Equilibrium prediction of CO₂ reforming of coke oven gas. Suitability for methanol production

J.M. Bermúdez, A. Arenillas*, J.A. Menéndez*

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

** Corresponding authors. Tel.: +34 985 118972; Fax: +34 985 297672*

E-mail address: aapuente@incarcsic.es; angelmd@incarcsic.es

Abstract

A thermodynamic study of the equilibrium of the CO₂ 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 CO₂/CH₄ 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 CH₄ and CO₂. 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.

Keywords

Coke oven gases; Methanol synthesis; Simulation; Energy; Environment

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 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; Bermúdez et al., 2011a; Bermúdez et al., 2011b). The CO_2 balance of the process is illustrated in Figure 1.

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

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

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carried out at such high temperatures, that sintering of the metal particles of the catalyst occurs, 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 as 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 CO₂ 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.

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, CO₂/CH₄ 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 CO₂ reforming of COG). Moreover, with this approach it is very difficult to analyze the presence of solid phases, such as 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).

Table 1. Possible reactions in the CO₂ reforming of coke oven gas

Number	Reaction	ΔH (kJ/mol)
1	$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2 \text{H}_2\text{O} + 2 \text{CO}$	247
2	$\text{H}_2 + \text{CO}_2 \leftrightarrow \text{H}_2\text{O} + \text{CO}$	42
3	$\text{H}_2\text{O} + \text{CH}_4 \leftrightarrow 3 \text{H}_2 + \text{CO}$	205
4	$\text{CH}_4 \leftrightarrow \text{C} + 2 \text{H}_2$	76
5	$\text{CO}_2 + \text{C} \leftrightarrow 2 \text{CO}$	173
6	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	131
7	$\text{C} + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2 \text{H}_2$	90
8	$\text{CH}_4 + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4 \text{H}_2$	165
9	$\text{CO} + 2 \text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$	-91
10	$\text{CO}_2 + 3 \text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-41
11	$\text{C}_2\text{H}_6 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2$	136
12	$\text{C}_n\text{H}_m \leftrightarrow n \text{C} + (m/2) \text{H}_2$	
13	$\text{C}_n\text{H}_m + n \text{H}_2\text{O} \leftrightarrow n \text{CO} + (n + m/2) \text{H}_2$	
14	$\text{C}_n\text{H}_m + n \text{CO}_2 \leftrightarrow 2n \text{CO} + (n/2) \text{H}_2$	
15	$3 \text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2$	-258
16	$\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \leftrightarrow 2 \text{CH}_3\text{OH}$	37
17	$\text{CH}_3\text{OCH}_3 + 3 \text{H}_2\text{O} \leftrightarrow 2 \text{CO} + 6 \text{H}_2$	136

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 H₂, CH₄, CO, CO₂, N₂, C₂H₄, C₂H₆, H₂O, 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) (Figure 2). These components are defined as follows:

1. COG: a stream representing the coke oven gas. In the basic scenario it includes H₂, CH₄, CO, CO₂ and N₂, and in the final case it also includes other hydrocarbons (C₂H₄ and C₂H₆) that may appear in small proportions.
2. CO₂: a stream representing the CO₂ 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.

Fig. 2. Scheme of the model

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 CO₂ and CH₄ were introduced in stoichiometric conditions and light hydrocarbons (C₂H₄ and C₂H₆) were excluded from the fed-in streams; a second scenario in which an excess of CO₂ over the estequiometric conditions (the CO₂/CH₄ 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 CH₄ over the stoichiometric conditions (the CO₂/CH₄ ratio was 40%/60%) was introduced in order to obtain a syngas with a higher content in H₂; and a final scenario with stoichiometric conditions of CO₂ and CH₄ and the presence of light hydrocarbons in the feeding streams. The feeding stream conditions employed in each scenario are summarized in Table 2.

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 ₂ H ₆	C ₂ H 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

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

1. CH₄ and CO₂ conversions (Eq. 1 and 2), which express the amount of each species reacted. These parameters were calculated as follows:

$$\text{CH}_4 \text{ conversion, \%} = 100 \cdot (\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out}) / \text{CH}_4 \text{ in} \quad (\text{Eq. 1})$$

$$\text{CO}_2 \text{ conversion, \%} = 100 \cdot (\text{CO}_2 \text{ in} - \text{CO}_2 \text{ out}) / \text{CO}_2 \text{ in} \quad (\text{Eq. 2})$$

2. H₂ 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 CH₄ and the light hydrocarbon is converted to H₂). This parameter was calculated as follows:

$$\text{H}_2 \text{ conversion, \%} = 100 \cdot (\text{H}_2 \text{ prod} / \text{H}_2 \text{ max}) \quad (\text{Eq. 3})$$

3. The H₂/CO ratio of the synthesis gas.
4. The R parameter of the synthesis gas (Eq. 4), which expresses the relation between the H₂, CO and CO₂ 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).

$$\text{R, dimensionless} = (\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2) \quad (\text{Eq. 4})$$

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 CO₂ reforming of coke oven gas (Bermúdez et al., 2010; Bermúdez et al., 2011a; Bermúdez et al., 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 text. The rest of the figures have been included as supplementary material.

3. Results and discussion

3.1. CO₂ 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 Figure 3. The figure shows the 3D surfaces and the contour plots obtained for these parameters as a function of temperature and pressure.

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.

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; Bermúdez et al., 2011a; Bermúdez et al., 2011b; Zhang et al., 2010). These suppositions are confirmed by the results in Figure 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 CO₂ 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 H₂/CO and the R parameter (Eq. 4) were evaluated. The H₂/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 H₂, as a result of which the process becomes less efficient.

As can be seen in Figure 5, the H₂/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 H₂/CO ratio is very high, the conversions are very low and H₂ production is almost zero, as a result of which these conditions should be 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 H₂ (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 N₂ or CH₄) it is necessary to include a purge in the recycling loop, which gives rise to a H₂-rich stream. Usually the H₂ 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.

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

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

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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 ($\text{CO}_2/\text{CH}_4 = 50/50$), the case with an excess of CO_2 ($\text{CO}_2/\text{CH}_4 = 60/40$) and the case with an excess of CH_4 ($\text{CO}_2/\text{CH}_4 = 40/60$). Figure 6 compares the different carbon and water productions for the three CO_2/CH_4 ratios while Figure 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.

Table 3. Comparison between the conversions of CH₄ and CO₂ and the H₂ 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								Scenario 3 – Excess of CH ₄								Scenario 4 – Presence of light hydrocarbons							
Difference in CH ₄ Conversion (%)								Difference in CH ₄ Conversion (%)								Difference in CH ₄ Conversion (%)							
P \ T	600	700	800	900	1000	1100	1200	P \ T	600	700	800	900	1000	1100	1200	P \ T	600	700	800	900	1000	1100	1200
1	7.2	3.2	5.2	3.9	2.0	0.8	0.3	1	-6.4	-2.8	-1.1	-0.5	-0.3	-0.4	-0.3	1	-2.8	-1.4	-0.6	-0.3	-0.2	-0.3	-0.3
5	12.8	8.4	4.7	8.5	7.8	4.4	2.3	5	-11.3	-7.4	-4.1	-2.1	-1.1	-1.0	-1.0	5	-4.6	-3.3	-2.0	-1.1	-0.6	-0.8	-0.8
10	14.5	10.7	7.0	7.0	10.9	7.8	4.4	10	-12.7	-9.4	-6.1	-3.5	-2.0	-1.7	-1.6	10	-5.1	-4.1	-2.9	-1.8	-1.0	-1.2	-1.3
15	15.4	12.0	8.4	5.3	12.0	10.2	6.3	15	-13.4	-10.5	-7.3	-4.6	-2.7	-2.2	-2.2	15	-5.3	-4.5	-3.4	-2.3	-1.4	-1.5	-1.8
20	15.9	12.8	9.4	6.3	12.2	11.9	7.9	20	-13.8	-11.1	-8.2	-5.4	-3.3	-2.7	-2.7	20	-5.5	-4.7	-3.7	-2.7	-1.7	-1.8	-2.2
Difference in CO ₂ Conversion (%)								Difference in CO ₂ Conversion (%)								Difference in CO ₂ Conversion (%)							
P \ T	600	700	800	900	1000	1100	1200	P \ T	600	700	800	900	1000	1100	1200	P \ T	600	700	800	900	1000	1100	1200
1	-6.5	-4.4	-6.5	-9.3	-8.9	-7.9	-7.0	1	5.9	4.0	1.5	0.4	0.1	0.1	0.1	1	-0.8	-0.4	-0.1	0	0	-0.1	-0.1
5	-7.5	-6.2	-4.1	-5.3	-7.2	-7.2	-6.7	5	6.6	5.5	3.5	1.5	0.5	0.3	0.2	5	-0.9	-0.7	-0.3	-0.1	0	-0.1	-0.1
10	-7.7	-6.7	-5.0	-3.7	-5.8	-6.5	-6.3	10	6.7	5.9	4.4	2.3	0.9	0.5	0.3	10	-0.9	-0.8	-0.5	-0.2	-0.1	-0.1	-0.2
15	-7.8	-6.9	-5.5	-3.3	-5.1	-5.9	-6.0	15	6.8	6.1	4.8	2.8	1.3	0.6	0.4	15	-0.9	-0.8	-0.5	-0.2	-0.1	-0.2	-0.2
20	-7.9	-7.1	-5.8	-3.8	-4.6	-5.5	-5.7	20	6.8	6.2	5.1	3.2	1.5	0.8	0.5	20	-1.0	-0.8	-0.6	-0.3	-0.1	-0.2	-0.3

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Difference in H ₂ Production (%)								Difference in H ₂ Production (%)								Difference in H ₂ Production (%)							
P \ T	600	700	800	900	1000	1100	1200	P \ T	600	700	800	900	1000	1100	1200	P \ T	600	700	800	900	1000	1100	1200
1	-2.8	-2.2	-3.1	-10.5	-15.2	-17.9	-19.3	1	2.5	2.0	0.7	0.1	0	-0.2	-0.1	1	2.8	1.3	0.5	0.2	0	-0.1	-0.1
5	-1.2	-1.7	-1.3	-0.8	-6.7	-12.8	-16.6	5	1.1	1.6	1.2	0.3	-0.1	-0.4	-0.5	5	4.6	3.0	1.6	0.7	0.3	-0.1	-0.3
10	-0.8	-1.2	-1.2	-0.2	-1.5	-8.0	-13.5	10	0.7	1.1	1.1	0.4	-0.1	-0.6	-0.8	10	5.2	3.8	2.3	1.2	0.5	-0.1	-0.5
15	-0.6	-0.9	-1.0	-0.4	-0.7	-4.6	-10.8	15	0.6	0.9	0.9	0.4	-0.2	-0.7	-1.1	15	5.6	4.3	2.8	1.6	0.7	0	-0.6
20	-0.5	-0.8	-0.9	-0.4	-1.6	-2.2	-8.6	20	0.5	0.7	0.8	0.4	-0.2	-0.8	-1.3	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% CO₂ / 50% CH₄), 2 (60% CO₂ / 40% CH₄) and 3 (40% CO₂ / 60% CH₄).

Fig. 7. Comparison between the results for the H₂/CO ratio (a) and R parameter (b) obtained in scenarios 1 (50% CO₂ / 50% CH₄), 2 (60% CO₂ / 40% CH₄) and 3 (40% CO₂ / 60% CH₄).

3.2.1. Excess of CO₂

When the CO₂ reforming of COG is carried out with an excess of CO₂ in the feed, the conversions are noticeably affected. In the case of CH₄ 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 CO₂ conversion. In this case, the results are worse than those obtained in the base case. The excess of CO₂ has increased

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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 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 behaviour 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 $\pm 3\%$).

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 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).

Figure 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.

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

The presence of light hydrocarbons has almost no influence on the parameters of the syngas produced. Figure 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.

Fig. 9. Comparison between the results for the H₂/CO ratio (a) and the R parameter (b) obtained in scenarios 1 (without light hydrocarbons) and 4 (with light hydrocarbons).

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 (H₂/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 CO₂/CH₄ ratios different from the stoichiometric proportion (50:50) yield worse results, since the conversions and H₂ 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 CO₂ and H₂O 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.

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