series of stages with perfect mix
C    Calculation based on intervals of 5 per 100 of recovery
C    Perm(7) are the permeabilities of the seven different components
C    fy(7) are the mole fractions in the feed of each of the components
C    X is the H2 recovery at each stage
C    suma_J is the total permeate flux
C    yf(7,100) are the molar fractions of each of the components in the feed at each stage
C    PJ(7,100) are the permeate flux per unit of membrane area at each stage
C    yp(7,100) are the molar fractions of each of the components in the permeate at each
stage
```

```
      Real Perm(7), fy(7), X, suma_J, yf(7,100), PJ(7,100),yp(7,100)

C     i are the stages and k the components
C     c and b are dummies for the iterations

      Integer i, k, b, c

C     yr(7,100) are the molar fractions in the retentate at each stage
C     alfa(7,100) is the membrane selectivity, denominator in Equation 9
C     d(100), e(100) are terms of the denominator of  Equation 9
C     sum_yp is the summation of the mole fractions in the permeate at each stage

      Real yr(7,100), d(100), e(100), alfa(7,100), sum_yp, Error

C     theta(100) are the stage-cuts
C     PJA(7,100) are the permeate molar flow rates of each component at each stage
C     F(100) are the feed molar flow rate at each stage
C     R(7,100) are the retentate molar flow rates of each component at each stage
C     A(100) is the cumulative membrane area of after each stage

      Real theta(100), PJA(7,100), F(100), R(7,100), A(100)

C     Rec(100) is the total recovery after each stage
C     PJA_ac(7) is the cumulative flow rate of retentate of each component after each
stage
C     yp_tot(7) are the final (overall)  mole fractions of each component in the permeate

      Real Rec(100), PJA_ac(7), yp_tot(7)

C     Values of the permeabilities in (mol·m)/(m^2·s·Pa) units

      Perm(1)=2*10**(-7.0)
      Perm(2)=2.3*10**(-8.0)
      Perm(3)=7*10**(-9.0)
      Perm(4)=6.2*10**(-9.0)
      Perm(5)=4*10**(-10.0)
      Perm(6)=6*10**(-7.0)
      Perm(7)=1.7*10**(-6.0)

C     Target total recovery

      XTOT=0.4

C     Reduced pressure

      Pr=PP/PF

C     Mole fractions in the feed
```

```
      fy(1)=YFH2
      fy(2)=YFCO
      fy(3)=YFCH4
      fy(4)=YFCO2
      fy(5)=YFN2
      fy(6)=YFMET
      fy(7)=YFH2O

C     H2 recovery after each stage

      X=0.05

C     First stage

      i=1

C     Initial permeate flux set equal to 0

      suma_J=0

C     Feed of the first stage

      F(i)= Feed

C     Mole fractions of the first stage
C     Initialising the program by calculating permeate flux
C     assuming maximum gradient

      do k=1,7,1
         yf(k,i)=fy(k)
         PJ(k,i)=Perm(k)*100*3600*PF*yf(k,i)
         suma_J= suma_J + PJ(k,i)
      end do

C     Mole fraction of H2 in the permeate assuming maximum gradient

      yp(1,i)=PJ(1,i)/suma_J


C     Initialising the iterative loop for the stage i

C     Calculation of mole fraction of H2 of retentate using Equation 8

  1   sum_yp=yp(1,i)
      yr(1,i)=(yf(1,i)*yp(1,i)-X*yf(1,i)*yp(1,i))/(yp(1,i)-X*yf(1,i))
      d(i)=(yp(1,i)-X*yf(1,i))*(yr(1,i)-Pr*yp(1,i))
      e(i)=yp(1,i)*(Pr*yp(1,i)+X*(1-Pr)*yf(1,i))
```

```
C     Calculation of mole fractions in the permeate using Equation 9
C     Calculation of mole fractions of in the retentate using Equation 8

      do k=2,7,1
         alfa(k,i)=e(i)+d(i)*(Perm(1)/Perm(k))
         yp(k,i)=yf(k,i)*yp(1,i)*yp(1,i)/alfa(k,i)
         yr(k,i)=(yf(k,i)*yp(1,i)-X*yf(1,i)*yp(k,i))/(yp(1,i)-X*yf(1,i))
         sum_yp= sum_yp + yp(k,i)
      end do

C     Convergence check: Calculate the error,

      Error=abs(1-sum_yp)

C     Continue or re-start the iterative loop for the stage

      if (error .GT. 0.0001) then
         yp(1,i)=yp(1,i)+(1-sum_yp)
         go to 1
      end if

C     Calculation of stage-cut

      k=1
      theta(i)=X*(yf(1,i)/yp(1,i))

C     Calculation of permeate and retentate molar flow rates at i stage

      do k=1,7,1
         PJ(k,i)=Perm(k)*100*3600*(PF*yr(k,i)-PP*yp(k,i))
         PJA(k,i)=theta(i)*F(i)*yp(k,i)
         R(k,i)=F(i)*yf(k,i)-PJA(k,i)
      end do

C     Calculation of the membrane area for the i stage

      A(i)=PJA(1,i)/PJ(1,i)

C     Calculation of the cumulative recovery after i stage

      Rec(i)=1-(R(1,i)/(Feed*fy(1)))

C     Finish or re-start iterative loop at  i+1 stage

      if (Rec(i) .LE. XTOT) then
         c=i+1
         F(c)=0

         do k=1,7,1
```

```
                yf(k,c)=yr(k,i)
                yp(1,c)=yp(1,i)
                F(c)=F(c)+R(k,i)
            end do

            i=i+1
            go to 1
        end if

C       Set final H2 recovery

        XTOT=Rec(i)

C       Calculate overall permeate flowrate and membrane area

        b=1
        k=1
        AREA=0

        do k=1,7,1
            PJA_ac(k)=0
        end do

        k=1

        do while (b .LE. i)
            A_tot=A_tot+A(b)

            do k=1,7,1
                PJA_ac(k)=PJA_ac(k)+PJA(k,b)
            end do

        b=b+1
        end do

        PJA_tot=0

        do k=1,7,1
            PJA_tot=PJA_tot+PJA_ac(k)
        end do

C       Calculate final permeate mole fractions

        k=1
        do k=1,7,1
            yp_tot(k)=PJA_ac(k)/PJA_tot
        end do

C       Calculate final recoveries
```

```
if (YFCO .EQ. 0) then
    COREC=0
    else
    COREC=PJA_ac(2)/(FEED*YFCO)
end if

if (YFCH4 .EQ. 0) then
    CH4REC=0
    else
    CH4REC=PJA_ac(3)/(FEED*YFCH4)
end if

if (YFCO2 .EQ. 0) then
    CO2REC=0
    else
    CO2REC=PJA_ac(4)/(FEED*YFCO2)
end if

if (YFN2 .EQ. 0) then
    N2REC=0
    else
    N2REC=PJA_ac(5)/(FEED*YFN2)
end if

if (YFMET .EQ. 0) then
    METREC=0
    else
    METREC=PJA_ac(6)/(FEED*YFMET)
end if

if (YFH2O .EQ. 0) then
    H2OREC=0
    else
    H2OREC=PJA_ac(7)/(FEED*YFH2O)
end if
```

4. CONCLUSIONES/ CONCLUSIONS

En la presente memoria de Tesis se estudia el reformado con CO_2 de gas de coquería con el objetivo de producir un gas de síntesis adecuado para la producción de metanol.

La conclusión general derivada de este trabajo es que la producción de metanol a través del reformado con CO_2 del gas de coquería puede ser un proceso competitivo, que ofrece varias ventajas sobre los procesos convencionales de producción de metanol, entre ellas, menores necesidades energéticas, reducción de emisiones de CO_2 y mayores rendimientos.

Las principales conclusiones de la Tesis se encuentran a continuación, divididas por objetivos según fueron planteados al inicio de la memoria.

1. *Del estudio del equilibrio termodinámico se concluyó que:*

- Para generar un gas de síntesis adecuado para la producción de metanol, mediante el reformado con CO_2 del gas de coquería, es necesario trabajar a temperaturas superiores a 800 ºC, a la presión más baja que permita la economía del proceso y con relaciones CH_4/CO_2 muy próximas a la estequiométrica. De lo contrario, los rendimientos del proceso son muy bajos y/o la composición del gas de síntesis (relación H_2/CO y parámetro R) no es la apropiada. Además, es necesario que el gas de coquería utilizado tenga proporciones de hidrocarburos de cadena corta lo más bajas posibles, para evitar una rápida desactivación del catalizador por depósitos de carbono.

2. *Las conclusiones derivadas del estudio de los catalizadores para el reformado con CO_2 del gas de coquería son:*

- El reformado con CO_2 de gas de coquería tiene lugar a través de dos vías de reacción diferentes. Por un lado, sucede a través de la descomposición de metano seguida de la gasificación de carbono y, por otro lado, a través de la reacción inversa de la *Water Gas Shift* seguida del reformado de metano con vapor de agua.

- Con catalizadores Ni/Al_2O_3 convencionales, el principal mecanismo por el que transcurre el proceso es la reacción inversa de la W*ater Gas Shift* seguida del reformado de metano con vapor de agua. Sin embargo, cuando se utiliza un carbón activo o mezclas de carbón activo con Ni/Al_2O_3 como catalizadores, es difícil determinar cuál de las dos vías es la predominante.

- El carbón activo no es un catalizador adecuado debido a las altas temperaturas necesarias para obtener conversiones y selectividades elevadas. Asimismo, las conversiones alcanzadas no son estables y decaen de forma continuada a lo largo de todo el experimento.

- El catalizador Ni/Al_2O_3 da lugar a elevadas conversiones y selectividades en todo el rango de temperaturas estudiadas, haciendo posible trabajar con velocidades espaciales muy superiores a las alcanzadas con el carbón activo. Las conversiones se mantienen estables durante, al menos, 50 horas, sin presentar síntomas de desactivación. No obstante, se detectó la formación de depósitos de carbono, lo que indica que si la reacción se prolongase por más tiempo, el catalizador podría desactivarse.

- Las mezclas de carbón activo y Ni/Al_2O_3 presentan un efecto sinérgico, que permite obtener mayores conversiones y menores producciones de subproductos que las predichas por la Ley de las Mezclas. La pérdida de superficie específica y microporosidad experimentada por estos materiales, cuando se utilizan conjuntamente, también es menor que la que presentan cuando se utilizan por separado. La presencia de elevadas proporciones de CO en el gas de coquería alimentado disminuye la intensidad de este efecto sinérgico.

- El gas de síntesis obtenido cuando se utilizan catalizadores Ni/Al_2O_3 convencionales o mezclas de éstos con carbón activo, tiene una relación H_2/CO y un parámetro R con valores apropiados para su utilización en la producción de metanol, al contrario que en el caso del gas obtenido utilizando el carbón activo como catalizador.

3. *Del estudio del reformado con CO_2 de gas de coquería utilizando calentamiento con microondas se concluye que:*

- El calentamiento con microondas no da lugar a mejores resultados en el reformado con CO_2 del gas de coquería que cuando se utiliza calentamiento convencional. Únicamente cuando se emplea carbón activo como catalizador es posible aumentar ligeramente las conversiones y selectividades del proceso.

- La presencia de elevadas proporciones de H_2, en combinación con el calentamiento con microondas, da lugar a microplasmas de elevada temperatura, que promocionan la sinterización del catalizador de Ni/Al_2O_3, dando lugar a menores conversiones y selectividades.

4. *Finalmente, las conclusiones obtenidas del estudio comparativo de la producción de metanol a partir del reformado con CO_2 de gas de coquería y las tecnologías convencionales de producción de metanol son:*

- La producción de metanol a través del reformado con CO_2 de gas de coquería da lugar a menores consumos energéticos que la producción convencional. Sin embargo, la tecnología convencional permite alcanzar mayores recuperaciones energéticas, lo que puede dar lugar a menores requerimientos energéticos.

- La producción de metanol a partir de gas de coquería permite reducir de forma considerable las emisiones de CO_2 propias de la producción convencional. De esta forma, el 40% del CO_2 producido, cuando el metanol es utilizado, se consume en su producción en el proceso basado en el gas de coquería, valor muy próximo al 50% teórico. La integración energética de la planta, así como su situación geográfica, determinará el grado de reducción de estas emisiones.

- Desde el punto de vista del aprovechamiento de las materias primas, la producción de metanol a partir de gas de coquería, mediante reformado con CO_2, permite obtener mayores rendimientos en carbono e hidrógeno que la tecnología convencional. Especialmente reseñable es el caso del rendimiento en H_2, que es hasta un 10% superior. La pureza del metanol obtenido también es mayor en el proceso de producción a partir de gas de coquería, reduciendo los costes asociados a la etapa de purificación. De hecho, es posible utilizar el metanol obtenido a partir del gas de coquería como combustible, sin necesidad de ningún proceso de purificación extra.

4. CONCLUSIONES

Para una posible futura implantación industrial de esta tecnología es necesario llevar a cabo, previamente, un análisis económico para determinar su viabilidad. Hay una serie de factores que sugieren que este análisis podría dar lugar a conclusiones favorables a la implantación de esta tecnología:

a) Se valorizan dos gases residuales: el gas de coquería y el CO_2. Actualmente el gas de coquería se quema en antorchas o se emite directamente, generando importantes emisiones de gases de efecto invernadero y dando lugar a bajas eficiencias económicas. Sin embargo, en este proceso es posible obtener un valioso producto, como es el metanol. Por su parte, los problemas asociados al CO_2 son bien conocidos. Con esta tecnología es posible reducir las emisiones de CO_2 asociadas a los procesos convencionales de producción de metanol, lo que puede dar lugar a beneficios económicos en los mercados de emisiones.

b) Los prometedores resultados obtenidos cuando se utilizan las mezclas de carbón activo y Ni/Al_2O_3 como catalizador pueden dar lugar a una reducción de los costes del proceso de reformado, ya que estas mezclas son más baratas que los catalizadores convencionales.

c) El reformado con CO_2 de gas de coquería tiene lugar, principalmente, a través de una vía de reacción diferente a la del reformado con CO_2 de metano, por lo que la velocidad de desactivación de los catalizadores puede ser considerablemente menor, tendiendo más bien hacia la propia del reformado de metano con vapor de agua. De esta forma, podría evitarse el principal obstáculo para la implantación industrial del reformado seco.

The present Thesis deals with the CO_2 reforming of coke oven gas with the aim of producing a syngas suitable for methanol production.

The general conclusion of this work is that the production of methanol via the CO_2 reforming of COG can be a competitive process that offers several technical advantages over conventional methanol production, including lower energy requirements, a reduction of CO_2 emissions and higher yields.

The main conclusions of the work are presented below. These conclusions try to answer the questions posed by the objectives presented at the beginning of the study and so they are divided according to these objectives.

1. *From the study of the thermodynamic equilibrium it has been concluded that:*

- The production of an appropriate syngas for methanol production by means of the CO_2 reforming of coke oven gas requires temperatures higher than 800ºC, the lowest possible pressure and a CH_4/CO_2 ratio as close to the stoichiometric ratio as possible. Otherwise, low yields and/or poor H_2/CO ratio and R parameter values are obtained. Moreover, the proportions of light hydrocarbons in the coke oven gas need to be minimal in order to minimize deactivation of the catalyst.

2. *The conclusions relating to the study of the catalysts for the CO2 reforming of COG are as follows:*

- The CO_2 reforming of coke oven gas takes place via two different reaction mechanisms. The first mechanism consists of methane decomposition followed by carbon gasification, whereas the second involves the reverse Water Gas Shift followed by methane steam reforming.

- When Ni/Al_2O_3 catalysts are used, the main reaction mechanism is the reverse Water Gas Shift followed by methane steam reforming. However, when activated carbon or mixtures of activated carbon and Ni/Al_2O_3 are employed as catalyst it is difficult to establish the predominant reaction mechanism.

- Activated carbon is not an appropriate catalyst due to the high temperatures required to obtain high conversions and selectivities. Moreover, the conversions achieved are not stable and decrease continuously as the experiment progresses.

- Ni/Al_2O_3 led to high conversions and selectivities over the entire range of temperatures studied, making it possible to work at considerably higher VHSVs than with activated carbon. The stability of the conversions was maintained over 50 hours with no signs of deactivation. However, carbon deposits were found, indicating that if the reaction had continued for a longer period of time, the catalyst might would have eventually lost its catalytic activity.

- Mixtures of activated carbon and Ni/Al_2O_3 have a synergetic effect, giving rise to higher conversions and lower water productions than those predicted by the law of mixtures. The loss of BET surface area and microporosity experienced by the materials when they are used in the mixtures is considerably lower than when they are used by themselves. The presence of high proportions of CO undermines the strength of the synergetic effect.

- The syngas produced from using Ni/Al_2O_3 and mixtures of activated carbon and Ni/Al_2O_3 as catalyst has appropriate H_2/CO ratio and R parameter values for methanol production, unlike the syngas obtained when activated carbon is used as catalyst.

3. *From the study of the microwave-assisted CO2 reforming of COG it has been concluded that:*

- Microwave heating does not enhance the CO_2 reforming of COG as it enhances the CO_2 reforming of methane. Only when activated carbon is used as catalyst is it possible to increase conversions and selectivities, but this increase is not significant.

- The presence of large amounts of H_2 in combination with microwave heating gives rise to microplasmas of very high temperatures that promote the sintering of the Ni/Al_2O_3 catalyst, resulting in poor conversions and selectivities.

4. *Finally, the conclusions derived from the comparison of the production of methanol by means of the CO2 reforming of COG with conventional production technology are:*

- Methanol production via the CO_2 reforming of COG leads to lower energy consumptions than conventional production. However, with conventional production higher energy recoveries are possible, which might eventually result in lower energy requirements than in the case of methanol production from COG.

- COG-based methanol production is able to reduce CO_2 emissions in a great extent in comparison with conventional production. Moreover, 40% of the CO_2 produced when methanol is used is consumed in the COG-based process, which is very close to the theoretical maximum of 50%. The energy integration of the plant and geographical location of the facilities determine the extent of reduction.

- From the viewpoint of raw material exploitation, methanol from COG via CO_2 reforming gives rise to higher carbon and hydrogen yields than conventional production. Especially noteworthy is the hydrogen yield, which is 10% higher in the case of COG based methanol production. The purity of the methanol produced by means of the CO_2 reforming of COG is also higher, leading to lower purification costs. Furthermore, it is possible to use COG-derived methanol directly as a fuel.

Any possible future industrial implantation of this technology will first require an economic analysis of its viability. Nevertheless, certain factors suggest that such an economic analysis would decide in favour of its implantation:

d) This technology valorises two residual gases: COG and CO_2. At present the surplus of COG is burnt away in torches or directly emitted to the air, contributing to the serious environmental problem of greenhouse gases emissions and resulting in low economic efficiency. In this process it is possible to obtain a valuable product from this waste gas. The problems associated with CO_2 are well known. With this process it is possible to reduce CO_2 emissions in comparison with conventional technologies. This could yield economic benefits in the emission markets.

e) The promising results obtained when mixtures of activated carbon and Ni/Al_2O_3 are used as catalyst could reduce the cost of the reforming process, since such mixtures are cheaper than conventional catalysts.

f) The CO_2 reforming of COG takes place mainly via a reaction mechanism different from the CO_2 reforming of methane, so the deactivation rate of the catalyst would be considerably lower than that of to the CO_2 reforming of methane tending towards that of steam reforming. Thus, the main obstacle to the industrial implantation of CO_2 reforming could be avoided.

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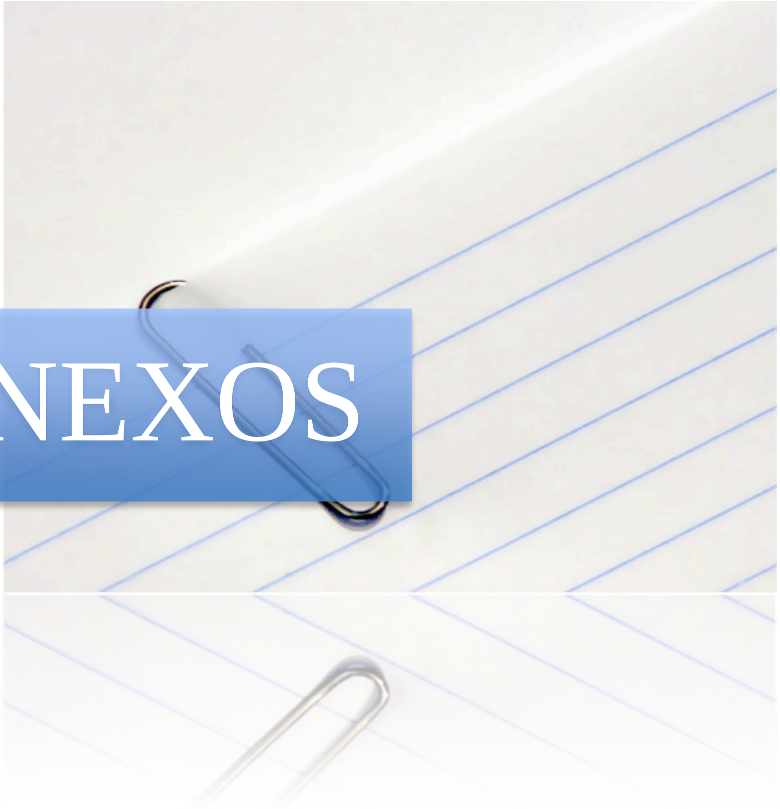
6. ANEXOS



ANEXO 1. OTROS CATALIZADORES PARA EL REFORMADO CON CO_2 DE METANO

En el transcurso de este trabajo se han utilizado otros catalizadores que, a pesar de dar lugar a buenas conversiones en el reformado de metano con CO_2, no permitieron obtener buenos resultados en el reformado con CO_2 de gas de coquería. Por este motivo, los resultados previos obtenidos en el reformado seco de metano con dichos catalizadores se muestran en este Anexo.

Tal y como se ha indicado en la Sección 3.2 *Catalizadores para el reformado con* CO_2 *de gas de coquería*, el carbón activo FY5 ha demostrado ser un catalizador efectivo para realizar el reformado con CO_2 de metano, en experiencias previas al trabajo realizado en esta Tesis. Durante los últimos años, los materiales carbonosos se están mostrando como una alternativa muy interesante a los catalizadores metálicos convencionales, en reacciones catalíticas heterogéneas. En el caso del reformado de metano con CO_2, los catalizadores metálicos convencionales presentan poca resistencia a la desactivación por depósitos de carbono (como es el caso de los catalizadores de Ni) o son caros y tienen una disponibilidad limitada (como es el caso de los metales nobles). Por su parte, los catalizadores carbonosos, especialmente los carbones activos, se caracterizan por una serie de propiedades físico-químicas que les otorgan una gran versatilidad para poder hacer frente a algunos de estos problemas asociados a los catalizadores metálicos. Entre estas propiedades destacan su bajo coste, elevada resistencia mecánica, gran superficie específica, la posibilidad de modificar fácilmente su distribución de tamaño de poros y su química superficial, buenas propiedades reductoras así como, en caso de ser utilizados como soporte catalítico en vez de cómo catalizadores por sí solos, la posibilidad de recuperar el metal activo de forma sencilla, simplemente quemando la fase carbonosa.

En varios trabajos realizados por el Grupo de Microondas y Carbones para Aplicaciones Tecnológicas, este carbón activo ha dado lugar a buenos resultados en diferentes situaciones: usándolo por sí solo en horno eléctrico y microondas[55, 72, 81, 87, 89, 90] o utilizándolo como soporte catalítico de Ni y en mezclas con escorias de alto horno. Los resultados de estos dos últimos casos se muestran en los artículos:

- *Synthesis of carbon-supported nickel catalysts for the dry reforming of* CH_4, publicado en Fuel Processing Technology (2010), 91 (7), 765-769.
  Mi participación en este trabajo consistió en la preparación de los catalizadores, así como en el análisis y discusión de los resultados.

- *Mixtures of Steel-Making Slag and Carbons as Catalyst for Microwave-Assisted Dry Reforming of CH_4,* publicado en Chinese Journal of Catalysis (2012), 33(7), 1115-1118.

  Mi participación en este artículo consistió en la caracterización de los materiales utilizados como catalizadores, así como en la realización de los test de reformado y en el análisis y la discusión de los resultados.

En el artículo *Synthesis of carbon-supported nickel catalysts for the dry reforming of CH_4* se estudia el efecto de las condiciones de síntesis del catalizador sobre sus propiedades catalíticas en el proceso de reformado seco de metano. Concretamente, se estudió:

1. La diferencia entre utilizar calentamiento convencional o calentamiento con microondas en la etapa de secado posterior a la impregnación de la fase activa.

2. El efecto de la temperatura de reducción, que se realizó a 300 y 500 ºC.

3. La influencia de la química superficial del carbón activo. Para ello se utilizó el carbón activo sin tratar y tras ser oxidado con una disolución saturada de $(NH_4)S_2O_8$ en H_2SO_4 2 M.

Los resultados del estudio mostraron que la oxidación previa favorece la interacción entre la superficie del soporte y el Ni, dando lugar a menores tamaños de partícula de Ni y una mejor dispersión del mismo. También la temperatura de reducción, afecta en este aspecto, ya que cuanto mayor es, menor es el tamaño de partícula y mejor la dispersión. Por su parte, el uso del microondas en la etapa de secado da lugar a una reducción importante del tiempo de operación así como a una disminución del tamaño de partícula. Por otro lado, la utilización del calentamiento con microondas también permite minimizar la influencia de la química superficial sobre las propiedades catalíticas del catalizador.

De cualquier forma, la necesidad de trabajar a temperaturas elevadas (al menos 800 ºC) para llevar a cabo el reformado seco, provoca una sinterización de las partículas de Ni, que hace que la mejora conseguida con los diferentes tratamientos, en cuanto a tamaño de partícula y dispersión, no afecte a los resultados del proceso.

Por su parte, en el artículo *Mixtures of Steel-Making Slag and Carbons as Catalyst for Microwave-Assisted Dry Reforming of* CH_4 se estudia la actividad catalítica de diferentes materiales y mezclas de los mismos (carbón activo FY5, coque metalúrgico, escorias siderúrgicas ricas en hierro y un catalizador convencional Ni/Al_2O_3) utilizando el microondas como medio de calentamiento.

En este estudio se pudo ver que, de entre los materiales carbonosos, el carbón activo FY5 funciona mucho mejor como catalizador que el coque metalúrgico, tanto por separado (el FY5 tiene buena actividad catalítica mientras que el coque apenas cataliza la reacción) como en las mezclas con las escorias metalúrgicas y el catalizador Ni/Al_2O_3 (en las que da lugar conversiones mayores y más estables).

En cuanto a los materiales no carbonosos, las escorias y el catalizador Ni/Al_2O_3, se pudo observar que el catalizador convencional es muy superior a la escoria. Para su calentamiento en microondas, ambos tienen que ser mezclados con un material carbonosos que actúe como captador, pero sea cual sea este captador, el catalizador convencional dio lugar a mejores conversiones que la escoria.

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Synthesis of carbon-supported nickel catalysts for the dry reforming of CH_4

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ABSTRACT

A series of carbon-based nickel (Ni) catalysts was prepared in order to investigate the effect of the preparation method on the dispersion of Ni and its final catalytic activity in the dry reforming of methane, i.e. $CH_4 + CO_2 = 2H_2 + 2CO$. Three parameters were studied: (i) the influence of the surface chemistry of the carbon used as support; (ii) the method of drying (conventional *vs.* microwave drying); and, (iii) the temperature of the reduction stage. In order to study the role of the surface chemistry of the commercial activated carbon used as support, the active carbon was tested as received and oxidized. Although a better Ni dispersion was achieved over the oxidized support, the conversions were much lower. It was also found that microwave drying offers various advantages over conventional drying, the main one being that less time is required to prepare the catalyst. Two reduction temperatures were used (300 and 500 °C), being found that it is necessary to adjust this parameter to prevent the Ni particles from sintering.

1. Introduction

During recent years the dry reforming of CH_4 to produce synthesis gas ($H_2 + CO$) has received a lot of attention, since this method offers certain advantages over other technologies, e.g. steam reforming or partial oxidation. One of these advantages is the fact that not only CH_4 but also CO_2, both of which are greenhouse gases, is consumed in the reaction. Secondly, a lower H_2/CO ratio is obtained, which is preferable for the synthesis of high hydrocarbon and oxygenated derivatives. Thirdly, a more efficient use in Chemical Energy Transmission Systems is achieved [1–5].

Research efforts in this field have been mainly focused on developing catalysts resistant to the deactivation resulting from carbon deposition. The way a catalyst is prepared determines its final properties. Thus, besides the metal used as catalyst, it is necessary to optimize the characteristics of the support, the interactions between the support and the metal and the parameters involved in each stage of preparation [1–5].

Nearly all of the metals in Group VIII have been studied over different supports, giving rise to good catalytic activity [1–5], nickel being the one which is leading the studies on this matter. Although Ni is more susceptible to coke formation, and therefore to deactivation than noble metals like Rh, Pt, Ru or Ir, its low cost and high availability, make it very attractive for possible future implementation on an industrial scale [1–5].

The choice of support is important in the preparation of a catalyst, because it can have a great influence on the activity and deactivation of the catalyst [1–5]. A variety of materials have been tested as Ni support in the reaction of dry reforming of CH_4, e.g. inorganic oxides [1,2,5] and carbon materials [3–5]. The use of carbon materials as supports of heterogeneous catalysts has grown in the last few decades. Activated carbons are probably the most frequently used carbon materials for this application, since they offer certain advantages, such as their low cost, high mechanical resistance, high surface area, the possibility of modifying the pore size distribution, good reductive properties, easy recovery of the active metal from the spent catalyst by burning off the support and the possibility of modifying easily their surface chemistry [3,4,6]. This last property is a key factor, since the surface chemistry has a strong influence on the interaction between the support and the catalytic metal during the impregnation step [6]. If the interaction between the support and Ni is strong, Ni is more likely to be firmly deposited and well dispersed over the surface of the support [6]. This Ni/support interaction can be enhanced by the presence of acidic oxygen groups on the surface of the carbon support. Thus, it is sometimes necessary to subject the support to pre-treatment in order to increase the presence of these groups [6].

Other preparation steps that have a significant influence on the final properties of a catalyst include drying and reduction [7–10]. The former is commonly carried out in conventional ovens, so that long periods of time are necessary for this process to be completed. A more attractive alternative technique is that of microwave drying. This method offers certain advantages over the conventional process, like the shorter drying times required (which contributes to lowering the cost of the process), and a more uniform heating (which leads to a better dispersion of the Ni over the surface of the support [7–10]). As far the reduction stage is concerned, it is necessary to determine the right reduction temperature in order to avoid sintering, as this produces catalysts with large metal particle sizes and a poor distribution.

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The aim of this work was to study the influence of the drying method, the reduction temperature and the surface chemistry of the activated carbons used as supports, upon the characteristics of the carbon-supported Ni catalysts and upon their final catalytic activity in the dry reforming of methane.

2. Experimental section

2.1. Catalysts preparation

A series of carbon-based Ni catalysts was prepared from a commercial active carbon in accordance with the following steps: (i) pre-treatment of the support; (ii) impregnation of the support; (iii) drying of the catalyst; and (iv) reduction of the catalyst.

2.1.1. Pre-treatment of the support

A commercial activated carbon (Filtracarb FY5), whose main characteristics are summarized elsewhere [11], was used as support for producing the catalysts. This activated carbon was employed as received (labeled as FY5) and oxidized (labeled as FY5ox). The commercial activated carbon was oxidized by dipping it in a saturated solution of $(NH_4)S_2O_8$ in H_2SO_4 2 M, in a proportion of 1 g of activated carbon per 10 mL of solution. The mixture was maintained under stirring for 17 h and, after this period of time, the oxidized carbon was filtered and washed with hot distilled water until the filtrate became neutral and then it was dried.

2.1.2. Impregnation of the support

FY5 and FY5ox were impregnated using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The concentration of the solution was such that the final catalyst would have a Ni content of 5 wt.%. The carbon supports were dipped into the solution in a proportion of 1 g of carbon to 5 mL of solution. The mixtures were then treated in an ultrasound bath for 7 h. After impregnation, the FY5 and FY5ox samples were labeled FY5Ni and FY5oxNi, respectively.

2.1.3. Drying of the catalyst

The samples were dried after the impregnating stage by using conventional or microwave heating. Thus, some impregnated samples were dried overnight in a conventional oven at 100 °C (labeled by adding E). Other samples were dried by means of microwave irradiation. The microwave devices used are described elsewhere [12,13]. The sample was heated up to 100 °C and maintained at this temperature for 12 min. These samples were labeled adding MW.

2.1.4. Reduction of the catalyst

The catalysts were reduced in a horizontal oven, under H_2 atmosphere (flow rate of 50 mL min^{-1}) at two different temperatures: 300 and 500 °C (these samples were labeled by adding 300 and 500, respectively). The temperature was increased from room temperature to the pre-set operating value at a heating rate of 10 °C min^{-1}, and held for 2 h before being allowed to cool down to room temperature. The final catalysts obtained and their corresponding preparation conditions are summarized in Table 1.

Table 1
Carbon-supported Ni catalysts studied and their preparation conditions.

Catalyst	Pre-treatment of the support	Drying method	Temperature of reduction (°C)
FY5Ni-E-300	None	Electric oven	300
FY5oxNi-E-300	Oxidation	Electric oven	300
FY5oxNi-E-500	Oxidation	Electric oven	500
FY5Ni-MW-300	None	Microwave oven	300
FY5oxNi-MW-300	Oxidation	Microwave oven	300
FY5oxNi-MW-500	Oxidation	Microwave oven	500

2.2. Catalyst characterization

Textural characterization was carried out by CO_2 adsorption–desorption isotherms at 0 °C and N_2 adsorption–desorption isotherms at −196 °C in a pressure range of 0–1 bar, in a Micromeritics Tristar 3000 instrument. The Dubinin–Raduskevich (DR) method [14] was applied to the N_2 and CO_2 adsorption isotherms, whereas the BET method was used for the N_2 adsorption isotherms [15].

The Ni particle size was evaluated by X-ray diffraction and Scherrer's equation [16]. The X-ray diffractograms were collected by a Bruker D8 Advance diffractometer equipped with a Göbel mirror and a Cu Kα radiation tube ($\lambda = 0.15406$ nm).

For the temperature-programmed reduction experiments (TPR), the samples were heated up to 400 °C at a heating rate of 5 °C min^{-1} in a stream containing 10% H_2 in Ar at a flow rate of 50 cm^3 min^{-1}. The sample was held at this temperature for 2 h. Once the sample had cooled down to room temperature, the gas was changed to pure argon in order to perform the temperature programmed-desorption (TPD) experiments. In the TPD tests, the amount of H_2 desorbed was evaluated by a mass spectrometer that analyzed the gases evolved when the sample was heated up to 800 °C at a rate of 15 °C min^{-1}.

2.3. Dry reforming experiments

The dry reforming experiments were carried out in a quartz reactor charged with the catalysts under study and heated in a cylindrical and vertical electric furnace up to 800 °C. The temperature was measured by placing a thermocouple inside the catalyst bed. The composition of the gas mixture fed into the system was 50% CH_4–50% CO_2 and the total volumetric hourly space velocity (VHSV) was 0.32 L g^{-1} h^{-1}. Before the reactant gases were introduced, the system was flushed with a nitrogen flow rate of 60 mL min^{-1} for 20 min and then heated up to the operating temperature (800 °C) under this inert atmosphere. The reaction was carried out for 150 min. The outflow gas was collected in Tedlar® sample bags and analyzed in a Varian CP-3800 gas-chromatograph equipped with a TCD detector and two columns connected in series.

The conversions of methane and carbon dioxide were calculated by means of Eqs. (1) and (2), respectively:

$$CH_4\text{conversion, vol.\%} = 100 \times [(H_2)_{out}/2]/[(CH_4)_{out} + (H_2)_{out}/2] \quad (1)$$

$$CO_2\text{conversion, vol.\%} = 100 \times [(CO)_{out}/2]/[(CO_2)_{out} + (CO)_{out}/2] \quad (2)$$

where $(CH_4)_{out}$, $(H_2)_{out}$, $(CO_2)_{out}$ and $(CO)_{out}$ are the methane, hydrogen, carbon dioxide and carbon monoxide concentrations in the effluent gas (vol.%), as determined by gas chromatography.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the N_2 adsorption–desorption isotherms of some of the carbon-based Ni catalysts prepared under different conditions and their corresponding carbon supports (i.e, as received activated carbon, FY5, and the oxidized support FY5ox). All the samples present type I isotherms according to the BDDT classification [17], indicating that they are microporous materials. The oxidized carbon support, FY5ox, shows an increase in N_2 adsorption capacity at low relative pressures compared to the original carbon FY5, indicating that the oxidation treatment produces an increase in microporosity. This is confirmed by an increase in the S_{BET} value by c.a. 95 m^2 g^{-1} (see Table 2). In relation to the textural properties of the carbon-based Ni catalyst, no significant differences can be observed among the samples dried by different methods or reduced under different temperatures, which indicates that neither of these variables has any relevant influence

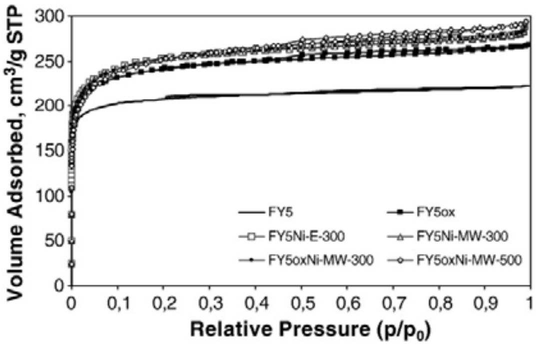

Fig. 1. N_2 adsorption–desorption isotherms at −196 °C of carbon supports (FY5 and FY5ox) and some of the Ni-based catalysts prepared.

on the final textural properties of the prepared catalysts. Also worthy of mention is the increase in the S_{BET} and pore volume observed for Ni catalysts obtained when using a non-oxidized activated carbon as support. The increase in the porosity of these samples could be due to the removal of adsorbed species from the carbon surface during the reduction treatment [18]. In the case of the Ni catalysts which were prepared over oxidized activated carbon, the same effect may have taken place. However, the increase in porosity could have been partially compensated by a decrease in this parameter due to the blockage caused by the larger Ni particles present in these samples.

Fig. 2 shows the Ni particle sizes obtained applying Scherrer's equation to the different X-ray diffractograms of the carbon-supported Ni catalyst. It can be seen that the surface chemistry of each carbon support, the drying method used to remove the solvent and reduction temperature of the catalyst have a strong influence on the size of the Ni particles supported on the carbon. The reduction temperature is the variable that has the greatest influence on the Ni particle size of the samples. Fig. 2 shows that a reduction temperature of 500 °C produces much larger Ni particle sizes (i.e. 130–170 Å) than the samples reduced at 300 °C. The TPR profiles of the different catalysts (not shown) show that a temperature of 300 °C is enough to reduce the Ni supported on the carbons studied. Higher reduction temperatures could produce the decomposition of some surface functional groups on the carbon support, promoting simultaneously the diffusion and sintering of the reduced Ni particles. It is this reason that at 500 °C large particle sizes are obtained. In contrast, the samples reduced at 300 °C present much lower particle sizes (i.e. 23–50 Å). In other words, in order to achieve an acceptable Ni dispersion, the reduction temperature needs to be adjusted.

Table 2
Textural parameters of carbon-supported Ni catalysts prepared under different conditions.

Sample	N_2 adsorption at −196 °C			CO_2 adsorption at 0 °C
	S_{BET} ($m^2 g^{-1}$) ±5	V_T ($cm^3 g^{-1}$)	W_0–N_2 ($cm^3 g^{-1}$) ±0.01	W_0–CO_2 ($cm^3 g^{-1}$) ±0.01
FY5	825	0.343	0.323	0.277
FY5ox	930	0.413	0.352	0.278
FY5Ni-E-300	974	0.437	0.370	0.221
FY5oxNi-E-300	975	0.446	0.374	0.239
FY5oxNi-E-500	953	0.452	0.361	0.221
FY5Ni-MW-300	969	0.431	0.365	0.230
FY5oxNi-MW-300	966	0.438	0.362	0.256
FY5oxNi-MW-500	949	0.451	0.355	0.219

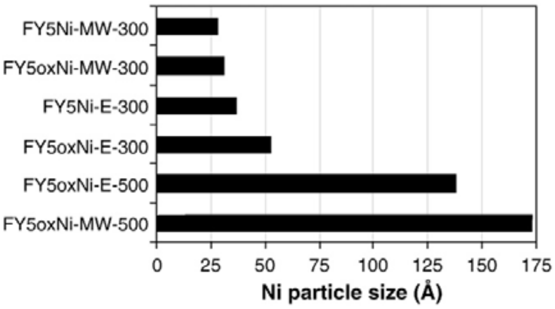

Fig. 2. Ni particle sizes in the carbon-supported Ni catalysts prepared under different conditions.

The influence of the surface chemistry of the carbon support and the drying method used on the preparation of the Ni catalyst was also studied for the samples obtained at the reduction temperature of 300 °C. It was observed that, independently of the surface chemistry of the carbon support, the use of microwave drying produces Ni catalysts with smaller particle sizes, compared to the samples dried by conventional drying. This means that microwave drying favours the dispersion of Ni particles over the carbon support. In addition, the time required to complete the drying stage is an important parameter which must be taken into account. The use of microwave oven greatly reduces the time required for this step (from several hours to approximately 15 min). As for the effect of surface chemistry, this variable was observed to have only a slight influence on the Ni particle size. In general, the Ni catalysts prepared with the oxidized support have larger Ni particle sizes. However, it should be noted that the influence of this variable seems to depend on the method used for the drying step. Thus, if microwave drying is used, the influence of the surface chemistry is not as pronounced as when conventional drying is employed. In fact, FY5Ni-MW-300 and FY5oxNi-MW-300 have similar particle sizes (i.e. 28 and 30 Å, respectively), whereas the samples dried using conventional drying show a wider range of particle sizes (i.e. 36 and 52 Å, for samples FY5Ni-E-300 and FY5oxNi-E-300, respectively). Therefore, microwave heating not only diminishes the Ni particle sizes and the time of preparation, compared to conventional heating, but it also reduces the effect of the surface chemistry on the Ni particle size.

Fig. 3 shows the H_2 temperature-programmed desorption profiles, between 50 and 800 °C, of the carbon-based Ni catalysts reduced at 300 °C. In the case of FY5 and FY5ox, no desorption peaks can be observed (not shown). However, the Ni catalysts obtained using the non-oxidized activated carbon as support (i.e. FY5Ni-E-300 and FY5Ni-MW-300) present two different peaks, the first one at low temperature,

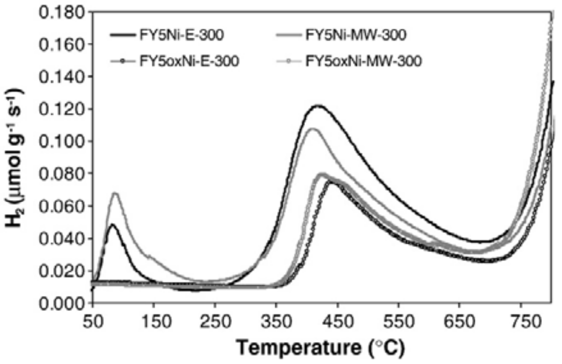

Fig. 3. Temperature-programmed hydrogen desorption profiles of carbon-supported Ni catalyst prepared under different conditions.

at around 80 °C for both catalysts, and the second one at around 410 °C. According to previous works [19,20], the first peak corresponds to hydrogen adsorbed onto the Ni which does not interact with the support. The second peak can be assigned to hydrogen that has been more thoroughly adsorbed, probably due to the presence of the spillover effect [21], as a result of a Ni/support interaction. Thus, it can be assumed that the higher the temperature of this peak, the greater the interaction between the nickel and the support. The Ni catalysts prepared using oxidized activated carbon as support (i.e. FY5oxNi-E-300 and FY5oxNi-MW-300) only show one peak at high temperature, i.e. the one corresponding to the hydrogen desorbed from the Ni with high interaction with the support. In addition, this peak appears at higher temperatures than for the Ni catalysts obtained using FY5 as support. This means that oxidation of the support favours the interaction between the Ni particles and the carbon surface. This can be explained taking into account that the incorporation of oxygen functional groups during oxidation produces a decrease in the PZC of the carbon supports, i.e., an O content of 2.8 wt.% dry basis and PZC = 10, in the case of FY5, and 16.4 wt.% dry basis and PZC = 1.8, in the case of FY5ox. Since the pH of the Ni impregnating solution is about 5, only in the cases where the PZC of the carbon support is lower than 5, the favourable electrostatic interactions between Ni cations and surface functional groups of carbon take place [22]. For this reason, when FY5ox is used as support practically all the nickel interacts with the carbon support, unlike the FY5 samples, where no attractive electrostatic interaction between the nickel and the carbon support occurs.

3.2. Catalytic activity

The catalytic properties of the samples studied were tested for the dry reforming reaction of CH_4. Ni catalysts supported on non-oxidized carbon and reduced at 300 °C show the best performance for dry reforming (see Fig. 4). In spite of the advantages of using microwave to prepare the carbon-based Ni catalysts, the catalytic activity of the

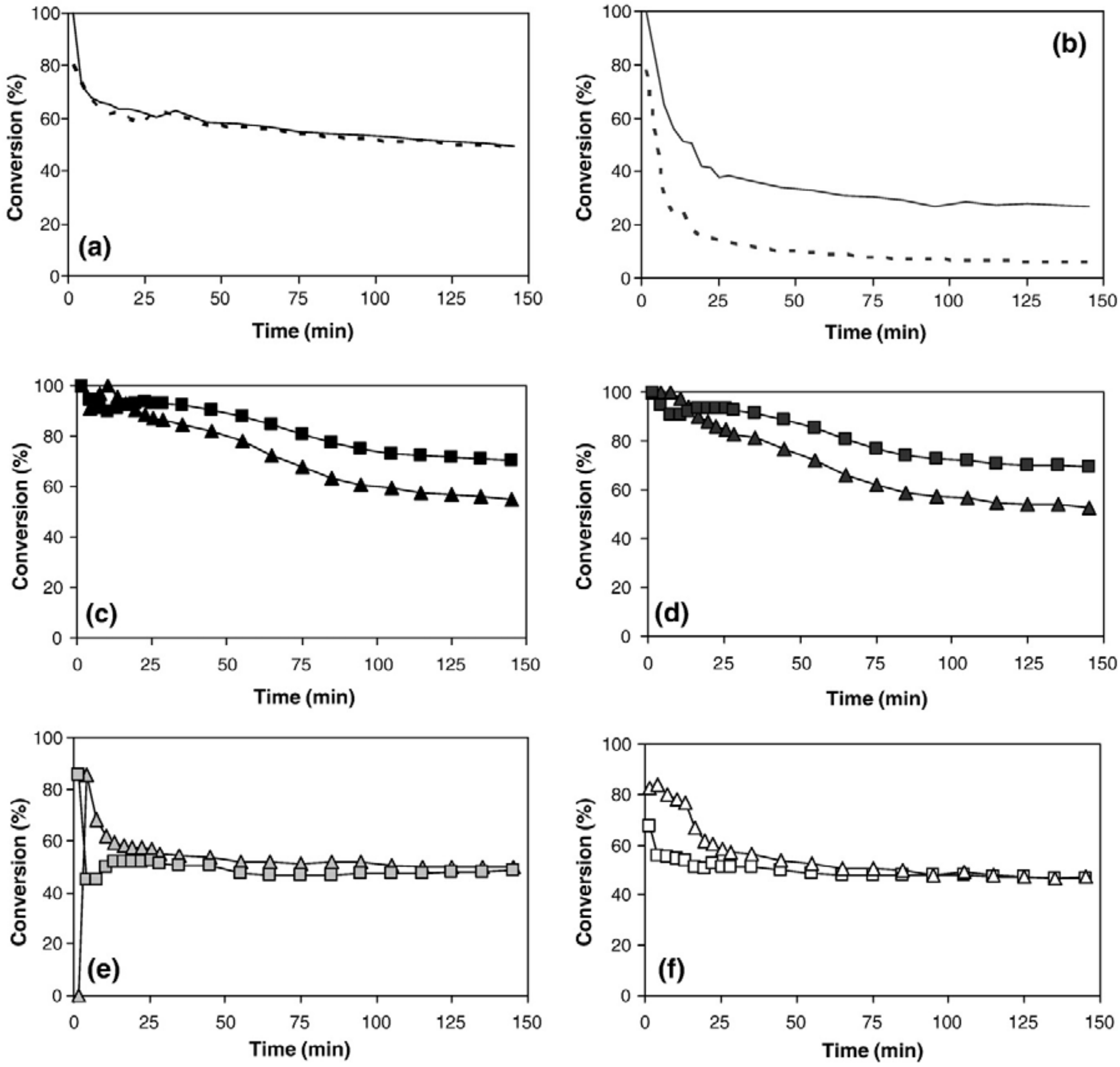

Fig. 4. CH_4 conversion (continuous line or triangles) and CO_2 conversion (dotted line or squares) corresponding to the dry reforming reaction carried out over carbon supports and some of the carbon-supported Ni catalyst prepared: (a) FY5; (b) FY5ox; (c) FY5Ni-MW-300; (d) FY5Ni-E-300; (e) FY5oxNi-MW-300; and, (f) FY5oxNi-MW-500.

catalyst dried in this device is very similar to that of the catalyst prepared using conventional heating (Fig. 4.c and d, respectively). Interestingly, no significant difference in catalyst performance was observed when the reduction temperature was changed from 300 to 500 °C (see Fig. 4e and f), although the particle sizes differ greatly. This may be due to the sintering of Ni particles which takes place at the operating temperature of dry reforming (800 °C), with the result that the final Ni particle sizes in both catalysts become similar. Therefore, although the reduction temperature needs to be adjusted to obtain an acceptable Ni dispersion, as explained above, this parameter could be considered irrelevant for the specific application of catalytic dry reforming reaction. Moreover, much lower conversions are attained when oxidized carbon is used as support instead of the as-received carbon. In fact, experiments carried out over FY5 and FY5ox (see Fig. 4a and b, respectively) demonstrated that the presence of oxygen surface groups reduced their catalytic activity dramatically. Thus, after 150 min, CH_4 conversion is 50% with FY5 and 30% with FY5ox, whereas CO_2 conversion is 50% and as low as 5%, respectively. It would seem, therefore, that the negative effect of the oxidation of carbon on the conversions of CH_4 and CO_2 is stronger than the positive effect, in terms of interaction between the Ni particles and carbon surface, achieved by using an oxidized support. Thus, conversions over oxidized carbon-based Ni catalysts (i.e., Fig. 4e or f) are higher than conversions achieved with non-impregnated FY5ox, but similar to, or even worse, than those achieved with the original FY5.

4. Conclusions

In this work, the influence of the surface chemistry of carbons used as supports, the drying method (i.e. microwave or conventional drying) and the temperature of the reduction stage on the Ni particle size, Ni dispersion and final catalytic activity in the dry reforming reaction of a series of carbon-based nickel catalysts has been studied. It was found that oxidation of the carbon support favours the interaction between Ni particles and carbon surface, and therefore Ni dispersion. Moreover, the reduction temperature also has a great influence on the Ni particle size. The use of microwave drying rather than conventional drying offers significant advantages in the preparation of carbon-supported Ni catalysts: the operating time is greatly reduced, smaller Ni particle sizes are obtained and the influence of the surface chemistry on the Ni particle size is minimised.

For the specific application of these catalysts to the dry reforming reaction, neither an improvement in Ni particle size nor Ni dispersion was found to be essential; due to the sintering of Ni particles that takes place at the reaction temperature (800 °C). Other factors can have a more important role on the catalytic activity of Ni-based catalysts in this reaction, including the oxidation of the carbon support, which reduces the catalytic properties considerably.

Acknowledgements

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Mixtures of Steel-Making Slag and Carbons as Catalyst for Microwave-Assisted Dry Reforming of CH_4

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Abstract: The use of steel-making slag as catalysts for microwave-assisted dry reforming of CH_4 was studied. Two carbon materials (an activated carbon and a metallurgical coke), mixtures of the carbon materials and Fe-rich slag, and mixtures of the carbon materials and Ni/Al_2O_3 were tested as catalysts. The mixtures of slag with carbons gave rise to higher and steadier conversions than those achieved over the carbon materials alone. In addition, the use of the metallurgical coke mixed with metal-rich catalysts gave rise to remarkable results. Thus, no CH_4 and CO_2 conversions were achieved when coke was used alone, whereas high conversions were obtained when it was mixed with the metal-rich catalysts.

Key words: steel-making slag; carbon catalyst; dry reforming; microwave heating
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In recent years, the process of dry reforming ($CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$) has been proposed as a promising technology, not only because syngas is produced with an adequate H_2/CO ratio for the production of liquid hydrocarbons but also because methane and carbon dioxide, both greenhouse gases, are converted into valuable feedstock [1]. One of the major obstacles for the industrial application of this technology is that there are no effective catalysts which operate without undergoing deactivation due to carbon deposition. Numerous attempts have been carried out in order to develop catalysts for this process. Noble metals have been addressed as the most efficient catalysts for the CO_2 reforming of CH_4 reaction. Nevertheless, Ni-based catalysts are preferred since they are cheaper and exhibit high activity for dry reforming with moderate resistance to carbon deposits [2]. Other conventional metal-based catalysts have also been evaluated, such as Fe catalysts. In general, Fe catalysts have shown poorer activity and selectivity than Ni-based catalysts [3]. However, the substitution of Ni by low contents of Fe (i.e. Ni-Fe catalysts) has promoted more stable catalysts [4].

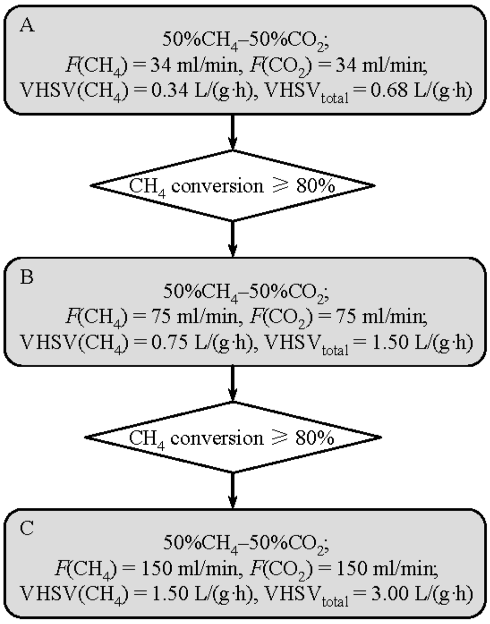
The use of carbon materials as catalysts for the dry reforming reaction has also been proposed [5,6], including chars from biomass residues [7]. Carbon-based catalysts offer some advantages over metal catalysts, such as availability, durability, and low cost. In addition, carbon materials usually have the ability to absorb microwaves, which makes them adequate catalysts for microwave-assisted CO_2 reforming of methane. Microwave heating, which is an alternative to conventional heating methods, is known to enhance heterogeneous and heterogeneous catalytic reactions [6,7].

The aim of this work is to investigate the catalytic activity of steel slag, a Fe-rich waste material produced during the process of steel making, in the microwave-assisted dry reforming of CH_4. In order to compare the performance of this residue as catalysts, alternative carbon catalysts and conventional Ni-based catalyst are also studied.

1 Experimental

Microwave-assisted CO_2 reforming of CH_4 was carried out using as catalyst Fe-rich steel-making slag (labeled as eFe, with 15.2 wt% of Fe content) mixed with a carbonaceous material (an activated carbon, FY5, or a metallurgical coke, CQ) in a proportion 1:1 (wt%). In order to evaluate the performance of the Fe-rich residue as catalyst, mixtures of the carbon materials with an in-lab prepared catalyst of Ni/Al_2O_3 (5 wt% of Ni content) were also tested.

Experiments were conducted in a quartz reactor charged with 6 g of catalyst, previously dried overnight at 100 °C, and heated up to 800 °C in a single mode microwave oven (MW). Details of this equipment setup have been described elsewhere [6]. As shown in Scheme 1, experiments were carried out in three steps of 180 min each, according to the operating conditions and conversion requirements.



Scheme 1. Protocol followed in the evaluation of the mixtures of metal-rich fraction with a carbonaceous material used as catalysts in the dry reforming reaction. $F(CH_4)$, flow rate of methane; $F(CO_2)$, flow rate of carbon dioxide; $VHSV(CH_4)$, methane volumetric hourly space velocity, defined as CH_4 flow rate (L/h)/mass of catalyst (g); $VHSV_{total}$, total volumetric hourly space velocity, defined as total flow rate (L/h)/mass of catalyst (g).

Produced gases were analyzed in a Varian CP-3800 gas-chromatograph equipped with a TCD detector. Concentrations in the effluent gas were used for calculating the conversions of CH_4 and CO_2 as follows.

$$CH_4 \text{ conversion} = [H_{2,out}/2]/[CH_{4,out} + H_{2,out}/2]$$

$$CO_2 \text{ conversion} = [CO_{out}/2]/[CO_{2,out} + CO_{out}/2]$$

2 Results and discussion

Preliminary heating tests of steel-making slag (eFe) showed that this residue does not absorb microwave energy, i.e. steel slag is not a microwave receptor. Therefore, it must be mixed with an absorber material (in the present work, a carbonaceous material) in order to be heated and used as catalyst for the microwave-assisted dry reforming reaction.

Proximate and elemental analyses of the carbon materials are summarized in Table 1. Chemical composition of the steel-making slag is reported in Table 2. Additionally, textural data of FY5 and Ni/Al_2O_3 are shown in Table 3. Data for the metallurgical coke and Fe-rich slag are not included since they showed no textural development (negligible BET surface area and pores volume).

Table 2 Chemical composition of the steel-making slag eFe

Composition	Content (wt%)
CaO	41.7
Fe_2O_3	21.7
SiO_2	15.0
MgO	3.7
MnO	3.5
Al_2O_3	2.3

Table 3 Textural properties of the materials used as catalysts

Sample	A_{BET}/ (m^2/g)	V_t/ (cm^3/g)	V_{mes}/ (cm^3/g)	V_{mic}/ (cm^3/g)	V_{umic}/ (cm^3/g)
FY5	826	0.34	0.03	0.32	0.25
Ni/Al_2O_3	166	0.51	0.50	0.07	—

A_{BET}: BET surface area; V_t: total pores volume; V_{mes}: mesopores volume; V_{mic}: micropores volume; V_{umic}: ultramicropores volume.

Conversions over FY5 and the mixture of FY5 + eFe and CQ and the mixture CQ + eFe are shown in Fig. 1. CO_2 and CH_4 conversions can be very different depending on the carbon material use as catalyst [5]. In general, active sites on carbon surface for dry reforming are high-energy surface defects. Initial catalytic activity of carbon materials seems to be related to the BET surface area or to the oxygen surface groups, specifically those are desorbed as CO in TPD experiments. The long-term stability of a carbon catalyst correlates with the BET surface area and the micropores volume, since the loss of catalytic activity of a carbon depends on the quantity of carbonaceous deposits that can accumulate before it becomes deactivated. Activated carbons present a high initial activity but they become rapidly deactivated as carbonaceous deposits block the pore mouths [8]. Thus, FY5, which has a large micropores volume, gave rise to high initial conversions followed by a rapid drop of conversion, especially in the case of CH_4 [6], whereas metallurgical coke CQ, with no textural development, was found to be a poor catalyst for dry reforming reaction. As can be seen, the mixtures of carbon + eFe gave rise to higher and steadier conversions than those obtained with the carbon materials alone. Interestingly, the mixture of slag

Table 1 Main chemical characteristics of the carbonaceous materials used as catalysts

Sample	Moist (wt%)	Ash content[a] (wt%)	Volatile matter content[a] (wt%)	Elemental content[a] (wt%)				
				C	H	N	S	O[b]
FY5	8.5	2.1	2.8	94.1	0.7	0.3	0.0	2.8
CQ	0.1	11.7	0.6	86.6	0.1	1.1	0.5	0.0

[a] Dry basis. [b] Calculated by difference.

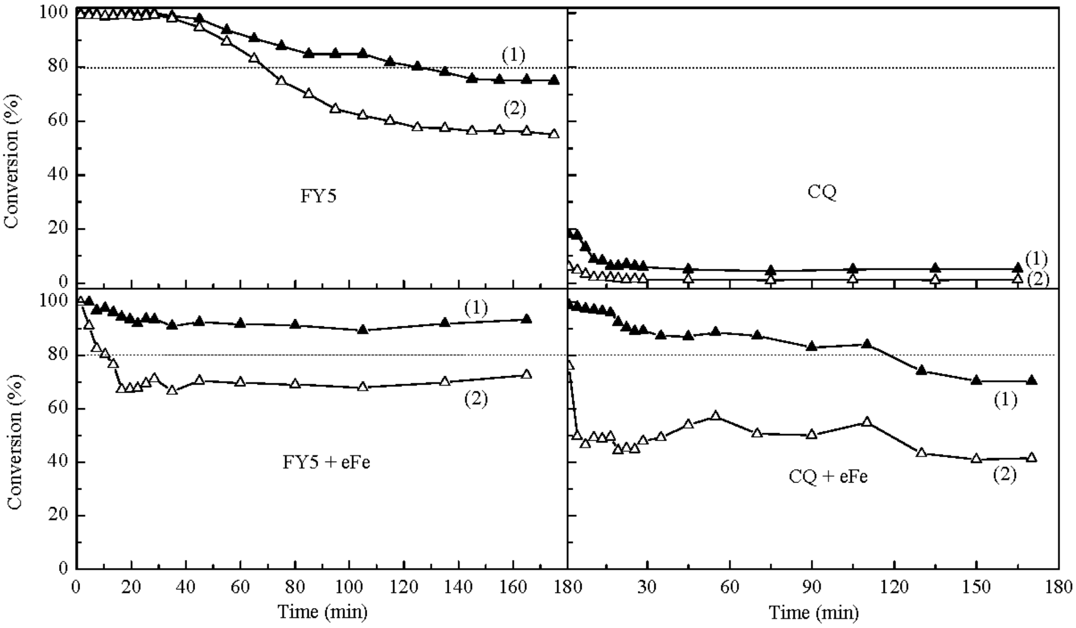


Fig. 1. CO_2 (1) and CH_4 (2) conversions for dry reforming carried out over FY5, FY5 + eFe, CQ, and CQ + eFe. All the experiments were carried out under the experimental conditions specified in the step A of the protocol that is shown in the Scheme 1.

and coke (CQ + eFe) gave rise to moderate but steady conversions (discarding first points). Thus, CH_4 and CO_2 conversions improved significantly regarding those achieved with CQ alone. In the case of FY5 + eFe, steady conversions were also obtained and the rapid deactivation observed over FY5 alone was avoided. Therefore, the addition of Fe-rich slag improved the activity of the catalytic mixtures. Nevertheless, the type of carbon material used had also a notably influence on the performance of the mixture. Thus, FY5 + eFe was better catalyst than CQ + eFe, which shows that the carbon fraction of the catalytic mixtures acted not only as microwave receptors but also as catalyst.

In order to assess the catalytic activity of steel-making slag, the mixtures of carbon + eFe were compared with mixtures of carbon + Ni/Al_2O_3. As it was expected, mixtures of carbon materials with Ni/Al_2O_3 were better catalysts than mixtures those with eFe. As can be seen in Fig. 2, it is possible to maintain conversions near to 100% by using the catalytic mixtures of carbons with Ni/Al_2O_3, even though $VHSV_{total}$ was increased stage by stage ($VHSV_{total}$ was about six times higher than that used with FY5 and CQ alone, and the mixtures with eFe).

It can be observed that conversions over mixtures with FY5 were again higher than over mixtures with CQ. Nevertheless, improvement in catalytic activity was much more significant for CQ, changing from no CH_4 conversion to about 80%, even after increasing $VHSV_{total}$. This result shows that residual fractions of metallurgical coke could be used as catalysts/microwave receptors for dry reforming.

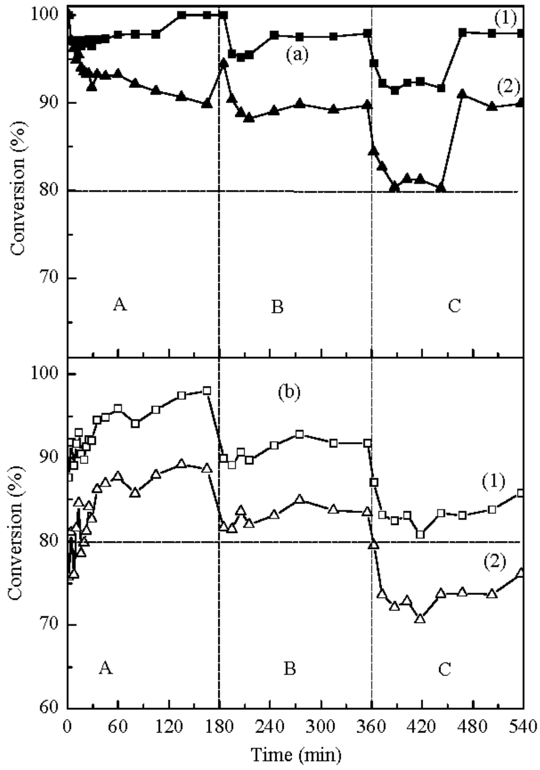


Fig. 2. CO_2 (1) and CH_4 (2) conversions for dry reforming carried out over mixtures of two different carbon materials and an in-lab prepared Ni-based catalyst. (a) FY5 + Ni/Al_2O_3; (b) CQ + Ni/Al_2O_3. Reaction conditions of A, B, and C are shown in Scheme 1.

3 Conclusions

Steel-making slag can be used as catalyst for microwave-assisted dry reforming. However, they must be mixed with a microwave absorber, i.e. a carbon material, since slag is not an absorber and therefore it does not heat in the microwave oven. Conversions achieved using mixtures of carbon material + Fe-rich slag are found to be higher and steadier than those obtained over the carbon materials alone. Catalytic activity of the mixtures depends on the carbon material selected. Thus, higher conversions are achieved using an activated carbon in the mixture than using a metallurgical coke. In fact, the activated carbon alone is better catalyst than the metallurgical coke, which shows no activity for the dry reforming reaction. Nevertheless, the activity of metallurgical coke is dramatically improved when a metal-rich fraction is added, specially mixed with Ni-based catalyst. Actually, mixtures of carbon materials with Ni/Al_2O_3 give rise to higher conversions than mixtures with slag, allowing $VHSV_{total}$ to be increased while high conversions are kept.

Acknowledgements

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ANEXO 2. MICROONDAS Y MATERIALES DE CARBONO

A pesar de que el calentamiento con microondas no dio lugar a buenas conversiones en el proceso de reformado seco del gas de coquería, como se reflejó en la Sección 3.3 *Reformado con CO_2 de gas de coquería asistido con microondas*, está tecnología ha dado buenos resultados en el reformado seco de metano en otros trabajos realizados en paralelo por nuestro grupo de investigación[55, 71, 72, 81, 87, 89, 90]. Estos resultados fueron los que motivaron la realización del estudio del reformado seco de gas de coquería asistido por calentamiento con microondas. Además, tanto en estudios realizados por nuestro grupo como por otros grupos de investigación, el calentamiento con microondas se ha mostrado como una alternativa eficiente al calentamiento convencional. En este Anexo se incluyen dos artículos publicados por nuestro grupo en los que se recoge una revisión de estos procesos y las mejoras obtenidas con el microondas, así como el estudio del principal fenómeno que ayuda a explicar dichas mejoras: la aparición de microplasmas.

El calentamiento con microondas es una tecnología con un creciente interés en investigación, en especial en lo que a los materiales carbonosos se refiere. La mayoría de los materiales de carbono son dieléctricos, por lo que cuando se introducen en un campo de microondas se produce su calentamiento por polarización de carga del espacio (también llamada polarización Maxwell-Wagner). Esto se debe a que estos materiales contienen cargas libres (como los electrones π) que se pueden desplazar dentro de los límites de la partícula cuando se encuentran bajo la influencia de un campo electromagnético. De esta manera, algunas regiones macroscópicas del material se cargan positiva o negativamente, generando resistencias eléctricas dentro del propio material, que provocan el calentamiento.

La interacción entre microondas y materiales de carbono ha dado lugar a mejoras en multitud de procesos, como disminución del tiempo de operación o incremento de los rendimientos. En el artículo *Microwave heating processes involving carbon materials*, publicado en Fuel Processing Technology, 2010, 91, 1-8, (que puede encontrarse en este Anexo) se resumen los principales logros alcanzados en diferentes procesos, en los cuales se utilizan materiales carbonosos, aplicando calentamiento con microondas en sustitución del calentamiento convencional. Los campos en los que se encuentran enmarcados dichos procesos abarcan desde la síntesis de materiales de carbono o la regeneración de carbones activos, hasta la mejora de procesos catalíticos heterogéneos, como el reformado con CO_2 de metano. Mi participación en este trabajo consistió en la revisión bibliográfica de la aplicación del calentamiento microondas en procesos catalíticos heterogéneos y la redacción y revisión en conjunto del trabajo.

La capacidad de las microondas para mejorar las reacciones en procesos catalíticos heterogéneos ha sido atribuida a la aparición de microplasmas durante el calentamiento, que generan puntos calientes. Estos microplasmas, que se observan a nivel macroscópico, son igniciones de la atmósfera circundante al material debidas a la presencia de arcos eléctricos. Estos arcos se pueden formar por diferencias en las propiedades dieléctricas dentro del material, por defectos geométricos o por la presencia de impurezas. Se les denomina microplasmas porque tienen lugar en pequeñas regiones del espacio durante una fracción de segundo. A estos microplasmas se les atribuye un efecto pseudo-catalítico, que es el que da lugar al aumento en la velocidad de reacción, y que mejora las conversiones y los rendimientos en los procesos catalíticos heterogéneos. Este efecto se debe a que, en esos puntos, la temperatura alcanzada por el sistema es considerablemente superior a la temperatura de operación.

En el artículo *Ball lightning plasma and plasma arc formation during the microwave heating of carbons*, publicado en Carbon, 2011, 49, 346-349 (mostrado al final del presente Anexo), se ha estudiado por primera vez la naturaleza de estos microplasmas en el caso de calentamiento de materiales carbonosos. Se ha observado que puede haber dos tipos de plasmas: plasmas cuasi-esféricos, más conocidos por el término *ball lightning plasmas*, y plasmas de arcos. Ambos tipos de plasma aparecieron en los distintos materiales de carbono utilizados en el estudio, con pequeñas diferencias de intensidad y frecuencia, dependiendo de la temperatura de trabajo y del grado de ordenamiento del material. Mi participación en este trabajo se centró en la realización de los distintos procesos de calentamiento con microondas de los materiales de carbono, así como grabación y tratamiento de las imágenes que aparecen en el artículo y en el material suplementario on-line.

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Review

Microwave heating processes involving carbon materials

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ABSTRACT

Carbon materials are, in general, very good absorbents of microwaves, i.e., they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties, to be used as microwave receptors, in order to heat other materials indirectly, or to act as a catalyst and microwave receptor in different heterogeneous reactions. In recent years, the number of processes that combine the use of carbons and microwave heating instead of other methods based on conventional heating has increased. In this paper some of the microwave-assisted processes in which carbon materials are produced, transformed or used in thermal treatments (generally, as microwave absorbers and catalysts) are reviewed and the main achievements of this technique are compared with those obtained by means of conventional (non microwave-assisted) methods in similar conditions.

Contents

1. Introduction to the microwave heating of carbons

Microwaves lie between infrared radiation and radiowaves in the region of the electromagnetic spectrum. More specifically, they are defined as those waves with wavelengths between 0.001 and 1 m, which correspond to frequencies between 300 and 0.3 GHz. The microwave band is widely used in telecommunications. In order to avoid interference with these uses, the wavelengths of industrial, research, medical and domestic equipment are regulated both at national and international levels. Thus, the main operating frequency in the majority of countries is 2.450 (+/−0.050) GHz [1,2].

Dielectric heating refers to heating by high-frequency electromagnetic radiation, i.e., radio and microwave frequency waves. The interaction of charged particles in some materials with the electric field component of electromagnetic radiation causes these materials to heat up. The heat resulting from this interaction is mainly due to two different effects. In the case of polar molecules, the electric field component of the microwaves causes both permanent and induced dipoles to rotate as they try to align themselves with the alternating field (2450 million times per second). This molecular movement generates friction among the rotating molecules and, subsequently, the energy is dissipated as heat (Dipolar Polarization). This is the case of water and other polar fluids. In the case of dielectric solid materials with charged particles which are free to move in a delimited region of the material, such as π-electrons in carbon materials, a current traveling in phase with the electromagnetic field is induced. As the electrons cannot couple to the changes of phase of the electric field, energy is dissipated in the form of heat due to the so-called Maxwell–Wagner effect (Interfacial or Maxwell-Wagner Polarization) [1,2].

The materials which interact with microwaves to produce heat are called microwave absorbers. The ability of a material to be heated in the presence of a microwave field is defined by its dielectric loss

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tangent: $\tan\delta = \varepsilon''/\varepsilon'$. The dielectric loss tangent is composed of two parameters, the dielectric constant (or real permittivity), ε', and the dielectric loss factor (or imaginary permittivity), ε''; i.e., $\varepsilon = \varepsilon' - i\varepsilon''$, where ε is the complex permittivity. The dielectric constant (ε') determines how much of the incident energy is reflected and how much is absorbed, while the dielectric loss factor (ε'') measures the dissipation of electric energy in form of heat within the material [1,2]. For optimum microwave energy coupling, a moderate value of ε' should be combined with high values of ε'' (and so high values of $\tan\delta$), to convert microwave energy into thermal energy. Thus, while some materials do not possess a sufficiently high loss factor to allow dielectric heating (transparent to microwaves), other materials, e.g. some inorganic oxides and most carbon materials, are excellent microwave absorbers. On the other hand, electrical conductor materials reflect microwaves. For example, graphite and highly graphitized carbons may reflect a considerable fraction of microwave radiation. In the case of carbons, where delocalized π-electrons are free to move in relatively broad regions, an additional and very interesting phenomenon may take place. The kinetic energy of some electrons may increase enabling them to jump out of the material, resulting in the ionization of the surrounding atmosphere. At a macroscopic level, this phenomenon is perceived as sparks or electric arcs formation. But, at a microscopic level, these hot spots are actually plasmas. Most of the time these plasmas can be regarded as microplasmas both from the point of view of space and time, since they are confined to a tiny region of the space and last for just a fraction of a second. An intensive generation of such microplasmas may have important implications for the processes involved.

The microwave heating of a dielectric material, which occurs through the conversion of electromagnetic energy into heat within the irradiated material, offers a number of advantages over conventional heating such as: (i) non-contact heating; (ii) energy transfer instead of heat transfer; (iii) rapid heating; (iv) selective material heating; (v) volumetric heating; (vi) quick start-up and stopping; (vii) heating from the interior of the material body; and, (viii) higher level of safety and automation [3]. Due to these advantages, microwaves are used in various technological and scientific fields in order to heat different kinds of materials [2–4]. Most of the industrial applications of microwave heating are based on heating substances that contain polar molecules, for example: food processing, sterilization and pasteurization, different drying processes, rubber vulcanization, polymerization or curing of resins and polymers by elimination of polar solvents, etc. In addition, solid materials with a high dielectric loss factor, i.e., microwave absorbers, can be subjected to different processes based on microwave heating. Among these materials, carbons are, in general, very good microwave absorbers, so they can be easily produced or transformed by microwave heating. Moreover, carbon materials can be used as microwave receptors to indirectly heat materials which are transparent to microwaves. Thus, carbon materials have been used as microwave receptors in soil remediation processes, the pyrolysis of biomass and organic wastes, catalytic heterogeneous reactions, etc. The high capacity of carbon materials to absorb microwave energy and convert it into heat is illustrated in Table 1, where the dielectric loss tangents of different carbons are listed. As can be seen, the loss tangents of most of the carbons, except for coal, are higher than the loss tangent of distilled water ($\tan\delta$ of distilled water = 0.118 at 2.45 GHz and 298 K). The search and compilation of these data is not a straightforward matter. Although this parameter is helpful for the study of microwave heating, few research groups have determined the dielectric loss tangents of carbons and the data that can be found are scattered throughout bibliography.

The first commercial microwave oven was developed in 1952, although it was during 1970s and 1980s when the widespread domestic use of microwave ovens occurred, as a result of Japanese technology transfer and global marketing [18]. Curiously, the industrial applications of microwaves were initiated by the domestic ovens. However, in recent years, the number of processes that combine the use of carbons and microwave heating to obtain benefits with respect to other traditional methods based on conventional heating has increased enormously. Thus, as can be seen from Fig. 1, the number of scientific publications related to these topics was very low until the late 1990s, but interest has risen drastically in the last decade and especially so in the last five years.

Table 1
Dielectric loss tangents for different carbon materials at a frequency of 2.45 GHz and room temperature, ca., 298 K.

Carbon material	$\tan\delta = \varepsilon''/\varepsilon'$	Reference
Coal	0.02–0.08	[5,6]
Carbon foam	0.05–0.20	[7]
Charcoal	0.11–0.29	[8,9]
Carbon black	0.35–0.83	[10,11]
Activated carbon	0.57–0.80	[9,12,13]
Activated carbon[a]	0.22–2.95	[14]
Carbon nanotube	0.25–1.14	[15,16]
CSi nanofibres	0.58–1.00	[17]

[a] Activated carbon at a mean temperature of 398 K.

The aim of this work is to review examples of different microwave-assisted processes involving carbon materials. In these processes, microwave heating is used either to produce or modify different carbon materials or is employed in combination with carbons acting as microwave absorbers to enhance different processes in technological applications. The amount of published work is relatively large, so an effort has been made to be representative rather than comprehensive. Thus, the synthesis of a wide range of carbon materials by microwave techniques is reviewed in Section 2. Due to the widespread use of activated carbons, their production, modification and regeneration is treated in a separate section (Section 3). The use of microwave heating in various metallurgical and mineral processes is presented in Section 4. Moreover, microwaves can be used not only to treat and modify solid carbons but also for purposes of revaluation, to obtain other products of high added value, such as gases. This is the case of thermal valorisation of biomass and biosolids, which is dealt with in Section 5. Finally, the use of microwaves to enhance the reactions catalyzed by carbons is growing in importance and is discussed in Section 6.

2. Synthesis of carbon materials

Microwave plasma-enhanced chemical vapor deposition (CVD) has been widely used for growing carbon nanotubes [19,20] or diamond deposition [21]. Although very few works have been

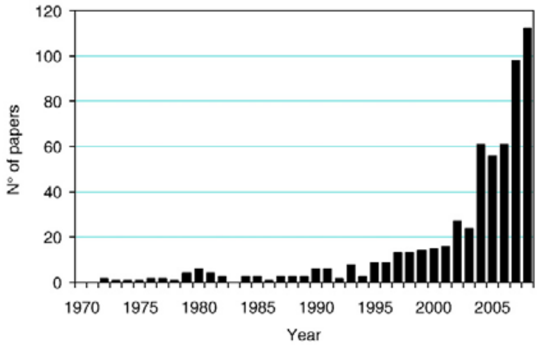

Fig. 1. Evolution of the number of research papers published on microwave-assisted processes involving carbon materials.
(Source: Scopus®).

described, the synthesis of nanocarbons by the direct microwave irradiation of catalyst particles on a solid support is another possibility for producing carbon nanofilaments by CVD [22,23]. Thus, carbon nanofilaments were formed through microwave-assisted CH_4 decomposition over an activated carbon, acting as catalyst and microwave receptor, using a combination of CH_4/N_2. The same method was also used to grow carbon nanofilaments on carbon fibres doped with Fe and Ni [23], giving rise to structures similar to those shown in Fig. 2. Mixtures of CH_4/CO_2 were also used to produce nanofilaments using a char as catalyst and microwave receptor [22]. Since no nanofilaments were observed after analogous tests carried out under conventional heating, it must be concluded that it is the different mechanism involved in heating the supports by microwaves that promotes the formation of nanofilaments.

Carbon materials can act not only as a support for growing nanostructures but also as the carbon-source for the synthesis of nanotubes and nanofibres via microwave heating. It has been reported that is possible to synthesize these nanostructures by simply microwave heating of graphite for 60 min [24] or of organometallic compounds like ferrocene, $Fe(C_5H_5)_2$, for just 30 min [25]. In addition, microwave irradiation seems to be an effective option for purifying nanotubes. Thus, the refining of raw samples of nanotubes, that is the elimination of the amorphous carbon formed during the synthesis and metal impurities (the remains of the catalyst), has been carried out by microwave heating, at 433 K for 30 min., in nitric acid. [26]. The microwave-induced functionalization of carbon nanotubes is another option. Reactions such as amidation and 1,3-dipolar cycloaddition have been performed in a matter of minutes, which is a significant reduction in time compared to conventional functionalization processes. In addition, the number of steps involved in the reaction procedure has been reduced, which opens the door to a fast and inexpensive process for producing functional singlewall carbon nanotubes [27]. The multifunctionalization of carbon nanotubes using a combination of two addition reactions, the 1,3-dipolar cycloaddition of azomethine ylides and the addition of diazonium salts, has also been achieved in solvent free conditions via a simple and fast microwave-induced method [28]. This method reduces not only the reaction time but it also avoids the need for using toxic solvents. Another example of the use of microwaves in the functionalization of carbon materials is the oxidation of carbon nanohorns [29]. Furthermore, carbon nanotubes can be incorporated into ceramic matrices using microwave irradiation. The use of a microwave-induced reaction may be able to overcome some of the problems of the conventional methods of synthesis, i.e., non-uniform dispersion and damage to the nanotubes during high temperature processing in the reacting media. As an example, a carbon nanotube–silicon carbide composite has been synthesized by this method in only 10 min at temperatures between 673 and 1173 K [30].

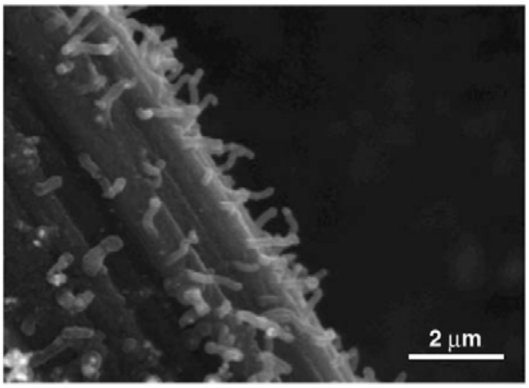

Fig. 2. Carbon nanofilaments grown on a carbon fibre. (Reprinted from Ref. [23] with permission from Elsevier).

Another application of microwave heating is the production of graphitic carbons from various precursors, such as isotropic or anisotropic pitch-based carbon powders [31]. Moreover, Mitsubishi Heavy Industries, Ltd. (MHI) has claimed[1] to have produced superior-grade graphite from carbon powder by using a microwave process at 3473 K. Expanded graphite, a modified graphite which retains its layered structure and is similar to natural graphite but with larger interlaying spacing and abundant multipores, has been produced by the microwave irradiation of both natural graphite, mixed with HNO_3 and $KMnO_4$ [32], and expandable graphite [33]. A microwave-based device specially designed for the production of expanded graphite has been patented [34]. It has also been claimed that powdered carborundum, i.e., silicon carbide, with diameters in the nanometer range, can be produced by a microwave-assisted process that involves reducing SiO_2 with various forms of carbon in a nitrogen atmosphere [35]. In a similar way, Changhong et al. used microwave heating to induce the direct reaction between silicon and charcoal powder, at temperatures lower than 1273 K, in order to synthesize silicon carbide [36].

Microwave irradiation has been used to synthesize ordered mesoporous carbon materials (OMC) by employing a nano-casting technique and ordered mesoporous silica as the template. Thus, microwave heating techniques have been applied to synthesize nano-structured materials such as zeolites and ordered mesoporous silica materials under hydrothermal conditions [37], the result being a remarkable enhancement in the efficiency of sol–gel synthesis, as manifested by the shorter time or lower temperature required for the synthesis, and the unique and uniform properties of the products. The ultrarapid production of OMC materials, which utilizes the intense heat generated by microwaves during the carbonization step, offers a number of advantages, such as energy saving, low temperature preparation (even at 673 K), controllable oxygen content, i.e., a wide range of hydrophilicity without the need for post-activation, and an enhancement of the conductivity of the carbon materials [38].

Another use of microwave heating in the synthesis of carbon materials is derived from the capacity of microwaves to interact with polar solvents (Dipolar Polarization). In this case, interaction can produce a more uniform dispersion of metal particles in the synthesis of carbon-supported catalysts by means of the so-called microwave-assisted polyol process [29,39,40]. Another advantage of the interaction of microwaves with polar solvents is that they can be eliminated by evaporation, thereby saving both energy and time. Thus, microwave heating can be used to facilitate the polymerization or curing of polymers by eliminating solvents. The application of microwave irradiation to polymer chemistry has also revealed potential advantages in its ability not only to drive chemical processes but also to perform them in a short time [41]. A particular case of industrial interest is the microwave-assisted vulcanization of rubber [42]. The use of microwave heating in rubber vulcanization is now a well-established technique. Interestingly microwave heating can also be used to devulcanize elastomer waste [43]. In the field of carbon materials, microwave heating has been applied in the drying step of the synthesis process of carbon xerogels [44,45]. Microwave drying has been used to prepare resorcinol–formaldehyde gels by employing methanol [44] and water [45] as solvents. By using microwave drying, the process for obtaining carbon gels has been greatly simplified. As with other drying methods, the textural properties can be controlled, but time has been considerably reduced by changing from conventional drying techniques to microwave drying (up to 90% reduction in the drying stage), no pre-treatment being necessary. Taking into account that one of the disadvantages of carbon gels, compared to

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[1] http://www.mhi.co.jp/en/news/sec1/e_0878.html.

other carbon materials, was the complexity, long time required and the high costs of the traditional synthesis methods, this improvement (i.e., the use of microwaves in the synthesis of carbon gels) makes these materials more economically competitive in a large number of applications.

3. Production, modification and regeneration of activated carbons

Activated carbons are, in general, produced from different organic precursors, such as biomass, coal, polymers, natural or synthetic fibres, etc, which are subjected to carbonization and activation processes. The activation process can be carried out by making steam, CO_2 or air react with a char or a carbonized material at relatively high temperatures, i.e., 873 to 1173 K. This kind of activation is commonly referred as physical or thermal activation. On the other hand, chemical activation consists in the simultaneous carbonization of the precursor with an activating agent, such as ZnO, H_3PO_4, KOH, etc, at temperatures ranging from 673 to 1073 K. Both microwave-assisted activation processes have been recently reviewed by Yuen and Hameed [46].

Since carbonaceous materials are good microwave absorbers, the microwave-assisted physical activation of chars from different organic precursors has been widely studied over the last few decades. Norman and Cha reported a method for producing highly microporous activated carbons by the CO_2 activation of coal chars [47]. More recently, a research group from Kunming University of Science and Technology in China has claimed to have obtained activated carbon by the steam activation of coconut shells in a pilot-scale device of 60 kW with considerable saving of time and energy [48], while another group from the University of Huddersfield in the United Kingdom has reported activating a phenolic resin-derived carbon in air using constant rate microwave thermogravimetry [49].

On the other hand, few attempts have been made to develop microwave-based processes for chemical activation. The non-carbonized organic precursors of activated carbons impregnated with activating agents are, in general, poor microwave absorbers. This characteristic makes it difficult to heat them up with microwaves to the high temperatures required, although this problem could be overcome by using microwave receptors, e.g. carbonaceous materials [50]. Additionally, Yagmur et al. [51] reported a microwave-induced impregnation method applied prior to the carbonisation stage saving both time and energy.

A way of exploiting the excellent dielectric properties of carbon materials, i.e., their high microwave absorption capacity, is the use of microwave heating to tailor their surface chemistry either by introducing or by removing surface functionalities. As was discussed in Section 2, the microwave-assisted functionalization of carbon nanotubes and nanohorns has already been successfully carried out. By contrast, in the case of activated carbons, microwave heating has mainly been used for the rapid elimination of surface functionalities that are often present on the carbon surface. Thus, microwave heating has been used to remove oxygen functionalities and produce a highly-basic activated carbon in just a few minutes, basic properties lasting upon air exposure [52]. Similar results were obtained for carbon fibres subjected to thermal treatments in a microwave oven [53,54]. In the case of granular activated carbons, the main advantage of employing microwave as opposed to conventional heating seemed to be the saving of time and energy, as the chemical changes observed on the carbon surface did not differ very much regardless of the method used, provided that similar temperatures were used [55]. However, whereas in the case of the activated carbons the porous texture remained more or less unaltered after microwave treatment, the carbon fibres subjected to microwave treatments exhibited a reduction in micropore volume and micropore size. This effect has been used to produce carbon molecular sieves (CMS) by subjecting acrylic textile fibres to microwave action [56]. This novel method of producing and improving the properties of molecular sieves of carbon fibres seems to be more economical than the conventional one. In particular, CMS produced by this method showed a very high selectivity for CO_2/CH_4 and O_2/N_2 gas separations [57].

Another topic of investigation has been the microwave-induced regeneration of exhausted activated carbons. Thus, Price and Schmidt [58] and Cha and Carlisle [59] have reported microwave-assisted regeneration processes of activated carbon saturated with volatile organic compounds (VOC). As well as of carbons used in gas-phase applications, the regeneration of activated carbons used in liquid phase adsorption has been studied. Thus, different activated carbons polluted with phenol [60] and pharmaceuticals [61] have been subjected to thermal regeneration under N_2 and CO_2 atmospheres, using both conventional and microwave heating. It was found that the rapid heating of the exhausted activated carbons by microwave energy leads to a quick regeneration. Furthermore, microwave technology allowed the activated carbons to be recycled and reused several times. Thus, it was shown that microwave heating preserves the porous structure of the regenerated activated carbons more efficiently than treatment in a conventional device. The use of this technique causes no damage to the carbon; rather, it increased the surface area, at least during the first regeneration cycles [62]. Fig. 3 illustrates the changes in the adsorptive capacity of a commercial activated carbon exhausted with phenol, after subsequent cycles of regeneration at 1123 K in N_2 and CO_2 atmospheres, using both conventional and microwave heating. Interestingly, regeneration in the microwave oven doesn't just preserves (or even increases) the adsorptive capacity of the activated carbon, the regeneration time is reduced by 90% as well.

One more example of the application of microwave-assisted regeneration of activated carbon is its use in certain gold recovery industries which is described in the next section.

4. Metallurgy and mineral processing

Microwave heating has been investigated for use in various metallurgical processes, including pyrometallurgy, hydrometallurgy [63] and mineral processing [3].

Yet in the particular case of processes involving carbons, the microwave-assisted reduction of metal oxides with different carbon materials has been extensively investigated. Thus, hematite fines and magnetite concentrates have been mixed with different carbons like charcoal or coke and then subjected to microwave heating up to 1273 K [64]. It was found that the process is influenced by the type of

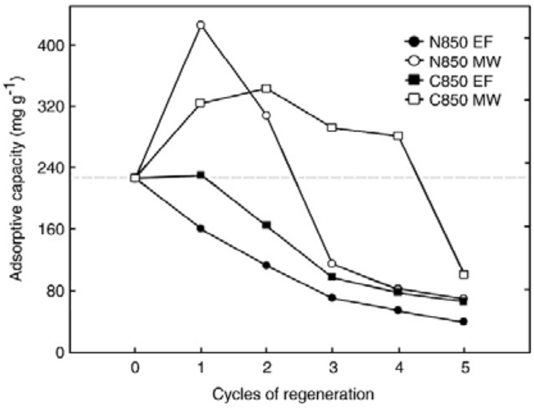

Fig. 3. Comparison of the phenol adsorptive capacities of an activated carbon after various cycles of regeneration: (N850EF) electric furnace at 1123 K in a N_2 atmosphere; (N850MW) microwave furnace at 1123 K in a N_2 atmosphere; (C850EF) electric furnace at 1123 K in a CO_2 atmosphere; (C850MW) microwave furnace at 1123 K in a CO_2 atmosphere. Adapted from reference [60].

carbon used and that, under similar conditions of temperature, microwave reduction produces better results than those attained by conventional heating. Recently, a process for carrying out the carbothermic reduction of iron oxides using microwave heating has been patented [65]. Similar processes that combine microwave heating with the use of various kinds of carbons as reducing agent and microwave absorbers are applied to other metallic oxides [66].

Microwave heating is also employed in the gold mining industry to recover gold from the activated carbon used in the so-called carbon-in-pulp process (CIP). The carbon, which is used to adsorb the gold cyanide molecule, is periodically removed from the adsorption tanks to allow removal of the gold by elution. Then, after the carbon is subjected to an acid wash to remove inorganic compounds, it is regenerated at 923–1123 K in a steam atmosphere to remove other foulants such as flotation reagents, lubricating oils and humic acids which would foul the carbon and undermine its performance. The regenerated carbon is then sized and returned to the CIP circuit. Regeneration is conventionally done in rotary kilns or vertical tube furnaces. However, it has been demonstrated that the use of microwave heating can be also an alternative economically feasible, with a saving of energy and time consuming [67].

Another field of application of microwave heating is the processing of coals. Coals are, in general, very poor microwave absorbers (see Table 1), since they do not possess graphene lattices of a size large enough to allow delocalized π-electrons to move in order to couple with the electromagnetic field of the microwaves (i.e., heating by interfacial polarization). Thus, only devolatized coals, chars or cokes, with a relatively large amount of delocalized π-electrons that move on the incipient graphenic structures, show good microwave absorbance properties (see Fig. 4).

Despite this, the microwave heating of coals is used in the industrial processing of coal. For example, a process for the microwave-assisted grinding of coals has been described [68]. In this process, coals of various ranks were exposed to microwave radiation to quantify the effect on grindability. Reductions of up to 50% of relative grindability were reported after 5 min of microwave exposure. These reductions are believed to be due to fracture mechanisms; inherent moisture within the coal structure absorbs microwaves changing phase, and producing considerable pressure and differential expansion by gangue mineral components. Another example is the microwave-assisted desulphurization of coals which is based on the fact that pyrite heats more rapidly than coal. This heating has the effect of enhancing the magnetic susceptibility of pyrite thereby improving the removal rates by magnetic separation [69]. In addition to these two industrial applications of microwave heating of coals, the possibility of using microwave heating of a high volatile bituminous coal for rapid coke making has been studied at the bench scale [70]. In the cited work it is suggested that devolatilization starts due to the moisture content and -OH bonds present in the coal, and then, when the aromaticity of the devolatilized material increases, the absorption of microwaves allows temperatures in excess of 1273 K, which produces graphitized coke in less than 2 h.

5. Thermal valorisation of biomass and biosolids

Microwave heating is a good alternative for carrying out the pyrolysis of biomass [71,72], coal [73,74], oil shale [75,76], glycerol [77] and various organic wastes [78]. In general, these materials are poor receptors of microwave energy, so they cannot be directly heated up to the high temperatures usually required to achieve total pyrolysis. However, microwave-induced pyrolysis is possible if the raw material is mixed with an effective microwave receptor, such as certain metal oxides [73,74] or carbon materials [50,71,72,75–78]. The latter are usually preferred for this particular application, not only because they are very good microwave absorbers, but also because they are inexpensive, easily available in different textures, sizes, forms, etc; and do not add any extra inorganic component to the solid residues obtained after pyrolysis. Moreover, the carbonaceous residue itself which is obtained from the pyrolysis of the organic materials can be used as an excellent microwave absorber [50,71,79,80].

A case of particular interest is the pyrolysis of sewage sludge [50,79–85], often called biosolids. Handling of this waste, which can be considered as biomass, represents a challenge in industrialized countries. So far, none of the methods used, from land reclamation, such as landfill or organic fertilisers, to incineration, are exempt from drawbacks, like collateral pollution or high costs of treatment. These high costs are in part due to the need to remove the high water content of the sludge. Microwave heating could be a highly efficient alternative for drying these biosolids [81]. Moreover, a process that uses the steam produced by microwave drying to gasify the products generated during subsequent pyrolysis has been described [80]. In this method, drying, pyrolysis and gasification of the sewage sludge take place at the same time, giving rise to a larger gas fraction with a high syngas ($CO + H_2$) content [79,84,85] and to an oil fraction with a low polycyclic aromatic hydrocarbons (PAHs) content [82,83]. In contrast, the oil from the conventionally heated sludge consists primarily of PAHs. Unlike other conventional pyrolysis methods and due to the high temperatures that are reached during the process, a partially vitrified solid residue can be obtained by microwave-assisted pyrolysis [80]. This is particularly useful in the case of sludges with high heavy metal content.

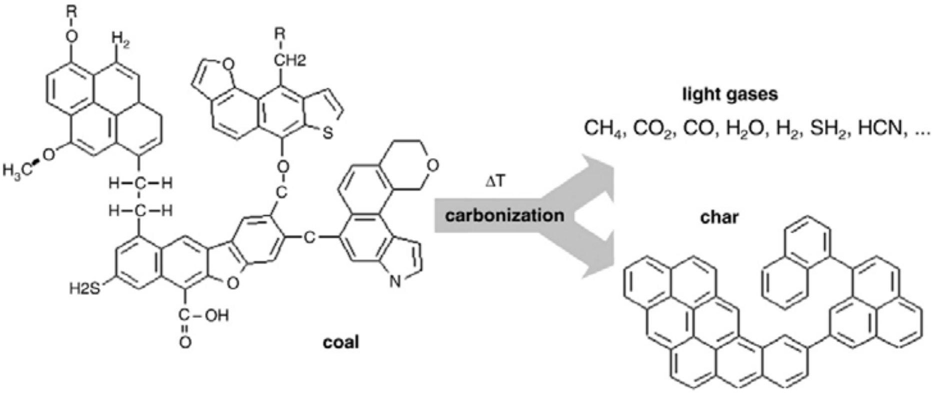

Fig. 4. Representative coal molecular structure and char after devolatilization. Coal doesn't possess many delocalized π-electrons. After devolatilization aromatic rings fuse giving rise to small graphitic planes with π-electrons free to move.

A unique characteristic of microwave-assisted thermal treatments of biomass and biosolids is that they produce a considerable higher amount of H_2 and CO (syngas) and much less CO_2 than similar treatments carried out using conventional heating. This feature is illustrated in Fig. 5, where the compositions of the gas fractions obtained from the pyrolysis of a biomass residue using both methods of heating are compared. Given that microwave-assisted pyrolysis maximizes the gas fraction obtained (oils are produced but in very small amounts) and the fraction of the carbonaceous residue can be used as microwave receptor and consumed by auto-gasification with the CO_2 obtained in the process [72], this method can be used for the thermal valorisation of biomass and biosolids, by producing mainly syngas-rich gases.

Microwave heating combined with the use of carbons as microwave receptors has also been used in soil remediation to eliminate organic pollutants. Thus, the use of graphite fibres, as microwave receptor, in microwave-assisted extraction (MAE) has been shown to be a successful method for the extraction of contaminants in soils, rivers and marine sediments [86]. Similar microwave-induced thermal treatments employing granular activated carbon as microwave absorber to achieve the appropriate temperature were used to decontaminate the soil [87].

6. Microwave enhancement of carbon-catalyzed reactions

Owing to their particularly strong interaction with microwave radiation and high thermal conductivity, graphite and certain other carbons are efficient sensitizers. They are capable of converting radiation energy to thermal energy, which is then transmitted instantaneously to supported chemical compounds. Two types of reaction are favored by carbon-microwave coupling: (i) reactions which require a high temperature, and (ii) reactions involving chemical compounds which, like the organic compounds, have a low dielectric loss and do not heat up sufficiently under microwave irradiation. Thus, microwave heating is a valuable, non-conventional energy source for organic synthesis, which can produce spectacular accelerations in many reactions [88]. Carbons and carbon-supported catalysts are used as sensitizer or sensitizer-plus-catalyst in several organic microwave-assisted synthesis reactions, such as Diels-Alder reactions, the thermolysis of esters, the decomplexation of metal complexes, the pyrolysis of urea, sterifications, etc. [89]. Carbon particles are used to selectively heat the catalyst and substrate without bulk heating the solution. A case of particular interest is fullerene chemistry under microwave irradiation [90], where fullerenes are subjected to different organic reactions in order to functionalize them.

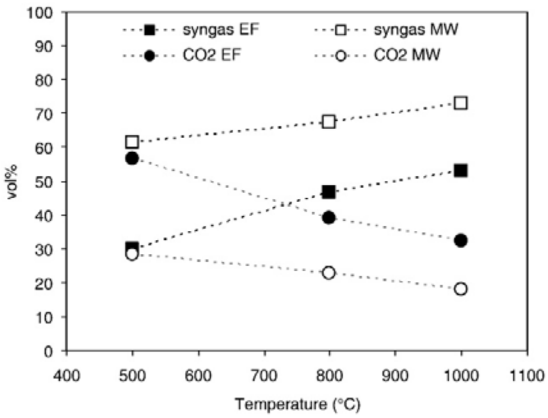

Fig. 5. Variation, with temperature, in the gas composition obtained from the pyrolysis of a biomass residue using conventional (closed symbols) and microwave-assisted (opened symbols) pyrolysis. Adapted from reference [72].

Carbons can be used as catalyst in a variety of heterogeneous gas-phase catalytic systems [91]. Besides, they are good microwave absorbers. These two characteristics have been combined to enhance various catalytic reactions, in which carbons play the double role of catalyst and microwave receptor. In fact, the interaction of microwave irradiation with some heterogeneous catalytic systems has been proven to enhance the reaction rates, the selectivities of the products and the conversion values [92–94].

NO_x reduction [95,96], SO_2 reduction [97], catalytic CH_4 decomposition for H_2 production [98,99] and CO_2 reforming of CH_4 (dry reforming) [100,101] are just some examples in which the use of carbon materials as catalyst and microwave receptor resulted in a considerable improvement in the yield of the reactions. A variety of carbon materials, such as activated carbons, metallurgical cokes, chars or anthracite, were used. Several microwave-enhanced heterogeneous catalytic reactions, in which carbons acted as catalyst and microwave receptor, are shown in Table 2.

The improvement in the results is attributed to the way the catalyst is heated by microwaves. Thus, in the case of microwave heating, the catalyst (i.e., the carbonaceous material) is heated directly by the action of the microwaves, and so it is at a higher temperature than the surrounding atmosphere. However, under conventional heating, heat is transferred through the surface of the catalyst, mainly by conduction and convection, resulting in a totally different temperature gradient. In addition to this, as mentioned before, microplasmas are commonly produced during the microwave irradiation of carbons. The temperature in these microplasmas (also called hot spots) is believed to be much higher than the overall temperature of the system, which usually favours heterogeneous reactions between the solid catalyst and the gases taking part in the reaction. It should therefore be possible to apply this technique to other catalytic reactions in which a carbon-based catalyst is used.

7. Conclusions

Carbon materials are, in general, very good microwave absorbers. This explains the increasing interest over the last decade in using them in a wide variety of microwave-assisted thermal processes. These processes include the synthesis of a wide variety of carbon materials (i.e., nanostructures, graphite, active carbons, polymers, etc.), the purification or even chemical and/or physical modification of carbons in a quick and controlled way, the enhancement of different processes involving coal, chars or even biomass/biosolids, and the clear improvement in the efficiency of some carbon-catalyzed reactions. These processes are attracting considerable attention given their possible use in commercial applications and some of them have already been demonstrated at pilot or even industrial scale. The main advantage of using microwaves, instead of traditional heating

Table 2
Examples of microwave-enhanced heterogeneous catalytic reactions, in which carbons are used as catalysts and microwave receptors.

Reaction	Catalyst/microwave receptor	Reference
$C + 2NO \rightarrow CO_2 + N_2$	Subbituminous coal char, anthracite, metallurgical coke	[95–97]
$C + NO \rightarrow CO + 1/2N_2$	Subbituminous coal char, anthracite	[95–97]
$C + SO_2 \rightarrow CO_2 + S$	Subbituminous coal char, anthracite	[97]
$2C + SO_2 \rightarrow 2CO + S$	Subbituminous coal char, anthracite	[97]
$C + CO_2 \leftrightarrow 2CO$	Biomass char	[72]
$CH_4 \rightarrow C + 2H_2$	Activated carbon	[98,99]
$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	Activated carbon	[100,101]

techniques, is because of the different mechanism involved in heating carbons, leading to, (i) a considerable decrease in the time scale, which in most cases implies a smaller consumption of energy, (ii) a reduction in the number of steps involved in the global process, eliminating the need for other reagents, devices, etc. and (iii) an increase in the efficiency of the global process. These advantages mean that the final products obtained from microwave-assisted processes will probably be more economically competitive than the ones obtained using traditional techniques.

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Ball lightning plasma and plasma arc formation during the microwave heating of carbons

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ABSTRACT

Microwave heating can be used to promote heterogeneous reactions with carbon materials, mainly because of the heating mechanism involved in microwave radiation and the phenomenon known as microplasmas. This work presents photographic evidence of plasma formation when different carbon materials are subjected to microwave heating. Two different kinds of plasmas were observed: ball lightning and arc discharge plasmas. The intensity of the plasmas in the less ordered carbon was significantly higher at the beginning of the process.

Microwave heating of carbons is used in processes such as the activation or regeneration of activated carbons, gas-phase chemical reactions, pyrolysis, carbonization, the synthesis of carbon gels, the generation of carbon nanofilaments, etc. [1].

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Fig. 1 – Experimental set-up.

In general, it has been reported that the use of microwave heating offers certain advantages over conventional heating. In most cases the process can be carried out in a much shorter time (e.g. pyrolysis, activation). Sometimes the products obtained are different or have different properties (e.g. pyrolysis, catalytic reactions, synthesis of carbons). Generally the differences between the microwave and conventional heating of carbon materials are attributed to the different heating mechanisms (dielectric heating vs. convection and conduction) and, especially, to the occurrence of a phenomenon referred to as "hot spots". When direct observation of the carbon bed during microwave heating is possible, it can be observed that small sparks or electric arcs are produced. These sparks are confined to a very tiny space and last only a fraction of a second. Hence they are often referred to as small localized plasmas or microplasmas [2–4]. However, there are no clear evidences that genuine plasmas are formed. The aim of this communication is to present photographic evidence that, at least, two different types of plasmas can appear when carbon materials are subjected to microwave heating, gaining some insight into the characteristics of such plasmas.

The experimental device used was a multimode cavity microwave oven equipped with a stainless steel ungrounded K-type thermocouple that not only allows the temperature of the sample to be measured, but is also connected to a PID controller so that the heating rate and final temperature can be programmed. A sample of approximately 3 g of carbon was placed on an alumina tray, which in turn was placed inside a 30 mm diameter quartz tube supported by a quartz wool layer. The tube was closed at both ends with perforated rubber stoppers that allowed a flow of N_2 (360 mL/min) to pass through the quartz tube, thus enabling an inert atmosphere to be maintained during the experiments. All the materials used were practically transparent to microwaves, with the exception of the thermocouple which reflected the microwaves and the carbon that absorbed them. This experimental set-up is shown in the photograph of Fig. 1. The experiments consisted in setting the final temperature at 700 °C and switching on the microwave at 50% maximum power (i.e., on/off pulses of 700 W of approximately 1 s duration). The experiment was video recorded through a window in the microwave door using a Cannon Ixus100 IS, HD 1280 × 720, 30 fps. Selected frames of the recorded films are shown in figures. The experiments were carried out on five different types of carbon which were ranked from the most ordered to the least ordered structures, according to their graphitic character, as follows: (i) graphite, (ii) metallurgical coke, (iii) anthracite, (iv) activated carbon and (v) a char from the pyrolysis of biomass. In all cases the carbon grains ranged from 0.5 to 3 mm.

In general, after 1 or 2 s of irradiation with microwaves, tiny flashes of light were observed to spread across the whole surface of the carbon bed, and also inside the carbon bed itself (this can be seen through the walls of the alumina tray, as in last picture of Fig. 2). Most of these flashes appeared to be no longer than 1 mm and to last only a fraction of a second. Occasionally longer flashes of about 10–30 mm were observed as well. This phenomenon is illustrated in the video as supporting material. At the beginning of the experiment the flashes of light were concentrated in certain regions of the carbon bed. Although the microplasmas occurred chiefly around the tip of the thermocouple, other regions (arbitrarily located depending on the experiment) were also prone to such occurrences, independently of the experiment performed. Moreover, in a number of experiments carried out without the use of a thermocouple, randomly located microplasmas were observed as well. The temperature in these regions increased more rapidly than in the rest of the carbon bed, i.e., such regions became incandescent before the rest. It has to be noticed, however, that the K-thermocouple is not a meaningful probe of the plasma temperature since the temperature in a plasma is a very complex issue as different species may be at different temperatures. The systems are not in thermal equilibrium and two temperatures can exits at the same place and time [4]. As the microwave radiation proceeded the entire carbon bed became incandescent and, the average temperature (i.e., the temperature as measured by the thermocouple) was similar in all parts of the bed. At this point, the frequency of occurrence and intensity of the microplasmas seemed to relapse. However this could be a false impression since in an incandescent carbon

Fig. 2 – Ball lightning plasma formation at the initial stages of the experiment, (average temperature as measured by a thermocouple: <400 °C). The experiment was carried out over activated carbon and in the presence of a thermocouple.

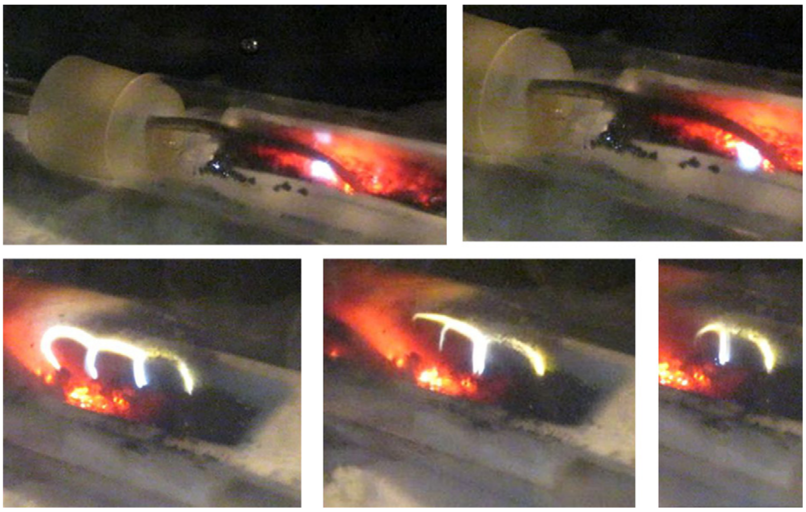

Fig. 3 – Ball lightning plasmas and plasma arcs after 1 min of irradiation (average temperature measured with the thermocouple: 400–700 °C). The experiment was carried out over activated carbon and in the presence of a thermocouple.

bed tiny plasmas are more difficult to be perceived. Nevertheless, these plasmas are still relatively abundant as illustrated in Fig. 3.

The microplasmas observed can be divided into two different types. Quasi-spherical plasmas, like those shown in Fig. 2 and in the two top pictures of Fig. 3 and electric arcs like those in the two bottom pictures. The spherical plasmas are examples of the formation, at laboratory scale, of the "unusual" and "controversial" ball lightning plasmas [5,6]. Ever since the earliest attempt to explain ball lightning plasmas made by Nikola Tesla in 1904[1] to the intriguing black hole hypothesis proposed by Rabinowitz [7] who suggested that small quiescent black holes are the core energy source of ball lightning plasmas, various theories have been put forward, but there is no widely-accepted explanation for the phenomenon [5]. These ball lightning plasmas are more abundant at the beginning of the experiments when the temperature of the carbon bed is still relatively low (<400 °C). On the other hand, electric arcs (or arc discharges), like those shown in the two bottom pictures of Fig. 3 appear at higher temperatures (400–700 °C). It should

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[1] http://tfcbooks.com/tesla/wireless01.htm.

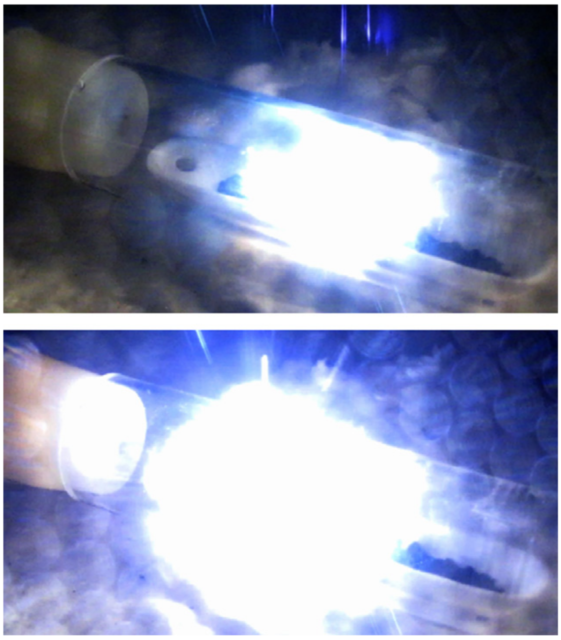

Fig. 4 – Ball lightning plasma formation at the initial stage of the experiment. While in the top picture the plasma appears to be confined inside the quartz tube, the plasma shown in the picture underneath appears to extend beyond the walls of the tube. The experiment was carried out over biomass char and in the absence of a thermocouple.

be mentioned that an electric arc is an electrical breakdown of a gas which produces an ongoing plasma discharge, resulting from a current flowing through normally non-conductive media such as air. These two types of plasma are very different not only as regards their shape, as can be seen in Figs. 2 and 3, but also, as mentioned above, as regards their nature.

All types of carbon, when subjected to the microwave heating, present a more or less similar behavior to that described above. However, it is known that different carbons heat to different extents in a microwave field depending on their structure and composition [1]. Thus, it was observed that, at the beginning of the experiment, before the carbon bed became incandescent, the intensity and size of the ball plasmas were higher in the less ordered carbons, i.e., the activated carbon and the biomass char. In these two carbons some of the ball plasmas reached a size of 10–30 mm. Surprisingly, in the case of the biomass char some of the ball lightning plasmas were observed to extend beyond the walls of the tube without apparently experiencing any alteration or obstruction (see Fig. 4). Possible overexposure of the camera sensor cannot be discarded as the cause of this effect. However, as can be seen in Fig. 4 (top) most of the large plasmas recorded with the camera appeared to be confined inside the quartz tube, plasmas like the one in the bottom picture of Fig. 4 being the exception rather than the rule. If confirmed, this phenomenon reported is extremely unusual since plasmas cannot penetrate through glass. However, an explanation of how ball lighting might be able to do so is given by Torchigin [8].

In sum, in the conditions described in this work the microwave heating of carbon materials was observed to give rise to the formation of two different kinds of plasma i.e., ball lightning or arc discharge plasmas.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.09.010.

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