



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

J.M. Bermúdez, B. Fidalgo, A. Arenillas, J.A. Menéndez \*

Instituto Nacional del Carbón, CSIC, Aparatado 73, 33080 Oviedo, Spain

## ARTICLE INFO

### Article history:

Received 19 October 2009

Received in revised form 11 January 2010

Accepted 12 January 2010

Available online 27 January 2010

### Keywords:

Coke oven gas

Dry reforming

Syngas

Methanol

## 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 as 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.

© 2010 Elsevier Ltd. All rights reserved.

## 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<sub>2</sub> (~55–60%), CH<sub>4</sub> (~23–27%), CO (~5–8%) and N<sub>2</sub> (~3–5%), along with other hydrocarbons, H<sub>2</sub>S and NH<sub>3</sub> 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<sub>2</sub> consumption. Another important advantage of the dry reforming of COG is the possibility of obtaining a syngas with a H<sub>2</sub>/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<sub>4</sub> and CO<sub>2</sub>. As can be seen in Fig. 1, the process can be considered as a way of “partial recycling” of CO<sub>2</sub> since it consumes, at least theoretically, half of the CO<sub>2</sub> 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<sub>2</sub>/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.

\* Corresponding author. Tel.: +34 985118972; fax: +34 985297672.

E-mail address: [angelmd@incar.csic.es](mailto:angelmd@incar.csic.es) (J.A. Menéndez).

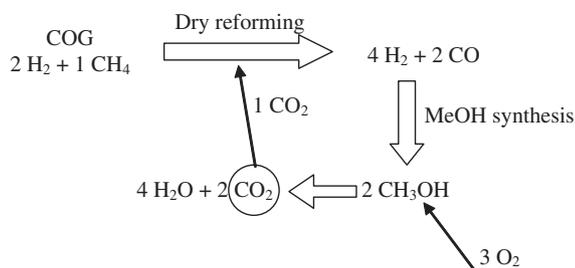


Fig. 1. Scheme of "partial recycling" of CO<sub>2</sub> in the process of dry reforming of COG for methanol production.

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<sub>4</sub> and CO<sub>2</sub> were fed in at a ratio of 1:1. In the rest of the experiments, H<sub>2</sub> was added in order to study the effect of the presence of H<sub>2</sub> in the feed stream on the process of dry reforming of methane. The addition of H<sub>2</sub> gave rise to a gaseous ternary mixture (GTM) composed of 54% H<sub>2</sub>, 23% CH<sub>4</sub> and 23% CO<sub>2</sub> (vol.%), in order that the H<sub>2</sub>/CH<sub>4</sub> ratio was within the range characteristic of COG (2–2.7). The CH<sub>4</sub> and CO<sub>2</sub> 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<sup>-1</sup> h<sup>-1</sup>, which represent 0.16, 0.22, and 0.32 L g<sup>-1</sup> h<sup>-1</sup> for the methane respectively, VHSV<sub>CH<sub>4</sub></sub>) 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<sub>2</sub> (flow rate of 60 mL min<sup>-1</sup> 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<sub>2</sub> and hydrocarbons (≥C<sub>2</sub>).

The CH<sub>4</sub> and CO<sub>2</sub> conversions and the selectivity to H<sub>2</sub> 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-linear equations and using the Solver Microsoft Excel® tool, and closing mass balances within a ±5% error margin. Selectivity to hydrogen gives an approximate idea of the amount of methane transformed into H<sub>2</sub> or into other species (such as light hydrocarbons, ≥C<sub>2</sub>, or water). The parameters were calculated according to Eqs. (1)–(3):

$$\text{CH}_4 \text{ conversion (\%)} = 100 \times \frac{\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out}}{\text{CH}_4 \text{ in}}, \quad (1)$$

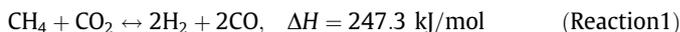
$$\text{CO}_2 \text{ conversion (\%)} = 100 \times \frac{\text{CO}_2 \text{ in} - \text{CO}_2 \text{ out}}{\text{CO}_2 \text{ in}}, \quad (2)$$

$$\text{H}_2 \text{ selectivity, } S \text{ (\%)} = 100 \times \frac{\text{H}_2 \text{ out} - \text{H}_2 \text{ in}}{2 \cdot (\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out})}, \quad (3)$$

where CH<sub>4 in</sub>, CO<sub>2 in</sub> and H<sub>2 in</sub>, are moles of each gas at the inlet of the reactor and CH<sub>4 out</sub>, CO<sub>2 out</sub> and H<sub>2 out</sub> are moles of each gas at the outlet.

### 3. Results and discussion

In a previous work by our group [20], the reforming of CH<sub>4</sub> with CO<sub>2</sub> (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<sub>2</sub> 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<sub>CH<sub>4</sub></sub> of 0.16 L g<sup>-1</sup> h<sup>-1</sup> (total VSHV of 0.32 L g<sup>-1</sup> h<sup>-1</sup>) and conversions of more than 40% were achieved.



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<sub>4</sub> and CO<sub>2</sub> conversions, and (ii) the reverse water gas shift reaction (RWGS) occurs (Reaction 2), giving rise to an increase in CO<sub>2</sub> conversion and the formation of water [16,21,22]. Both effects result in a decrease in hydrogen production.

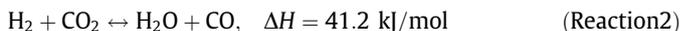


Table 1  
Main chemical characteristics and textural properties of the activated carbon FY5.

Proximate analysis (wt.%)				Ultimate analysis (wt.%) <sup>a</sup>							
Moisture	Ash <sup>b</sup>	Volatile matter <sup>a</sup>		C	H	N	S	O <sup>b</sup>	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 <sup>a</sup> )											
SiO <sub>2</sub>	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	SO <sub>3</sub>	MgO	TiO <sub>2</sub>	Ni	Co	
39.79	25.40	9.06	9.04	6.4	3.01	2.77	2.71	1.18	n.d. <sup>c</sup>	n.d. <sup>c</sup>	
Textural properties											
S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>t</sub> (cm <sup>3</sup> /g) <sup>d</sup>	V <sub>m</sub> (cm <sup>3</sup> /g) <sup>e</sup>	V <sub>s</sub> (cm <sup>3</sup> /g) <sup>f</sup>								
825	0.34	0.32	0.25								

<sup>a</sup> Dry basis.

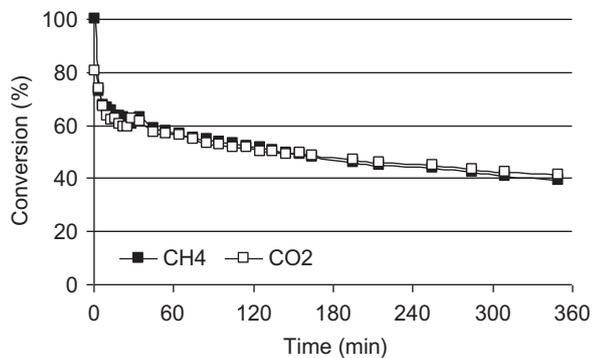
<sup>b</sup> Calculated by difference.

<sup>c</sup> Not detected.

<sup>d</sup> Total specific pore volume.

<sup>e</sup> Specific volume of micropores (pores of internal width < 2 nm).

<sup>f</sup> Specific volume of small micropores (pores with an internal width < 0.7 nm).

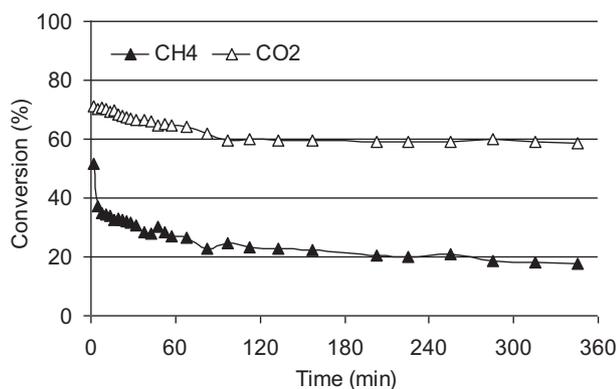


**Fig. 2.** CH<sub>4</sub> and CO<sub>2</sub> conversions for the dry reforming of CH<sub>4</sub> at 800 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1, VHSV<sub>CH<sub>4</sub></sub> = 0.16 L g<sup>-1</sup> h<sup>-1</sup>, VHSV = 0.32 L g<sup>-1</sup> h<sup>-1</sup> and 1 atm (adapted from [20]).

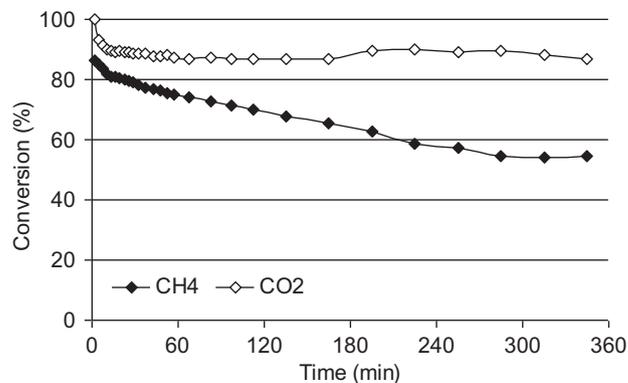
Both phenomena occurred in the case of the dry reforming of the GTM at 800 °C, and led to changes in the CH<sub>4</sub> and CO<sub>2</sub> conversions resulting from the dry reforming of CH<sub>4</sub>. As can be seen in Fig. 3, methane conversion fell to below 40% from the very beginning of the reaction, 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<sub>2</sub> production and changing the H<sub>2</sub>/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<sub>4</sub> conversion is higher than 50% throughout the experiment, a level of conversion never reached in tests carried out at 800 °C. CO<sub>2</sub> 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<sub>2</sub> 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 re-

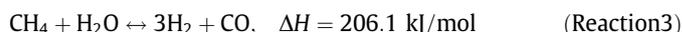


**Fig. 3.** CH<sub>4</sub> and CO<sub>2</sub> conversions for the dry reforming of the GTM at 800 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1, VHSV<sub>CH<sub>4</sub></sub> = 0.16 L g<sup>-1</sup> h<sup>-1</sup>, VHSV = 0.75 L g<sup>-1</sup> h<sup>-1</sup> and 1 atm.



**Fig. 4.** CH<sub>4</sub> and CO<sub>2</sub> conversions for the dry reforming of the GTM at 900 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1, VHSV<sub>CH<sub>4</sub></sub> = 0.16 L g<sup>-1</sup> h<sup>-1</sup>, VHSV = 0.75 L g<sup>-1</sup> h<sup>-1</sup> and 1 atm.

sults 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.



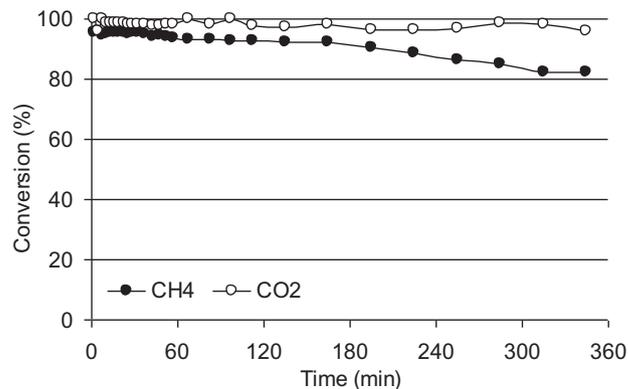
However, this mechanism seems less probable since it would lead to similar increments in both CH<sub>4</sub> and CO<sub>2</sub> conversions which did not take place, as can be seen in Fig. 4. Nevertheless, the sum of RWGS reaction (Reaction 2) and steam reforming reaction (Reaction 3) gives rise to the 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<sub>4</sub> and 95% for CO<sub>2</sub> 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<sup>-1</sup> h<sup>-1</sup>, respectively) are shown in Fig. 6. As can be seen, both CH<sub>4</sub> and CO<sub>2</sub> conversions



**Fig. 5.** CH<sub>4</sub> and CO<sub>2</sub> conversions for the dry reforming of the GTM at 1000 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1, VHSV<sub>CH<sub>4</sub></sub> = 0.16 L g<sup>-1</sup> h<sup>-1</sup>, VHSV = 0.75 L g<sup>-1</sup> h<sup>-1</sup> and 1 atm.

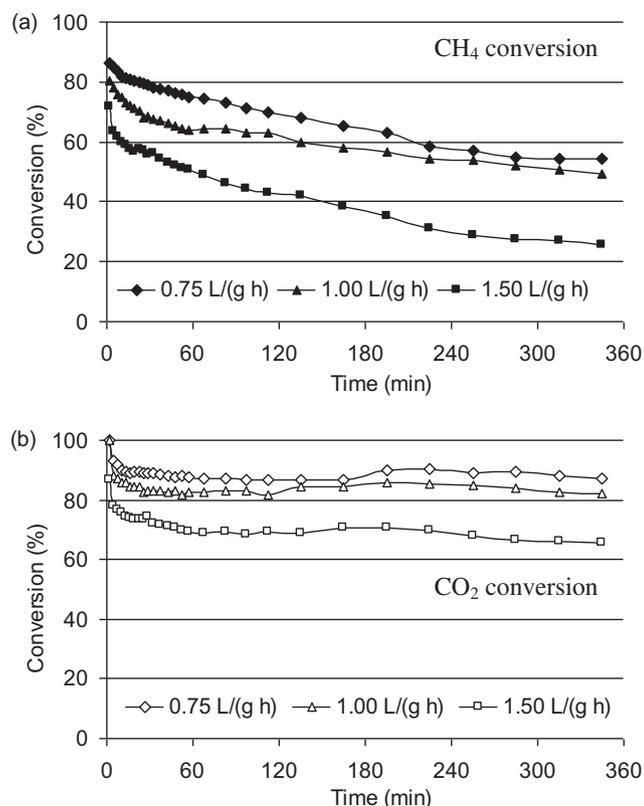


Fig. 6. Influence of the VHSV on (a) CH<sub>4</sub> conversion and (b) CO<sub>2</sub> conversion, for the dry reforming of the GTM at 900 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1 and 1 atm.

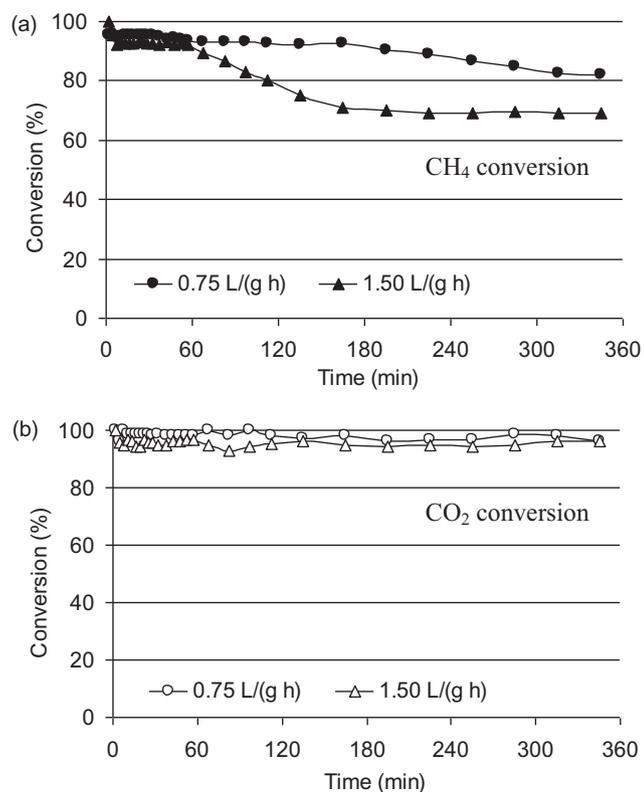


Fig. 7. Influence of the VHSV on (a) CH<sub>4</sub> conversion and (b) CO<sub>2</sub> conversion, for the dry reforming of the GTM at 1000 °C, CH<sub>4</sub>/CO<sub>2</sub> = 1 and 1 atm.

are affected by changes in VHSV. Thus, the levels of conversions diminish as the VHSV increases. However, the decrease in the CH<sub>4</sub> conversion is greater than in the case of CO<sub>2</sub>. The loss of conversion due to dry reforming reaction and to the increase in VHSV is similar both for CH<sub>4</sub> and CO<sub>2</sub> [20]. Whereas, the consumption of CO<sub>2</sub> due to the RWGS reaction, which seems to be higher at elevated VHSVs, led to a smaller decrease in CO<sub>2</sub> conversion. Thus, high amounts of water were collected when the VHSV increased (50% higher in the experiment at 1 L g<sup>-1</sup> h<sup>-1</sup> and twice the amount in the experiment carried out at 1.5 L g<sup>-1</sup> h<sup>-1</sup>, compared to the experiment at 0.75 L g<sup>-1</sup> h<sup>-1</sup>), owing to the more vigorous RWGS reaction as VHSV increased. This may be due to an increase in the CO<sub>2</sub> concentration throughout the reactor. Since there is a high amount of H<sub>2</sub> present, CO<sub>2</sub> could be the species which limits the RWGS reaction. Consequently, high conversions of CO<sub>2</sub> 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<sup>-1</sup> h<sup>-1</sup> and 1.50 L g<sup>-1</sup> h<sup>-1</sup>, respectively. As was explained above, no water production was observed at 1000 °C and 0.75 L g<sup>-1</sup> h<sup>-1</sup>. When the VSHV was increased to 1.50 L g<sup>-1</sup> h<sup>-1</sup>, some water was produced due to the increase in the concentration of CO<sub>2</sub> 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<sub>2</sub> 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<sub>4</sub> is converted into H<sub>2</sub> or into other species, it is necessary to evaluate the selectivity (Eq. (3)). Selectivity to H<sub>2</sub> 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<sub>2</sub> 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<sup>-1</sup> h<sup>-1</sup>), 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.

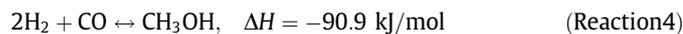
To determine whether a syngas is suitable for methanol production, the H<sub>2</sub>/CO ratio after the process of reforming must be taken into account. The appropriate H<sub>2</sub>/CO ratio for the synthesis of methanol (Reaction 4) is 2 [17,18]. Both steam and dry reforming of methane give rise to 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<sub>2</sub>/CO ratio, *R* parameter and selectivity to H<sub>2</sub> (*S*) for the dry reforming of the GTM at different temperatures and VHSV.

Temperature (°C)	VHSV (L g <sup>-1</sup> h <sup>-1</sup> )	H <sub>2</sub> /CO	<i>R</i>	<i>S</i> <sup>a</sup> (%)
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

<sup>a</sup> Range of variation of the selectivity to H<sub>2</sub> from *t* = 0 to 6 h.

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.



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]:

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

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 influ-

ence 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  $1.5 \text{ L g}^{-1} \text{ h}^{-1}$ , the activated carbon FY5 is a good catalyst for the dry reforming of COG as means of producing syngas for the production of methanol.

#### Acknowledgments

The authors wish to thank PCTI – Asturias for the financial support received under Project PEST08-03. B.F. and J.M.B. acknowledges the support received from the CSIC I3P and JAE Programmes, respectively.

#### References

- [1] van der Drift A, Boerrigter H. Synthesis gas from biomass for fuels and chemicals, IEA bioenergy agreement task 33: thermal gasification of biomass. Stockholm, Sweden: International Energy Agency; 2006.
- [2] Zahedi M, Rowshanzamir S, Eikani MH. Autothermal reforming of methane to synthesis gas: modelling and simulation. *Int J Hydrogen Energy* 2009;34:1292–300.
- [3] Domínguez A, Fernández Y, Fidalgo B, Pis JJ, Menéndez JA. Biogas to syngas by microwave-assisted dry reforming in the presence of char. *Energy Fuels* 2007;21(4):2066–71.
- [4] Li YB, Xiao R, Jin B. Thermodynamic equilibrium calculations for the reforming of coke oven gas with gasification gas. *Chem Eng Technol* 2007;30(1):91–8.
- [5] Guo J, Hou Z, Gao J, Zheng X. Production of syngas via partial oxidation and  $CO_2$  reforming of coke oven gas over a Ni catalyst. *Energy Fuels* 2008;22(3):1444–8.
- [6] Asp B. Masters Thesis. Luleå University of Technology, Luleå, Sweden, 2007. Available from: <http://epubl.ltu.se/1402-1617/2007/189/LTU-EX-07189-SE.pdf>.
- [7] Zhang JY, Zhou JM, Yan HJ. Kinetic model on coke oven gas with steam reforming. *J Cent South Univ Technol* 2008;15(1):127–31.
- [8] Josecka F, Wang M, Wub Y. Potential energy and greenhouse gas emission effects of hydrogen production from coke oven gas in US Steel mills. *Int J Hydrogen Energy* 2008;33(4):1445–54.
- [9] Modesto M, Nebra SA. Exergoeconomic analysis of the power generation system using blast furnace and coke oven gas in a Brazilian steel mill. *Appl Therm Eng* 2009;29(11–12):2127–36.
- [10] Yang J, Lee C-H. Adsorption dynamics of a layered bed PSA for  $H_2$  recovery from coke oven gas. *AIChE J* 1998;44(6):1325–34.
- [11] Shen J, Wang Z-Z, Yang H-W, Yao R-S. A new technology for producing hydrogen and adjustable ratio syngas from coke oven gas. *Energy Fuels* 2007;21(6):3588–92.
- [12] Onozaki M, Watanabe K, Hashimoto T, Saegusa H, Katayama Y. Hydrogen production by the partial oxidation and steam reforming of tar from hot coke oven gas. *Fuel* 2006;85(2):143–9.
- [13] Zhang Y, Li Q, Shen P, Liu Y, Yang Z, Ding W, et al. Hydrogen amplification of coke oven gas by reforming of methane in a ceramic membrane reactor. *Int J Hydrogen Energy* 2008;33(13):3311–9.
- [14] Yang S, Xu X, Tian W. Simulation for hydrogen production from sorption enhanced coke-oven gas steam reforming based on chemical looping combustion. *J Chem Ind Eng* 2007;58(9):2363–8.
- [15] Hashimoto T, Onozaki M. Reforming of hot coke oven gas. *J Jpn Inst Energy* 2006;85(5):364–70.

- [16] Zhang G, Dong Y, Feng M, Zhang Y, Zhao W, Cao H. CO<sub>2</sub> reforming of CH<sub>4</sub> in coke oven gas to syngas over coal char catalyst. *Chem Eng J* 2009. doi:10.1016/j.cej.04.005.
- [17] Olah GA, Goepfert A, Prakash GKS. *Beyond the oil and gas: the methanol economy*. Weinheim, Germany: Wiley-VCH; 2006. p. 209–45.
- [18] Yin X, Leung DY, Chang J, Wang J, Fu Y, Wu C. Characteristics of the synthesis of methanol using biomass-derived syngas. *Energy Fuels* 2005;19(1):305–10.
- [19] Maruoka N, Akiyama T. Exergy recovering from steelmaking off-gas by latent heat storage for methanol production. *Energy* 2006;31(10–11):1632–42.
- [20] Fidalgo B, Domínguez A, Pis JJ, Menéndez JA. Microwave-assisted dry reforming of methane. *Int J Hydrogen Energy* 2008;33(16):4337–44.
- [21] Xu J, Froment GF. Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics. *AIChE J* 1989;35(1):88–96.
- [22] Ginsburg JM, Pia J, El Solh T, De Lasa HI. Coke formation over a nickel catalyst under methane dry reforming conditions: thermodynamic and kinetic models. *Ind Eng Chem Res* 2005;44(14):4846–54.
- [23] Sun JT, Metcalfe IA, Sahibzada M. Deactivation of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst by sintering. *Ind Eng Chem Res* 1999;38(10):3868–72.
- [24] Hamelinck CN, Faaijk APC. *Future prospects for production of methanol and hydrogen from biomass*. Utrecht, The Netherlands: Utrecht University; 2001. Available from: [http://www.mtholyoke.edu/courses/tmillett/course/geog\\_304B/e2001-49.pdf](http://www.mtholyoke.edu/courses/tmillett/course/geog_304B/e2001-49.pdf).
- [25] Tjatjopoulos GJ, Vasalos IA. Feasibility analysis of ternary feed mixtures of methane with oxygen, steam, and carbon dioxide for the production of methanol synthesis gas. *Ind Eng Chem Res* 1998;37(4):1410–21.