**Abstract**

A conceptually similar approach to dry reforming of CH$_4$ (DRM) called Catalytic Decomposition of Biogas (CDB) is proposed. CDB is based on the direct decomposition of CH$_4$ and CO$_2$, which are the most abundant components in biogas (typically with CH$_4$:CO$_2$ molar ratios higher than 1). The main difference between DRM and CDB lies in the desired products obtained in each process. While in DRM carbon formation is not desired and thus avoided, in CDB carbon accumulation in form of filamentous structures is promoted. In this work, the effect of CH$_4$ and CO$_2$ partial pressures on the initial reaction rates of CDB was studied using a Ni/Al$_2$O$_3$ catalyst. Furthermore, a deactivation study was carried out in order to determine the experimental conditions (CH$_4$ and CO$_2$ partial pressures and temperature) at which carbon formation did not deactivate the catalyst. It was proved that after a certain time on stream, CDB can reach the steady state even though the CH$_4$:CO$_2$ molar ratio is higher than one (typical biogas conditions). In addition, temperature increased reaction rates since CDB is an endothermic process, but it had no effect on catalyst deactivation.
**Keywords:** Catalytic Decomposition of Biogas, CH₄-CO₂ reaction, Ni/Al₂O₃ catalyst, deactivation study, nanostructured carbon.
1 Introduction

Due to the finite nature of fossil fuels, it is necessary to change from our current energy system to a new long term sustainable system in which all the energetic sources should be considered. Biogas, a gas composed mainly of methane (40-70%) and carbon dioxide (30-60%) [1], can be used as feedstock in the dry reforming of CH$_4$ (DRM) to produce syngas and because of its renewable character, the process is classified as CO$_2$ neutral.

DRM (CH$_4$ + CO$_2$ $\rightarrow$ 2H$_2$ + 2CO) is a highly endothermic reaction ($\Delta H^o = 247$ kJ·mol$^{-1}$) that takes place catalytically in a temperature range between 600-800 °C, producing a syngas with a theoretical H$_2$:CO molar ratio of 1:1 [2-10]. Nowadays, a general rate expression is not yet established for the CH$_4$-CO$_2$ reaction and different expressions can be found in the literature [11-16]. However, there is a general consensus on the elementary reaction steps [17]: CH$_4$ decomposition takes place on the leading face of the catalyst particle (active face), initially generating CH$_x^*$ species and then chemisorbed carbon (C$^*$) and atomic hydrogen (H$^*$) {1-3}. At the same time, direct CO$_2$ decomposition {4} takes place followed by C$^*$ and CH$_x^*$ oxidation {5-6}, CO generation {7-8}, H$_2$ generation {9} and the reverse water gas shift reaction {10}.

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3^* + \text{H}^* \{1\} \\
\text{CH}_x^* & \rightarrow \text{CH}_{x-1}^* + \text{H}^* \{2\} \\
\text{CH}^* & \rightarrow \text{C}^* + \text{H}^* \{3\} \\
\text{CO}_2 & \leftrightarrow \text{CO}^* + \text{O}^* \{4\} \\
\text{C}^* + \text{O}^* & \leftrightarrow \text{CO}^* \{5\} \\
\text{CH}^* + \text{O}^* & \leftrightarrow \text{CHO}^* \{6\}
\end{align*}
\]
CHO$^*$ $\leftrightarrow$ CO$^*$ + H$^*$ \{7\}

CO$^*$ $\leftrightarrow$ CO \{8\}

2H$^*$ $\leftrightarrow$ H$_2$ \{9\}

CO$_2$ + H$_2$ $\leftrightarrow$ H$_2$O + CO \{10\}

Generally, when CH$_4$-CO$_2$ reaction is studied, efforts are devoted to avoid carbon formation in order to disregard its possible effects on the catalyst behaviour. Recently, a conceptually similar approach to DRM called Catalytic Decomposition of Biogas (CDB) has been proposed [18, 19]. CDB basically consists on the direct decomposition of CH$_4$ and CO$_2$ mixtures and comprises the main reaction steps considered for the DRM. The main difference between DRM and CDB lies in the desired products obtained in each process. As opposed to DRM reaction, CDB promotes carbon growth under optimized conditions in form of filamentous structures such as carbon nanofibers (CNF) that allow carrying out the reaction without catalyst deactivation. For that reason, another step on the mechanistic scheme of the CH$_4$-CO$_2$ reaction is added when using a Ni catalyst: C$^*$ diffusion and precipitation on the trailing face of the catalyst particles to form filamentous carbon structures \{11\} [20]. It is generally accepted that C$^*$ diffusion through the catalyst particle is the rate determining step in the growth of filamentous carbon [21].

C$^*$ $\rightarrow$ C$_{\text{filamentous}}$ \{11\}

Catalyst deactivation occurs when C$^*$ produced after the breaking of the four C-H bonds of CH$_4$ \{1-3\} and located on the leading face of a catalyst particle is not able to diffuse to the trailing face \{11\} or to be oxidized with atomic oxygen (O$^*$) \{5-6\}. As a result, C$^*$ accumulation takes place on the leading face, encapsulating catalyst particles.
However, if the different reaction rates involved in the process (equations \{3\}, \{5\} and \{11\}) are well balanced, then filamentous carbon structures may grow without catalyst deactivation.

In this work, two different approaches regarding the CH\textsubscript{4}-CO\textsubscript{2} reaction are analysed. Firstly, reaction rates were calculated at the beginning of the reaction, when carbon accumulation on the leading face of the catalyst particles can be considered negligible and therefore the effect of CH\textsubscript{4} and CO\textsubscript{2} partial pressures on the reaction rates can be analyzed. Secondly, the evolution of reaction rates at longer reaction times was considered. As the reaction takes place, carbon formation starts to influence on the catalyst behaviour. Depending on the experimental conditions (CH\textsubscript{4} and CO\textsubscript{2} partial pressures and temperature) deactivation of the catalyst may occur. For that reason, it is necessary to understand under which experimental conditions is possible to promote the formation of filamentous carbon structures avoiding catalyst deactivation.

2 Experimental

2.1 Catalyst preparation

A Ni based catalyst using Al\textsubscript{2}O\textsubscript{3} as textural promoter with a Ni:Al molar ratio of 2:1, previously developed for the Catalytic Decomposition of Methane (CH\textsubscript{4} → 2H\textsubscript{2} + C) (CDM) by our research group [22] and denoted as Ni/Al\textsubscript{2}O\textsubscript{3}, was prepared by the fusion method previously described in [23]: briefly, nitric salts of nickel and aluminium were crushed, followed by the decomposition of the mixture at 350 °C for 1h and calcination at 450 °C for 8h. The powder sample was ground and sieved to allow the selection of different particle sizes: >40, 40-100 and 100-200 µm. The nickel domain size of the calcined fresh catalyst was 19 nm while after the reduction pre-treatment (under a H\textsubscript{2}}
flow at 550 °C) and passivation (under a 1% O₂-99% N₂ flow at room temperature) was 31 nm. This catalyst has been extensively used and a thorough characterization can be found in previous works of our research group [19, 24].

2.2 Experimental procedure

Tests were carried out in a fixed-bed quartz reactor, 15 mm i.d, 690 mm height, heated by an electric furnace. Before each test, catalyst was reduced in-situ with a H₂ flow at 550 °C for 1h. X-ray analyses of the reduced catalyst confirmed the complete reduction of the active phase (Figure not shown).

To guarantee the rate controlling regime, internal and external mass transfer limitations were analysed through the Madon-Boudart criterion [25]. To avoid difusional effects, activity tests were carried out at atmospheric pressure, with a catalyst particle size of 100-200 µm and a total feed flow rate of 12 L_N·h⁻¹. The WHSV (Weight Hourly Space Velocity) was fixed at 1200 L_N·g_cat⁻¹·h⁻¹ and thus, the amount of catalyst used in each activity test was 0.01 g. The partial pressures influence was determined by keeping the partial pressure of one reactant (0.15 atm for CO₂ and 0.25 atm for CH₄) and varying the other one between 0.10 and 0.45 atm at 600 °C. N₂ was used to adjust the balance and to keep a total pressure of 1 atm. To study the temperature effect, CH₄ and CO₂ partial pressures were fixed at 0.10 atm (N₂ balanced) and temperature was varied between 600 and 700 °C. As previously stated, one of the main targets in CDB is the production of carbon nanofilaments and in [18], a thermodynamic study was carried out revealing that this temperature range was the temperature condition at which carbon formation was more favoured. Each experiment lasted one hour and allowed to determine the carbon formation effect on the catalyst activity. Table 1 shows the experimental conditions
used in each run. CH$_4$ and CO$_2$ conversions, $X_i$ (Eq.1) and reaction rates, $(-r_i)$ (Eq.2), were calculated as follows:

$$X_i = \frac{\text{mole}_{\text{in},i} - \text{mole}_{\text{out},i}}{\text{mole}_{\text{in},i}} \quad (\text{Eq.1})$$

$$(-r_i) = \frac{X_i}{W/F_i} \quad (\text{Eq.2})$$

In Eq.1, mole$_{\text{in},i}$ represents CH$_4$ or CO$_2$ moles introduced in the reactor and mole$_{\text{out},i}$ represents CH$_4$ or CO$_2$ moles leaving the reactor. In Eq. 2, $W$ represents the grams of catalyst initially loaded in the reactor and $F_i$, the CH$_4$ or CO$_2$ molar flow, being i: CH$_4$ or CO$_2$.

In order to determine the outlet gases composition, bag samples were taken and analysed by means of gas chromatography in a HP 5890 chromatograph equipped with two packed columns (Molecular Sieve and Porapack) and a TCD detector. Carbon samples obtained after experiments were analysed with a scanning electron microscope (SEM) (Hitachi S-3400) coupled to a Si/Li detector for energy dispersive X-ray (EDX) analysis.

3 Results and discussion

The effect of the CH$_4$ and CO$_2$ partial pressures on the Catalytic Decomposition of Biogas (CDB) initial reaction rates was studied using a Ni/Al$_2$O$_3$ catalyst. Furthermore, a deactivation study was carried out in order to determine the experimental conditions (CH$_4$ and CO$_2$ partial pressures and temperature) at which carbon formation do not deactivate the catalyst.

3.1 P$_{\text{CH4}}$ and P$_{\text{CO2}}$ influence: initial rates
In a first approach, reaction rates were calculated at the beginning of the reaction (initial reaction rates) to avoid carbon accumulation on the leading face of the catalyst particles. To elucidate the effect of CH₄ and CO₂ partial pressures, from now on P(CH₄) and P(CO₂) respectively, net CH₄ (−r(CH₄)) and CO₂ (−r(CO₂)) consumption rates are firstly represented as a function of P(CO₂) in Figure 1, keeping constant P(CH₄) at 0.25 atm. Initially, (−r(CH₄)) increased with P(CO₂) up to P(CO₂) values of 0.25 atm (CH₄:CO₂ molar ratio ≥1). At higher P(CO₂), (−r(CH₄)) remained almost constant (ca. 85 mmol·g_{cat}⁻¹·min⁻¹). It is likely that from 0.25 atm and onwards, the quantity of O⁺ produced on CO₂ decomposition reaction {4} was enough to oxidize the entire C⁺ formed on CH₄ decomposition reactions {1-3}, thus explaining the steady state reached by (−r(CH₄)) when CH₄:CO₂ molar ratio ≤1. This agrees with results obtained by other authors [14, 16] which showed that when Ni active sites are the most abundant surface species, (−r(CH₄)) did not depend on P(CO₂). However, at P(CO₂)<0.25 atm (CH₄:CO₂ molar ratio>1) low O⁺ concentration produced on reaction {4} due to the low P(CO₂), along with high CH₄ conversions obtained (X(CH₄)>30%, Table 1) that cause a high carbon formation rate, may provoke that C⁺ at the surface of the catalyst cannot be considered negligible even at the beginning of the reaction. As a consequence, a reduction in the number of Ni active sites can take place, thus explaining the lower (−r(CH₄)) values observed.

As regard (−r(CO₂)), at low pressures, (−r(CO₂)) increased linearly until P(CO₂) reached 0.25-0.30 atm. From this pressure and onwards, (−r(CO₂)) remained constant. This can be tentatively explained taking into account that the amount of O⁺ needed to react with the entire C⁺ was achieved at CO₂ pressures above 0.25 atm when CH₄:CO₂ molar ratio is ≤1 and therefore reaction {4} was equilibrated provoking a constant (−r(CO₂)). On the other hand, at P(CO₂)<0.25 (CH₄:CO₂ molar ratio>1), even though the amount of C⁺ in the catalyst surface is expected to be constant since P(CH₄) is fixed at 0.25 atm, the amount of
O* produced from CO\textsubscript{2} decomposition reaction \{4\} decreased as P\textsubscript{CO2} did, explaining the decrease in (–r\textsubscript{CO2}). Even though, RWGS \{10\} could influence on (–r\textsubscript{CO2}), it is considered quasi-equilibrated in DRM [16, 17] and therefore, an important influence on (–r\textsubscript{CH4}) and (–r\textsubscript{CO2}) is not expected.

In Figure 2, the effect of P\textsubscript{CH4} is analyzed keeping constant P\textsubscript{CO2} at 0.15 atm. An increase of (–r\textsubscript{CH4}) was observed as P\textsubscript{CH4} increased. Many studies [11, 14, 16] concluded that CH\textsubscript{4} and/or CH\textsubscript{x}\* decomposition are the rate determining steps (RDS) of the CH\textsubscript{4}-CO\textsubscript{2} reaction and thus, an increase in P\textsubscript{CH4} provokes an increase in (–r\textsubscript{CH4}). This statement is valid as long as catalyst behaviour is not affected by C\* accumulation at the surface of the catalyst particles. In Figure 2, (–r\textsubscript{CH4}) trend coincides with the expected one. However, and according with results presented before (Figure 1), a slight contribution of the deactivation phenomenon can take place when CH\textsubscript{4}:CO\textsubscript{2} molar ratio>1 since carbon accumulation on the leading face of the catalyst could provoke a decrease of the initial (–r\textsubscript{CH4}).

On the other hand, (–r\textsubscript{CO2}) was constant and did not depend on P\textsubscript{CH4}, excepting at P\textsubscript{CH4}=0.10 atm, where a lower value was observed. At P\textsubscript{CH4}≥0.15 atm, (–r\textsubscript{CH4}) increased and therefore the amount of C\* and CH\* in the surface of the catalyst particle also did. These products, in turn, react with the O\* produced on reaction \{4\} generating CHO\* and finally CO\*\. Even if (–r\textsubscript{CO2}) was expected to increase due to the shift of reaction \{4\} provoked by O\* consumption, it remained constant (ca. 60 mmol·g\textsubscript{cat}^{-1}·min\textsuperscript{-1}). A simultaneous production of CO\* takes place (reaction \{5\} and \{7\}) and as a result reaction \{4\} was equilibrated. Nevertheless, when P\textsubscript{CH4}=0.10 atm, the amounts of C\* and CH\* produced on CH\textsubscript{4} decomposition reactions \{1-3\} may be insufficient to react
with the $O^*$ produced on CO$_2$ decomposition reaction \{4\} and thus the equilibrium was shifted causing a decrease of ($-r_{CO_2}$).

### 3.2 Catalyst deactivation study

To study the catalyst deactivation phenomenon, ($-r_{CH_4}$) and ($-r_{CO_2}$) evolution with time were analyzed as a function of $P_{CH_4}$ and $P_{CO_2}$, by keeping constant the other pressure. In this section, only results related with $P_{CH_4}$ are shown. Results obtained as a function of $P_{CO_2}$ (at constant $P_{CH_4}$) were found to present the same trend as the ones obtained as a function of $P_{CH_4}$ and are therefore not included.

In Figure 3, ($-r_{CH_4}$) is plotted as a function of $P_{CH_4}$ and time on stream (TOS) at 600 °C. $P_{CO_2}$ was kept constant at 0.15 atm. To complete Figure 3, ($-r_{CH_4}$) and ($-r_{CO_2}$) values as a function of TOS are showed in Table 2. At $P_{CH_4}=0.10$ and 0.15 atm (dash lines), which correspond to CH$_4$:CO$_2$ molar ratio $\leq 1$, a slight deactivation was observed in the first 5 minutes of reaction. Thereafter, catalyst seemed to reach a steady state since ($-r_{CH_4}$) remained almost invariable after 15, 30 and 60 minutes TOS. In these cases, it was found that ($-r_{CH_4}$)$\leq$($-r_{CO_2}$) and thus $C^*$ from CH$_4$ decomposition reactions \{1-3\} can be considered to be completely removed from the leading face of the catalyst particles, avoiding encapsulation and deactivation. $C^*$ may either diffuse to the trailing face of the catalyst particle to form filamentous carbon \{11\} or be oxidized by the $O^*$ \{5-6\} produced on CO$_2$ decomposition reaction \{4\}.

On the other hand, from $P_{CH_4}=0.20$ atm and onwards (CH$_4$:CO$_2$ molar ratio $> 1$), a clear deactivation, more significant as $P_{CH_4}$ augmented, was observed in the first 5 minutes TOS. Between 15 and 30 min TOS, catalyst deactivation was still present but the drop of ($-r_{CH_4}$) was less pronounced. Subsequently, ($-r_{CH_4}$) remained almost constant and a
steady state was probably reached. To explain this behaviour, \((-r_{\text{CH}_4})\) and \((-r_{\text{CO}_2})\) have to be considered. In cases where CH$_4$:CO$_2$ molar ratio>1, initial \((-r_{\text{CH}_4})\) were higher than initial \((-r_{\text{CO}_2})\) (Table 2), and an accumulation of C* on the leading face of the catalyst may take place in the first minutes reaction since the amount of O* produced on reaction \{4\} was probably not enough to oxidize the entire C*. This accumulation is expected to be greater as P$_{\text{CH}_4}$ increased, since differences between the initial \((-r_{\text{CH}_4})\) and \((-r_{\text{CO}_2})\) were bigger. As a consequence, a reduction of the Ni active sites can take place and hence \((-r_{\text{CH}_4})\) underwent a reduction. As TOS increased (30 and 60 minutes), \((-r_{\text{CH}_4})\) became more similar to \((-r_{\text{CO}_2})\) and as a result, the amount of C* produced equalled the amount of O*.

Summarizing, \((-r_{\text{CH}_4})\) decreased when deactivation occurred. This fact was more significant as the CH$_4$:CO$_2$ molar ratio increased. At P$_{\text{CH}_4}$=0.35 atm, the initial \((-r_{\text{CH}_4})\) was 83 mmol·g$_{\text{cat}}^{-1}$·min$^{-1}$ while after 60 minutes was 39 mmol·g$_{\text{cat}}^{-1}$·min$^{-1}$. A drop over a 50% took place. In contrast, if deactivation did not occur (CH$_4$:CO$_2$ molar ratio\(\leq 1\)), \((-r_{\text{CH}_4})\) remained almost constant and even if the initial \((-r_{\text{CH}_4})\) was lower compared with tests where CH$_4$:CO$_2$ molar ratio>1, after a certain TOS the trend could be reversed. For example, at P$_{\text{CH}_4}$=0.15 atm, \((-r_{\text{CH}_4})\) was approximately 60 mmol·g$_{\text{cat}}^{-1}$·min$^{-1}$ for the entire experiment. This value was higher than the one obtained at P$_{\text{CH}_4}$=0.35 atm after 60 minutes (i.e. 39 mmol·g$_{\text{cat}}^{-1}$·min$^{-1}$). However, in biogas the CH$_4$:CO$_2$ molar ratio is usually equal or higher than one depending on the biogas source. Results here presented are very promising since it has been proved that at CH$_4$:CO$_2$ molar ratio\(\geq 1\) and after a certain TOS (ca. 30 minutes), a steady state was achieved regardless the CH$_4$:CO$_2$ molar ratio.

In all the CDB experiments and regardless the CH$_4$:CO$_2$ molar ratio used, carbon formation was observed. However, a SEM micrograph of the carbon material obtained
after CDB (P_{CH4}=P_{CO2}=0.15 \text{ atm} \text{ and } 600 \text{ °C}) is shown in Figure 4 confirming that carbon nanofilaments formation is possible avoiding catalyst deactivation. SEM study revealed that carbon appeared as long nanofilaments few microns long with a high degree of structural order as it was proved in previous works [18, 19]. This material can be used in different areas as graphitic precursor for subsequent application as anode in the rechargeable lithium-ion batteries [26], as catalyst support in PEM fuel cells applications [27], or as additive in epoxy-based composites [28], among other applications.

3.3 Temperature effect

The effect of temperature on (–r_{CH4}) and (–r_{CO2}) was studied along with catalyst deactivation. In the previous section, it was established that CH₄-CO₂ reaction could be carried out without catalyst deactivation at 600 °C if CH₄:CO₂ molar ratio≤1. Thus, the partial pressure of both reactants, CH₄ and CO₂, was kept at 0.1 atm (N₂ balanced) in order to elucidate the temperature effect on initial reaction rates and catalyst deactivation with time. With that purpose temperature was varied from 600 to 700 °C.

In Figure 5, (–r_{CH4}) and (–r_{CO2}) at the beginning of the reaction (initial rates) are plotted as a function of temperature. The main reactions involved in the CH₄-CO₂ reaction are endothermic [29] and for that reason, when temperature increased, both (–r_{CH4}) and (–r_{CO2}) increased. Furthermore, it was observed that both reaction rates were very similar, (–r_{CH4})≈(–r_{CO2}), and according to results presented in section 3.2, deactivation is not expected. To confirm that, (–r_{CH4}) is represented as a function of TOS for different temperatures ranging from 600 to 700 °C in Figure 6. Firstly, a slight deactivation was observed in the first 15 minutes TOS; however, no trend was appreciated as a function of temperature. For example, the reduction of (–r_{CH4}) after 15 minutes at 620 °C was
mmol·g_{cat}^{-1}·min^{-1} (8%) while at 660 °C was 4 mmol·g_{cat}^{-1}·min^{-1} (3%) and at 700 °C was 10 mmol·g_{cat}^{-1}·min^{-1} (7%). Secondly, the drop of (–r_{CH4}) between 15 and 30 minutes was reduced for all the temperatures, representing a reduction of the catalyst deactivation. Finally, between 30 and 60 minutes, a steady state was almost achieved at all the temperatures studied and catalyst deactivation was negligible. Therefore, even if a slight deactivation was observed at the beginning of the reaction, after one hour TOS catalyst stability seemed to be achieved regardless of the temperature when feeding a CH_{4}:CO_{2} molar ratio=1.

4 Conclusions

Depending on CH_{4}:CO_{2} molar ratio, two different behaviours according to catalyst deactivation were observed. Firstly, when CH_{4}:CO_{2} molar ratio≤1 (P_{CH4}≤P_{CO2}), the amount of C* accumulated on the leading face of the catalyst was negligible and as a result, catalyst deactivation did not take place. Secondly, when CH_{4}:CO_{2} molar ratio>1 (usual biogas conditions), a clear deactivation, more important as CH_{4}:CO_{2} molar ratio increased, was observed at the beginning of the reaction. However, after a certain TOS, (–r_{CH4}) equalled (–r_{CO2}) and the steady state was also achieved in these conditions. Partial pressures and deactivation studies revealed that after a certain TOS and regardless the CH_{4}:CO_{2} molar ratio, CH_{4}-CO_{2} reaction could be carried out with a Ni/Al_{2}O_{3} catalyst producing simultaneously syngas and filamentous carbon structures without catalyst deactivation. Besides, temperature study performed at P_{CO2}=P_{CH4}=0.10 atm revealed that temperature did not affect catalyst deactivation in the temperature range between 600 and 700 °C. However and due to the endothermicity of the process, an increase in the reaction rates was observed as the temperature increased.
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References

Table 1. Experimental conditions of each activity test.

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<th>$P_{CO2}$ (atm)</th>
<th>$W:F_{CH4}$ (gcat·min·mmol$^{-1}$)</th>
<th>$W:F_{CO2}$</th>
<th>Temp. ($^\circ$C)</th>
<th>CH$_4$:CO$_2$</th>
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Table 2. (–rCH₄) and (–rCO₂) values as a function of TOS and PCH₄. PCO₂=0.15 atm and T=600 ºC.

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<th>PCH₄ (atm)</th>
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<td>TOS (min)</td>
<td>-rCH₄</td>
<td>-rCO₂</td>
<td>-rCH₄</td>
<td>-rCO₂</td>
<td>-rCH₄</td>
<td>-rCO₂</td>
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Figure captions

**Figure 1.** Initial (−r_{CH4}) and (−r_{CO2}) as a function of the P_{CO2} at 600 °C (P_{CH4}=0.25 atm).

**Figure 2.** Initial (−r_{CH4}) and (−r_{CO2}) as a function of the P_{CH4} at 600 °C (P_{CO2}=0.15 atm).

**Figure 3.** (−r_{CH4}) as a function of the time on stream for different P_{CH4} at 600 °C (P_{CO2}=0.15 atm).

**Figure 4.** SEM micrograph of the carbonaceous product generated during the CH₄-CO₂ reaction (P_{CH4}=P_{CO2}=0.15 atm and 600 °C).

**Figure 5.** Initial (−r_{CH4}) and (−r_{CO2}) as a function of the temperature (P_{CH4}=P_{CO2}=0.10 atm).

**Figure 6.** (−r_{CH4}) as a function of the time on stream for different temperatures (P_{CH4}=P_{CO2}=0.10 atm).
Figure 1
Figure 2
Figure 3
Figure 5
Figure 6