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## Article

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# Catalytic bi-reforming of methane for carbon dioxide ennoblement

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## Abstract

New processes that may reduce the net carbon emissions and contribute to a more circular economy are needed. Bi-reforming of methane (BRM) is a promising method for syngas production, with a hydrogen-to-carbon monoxide ratio of two in the reaction products, relevant for example when the purpose is methanol synthesis. In this work, reaction studies were carried out over a nickel-based catalyst varying the temperature (798–1123 K). Three main temperature zones have been identified; a low temperature zone where the conversion of carbon dioxide is almost null, a middle temperature range where steam reforming of methane (SRM) is dominant while the conversion of carbon dioxide via dry reforming of methane (DRM) is low, and finally a high temperature range where DRM becomes more significant. The results show that syngas can be successfully produced using this process. For the range of operating conditions studied, the carbon dioxide and methane conversions increase with temperature, reaching 40% and 100%, respectively at the largest temperature studied. However, the production of syngas in a molar ratio of 1:2 for CO-to-H<sub>2</sub> requires the use of high temperatures. Most probably the nickel agglomerates on top of the  $\gamma$ -alumina support are responsible for the poor catalyst performance.

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**Keywords:** Bi-reforming of methane; BRM; CO<sub>2</sub> ennoblement; Syngas production; Methanol

## 1. Introduction

The current dependence on non-renewable resources, in particular oil, to obtain energy and most chemicals needed to support modern lifestyles has resulted in growing negative environmental impacts. Climate change, due to the emission of greenhouse gases (GHG), especially CO<sub>2</sub> and CH<sub>4</sub>, is considered one of the most significant impacts. Currently, one of the strategies seen as more interesting to minimize the effects of climate change involves

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the capture of CO<sub>2</sub> and the utilization of renewable energy, either to power the conversion process or to obtain hydrogen to combine with the CO<sub>2</sub>, to obtain other compounds that can be further used as fuels or as basic feedstocks [1]. Besides contributing to a more circular economy, as the generated carbon is again incorporated in the production cycles and there is an increase in the renewable energy usage, this process also contributes to the Sustainable Development Goals, SDG, in particular goals 7 and 13, and to fulfill the goals of the Paris Agreement to reduce the net carbon emissions [2,3].

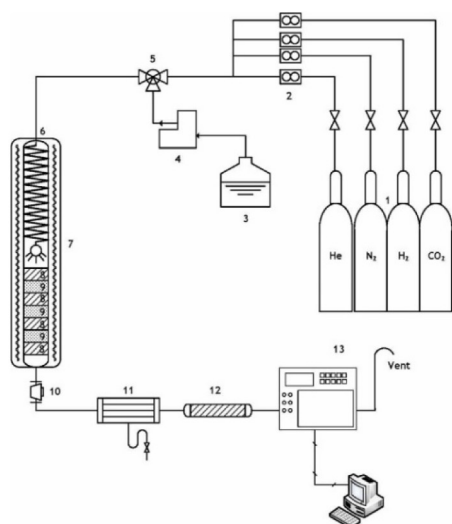
Methanol is currently seen as a good option, as it can be used both as an energy carrier and as a chemical feedstock to obtain other compounds or products [4,5]. Currently, steam reforming (SR) of natural gas and light oil fractions are used to produce synthesis gas (syngas), required for methanol synthesis after adequate hydrogen-to-carbon monoxide adjustment. The use of waste streams containing GHG, namely CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub>, combined with natural gas and/or biogas if necessary, are suitable sources for producing syngas via bi-reforming of methane (BRM). That reaction is in fact a combination of two reactions: steam reforming of methane (SRM) expressed by Eq. (1), and dry reforming of methane, (DRM), expressed by Eq. (2), being the BRM expressed by Eq. (3).



Despite the potential of BRM as a carbon emissions mitigator, research efforts in BRM are scarce. Hence, in this work the BRM reaction was studied varying the temperature, in order to help identify the most adequate conditions to perform it. The results obtained will be used to establish a reaction mechanism and to determine a kinetic model and obtain the numerical values of the kinetic constants, to describe the observed experimental behavior and support the future industrial implementation of the BRM reaction.

## 2. Materials and methods

A commercial 15 wt% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Octolyst 1001), gently supplied by Evonik (earlier Degussa AG) in the form of extrudates was used in this work as catalyst [6]. A detailed discussion on the characterization of the catalyst can be found in previous reports [6–8]. The experiments were performed at temperatures in the range of 798 to 1123 K, in 25 K intervals, at atmospheric pressure in a continuous flow tubular reactor. The reactor setup is shown in Fig. 1. Details about the reactor setup can be found in a previous study [6]. The feed had a carbon-to-water molar ratio of 2 [(3 CH<sub>4</sub> + 1 CO<sub>2</sub>): 2 H<sub>2</sub>O] corresponding to flowrates of 30 cm<sup>3</sup>/min of CH<sub>4</sub>, 20 cm<sup>3</sup>/min of H<sub>2</sub>O and 10 cm<sup>3</sup>/min of CO<sub>2</sub> with no inert added. A mass of catalyst of 15 g was used in all experiments.



**Fig. 1.** Reactor setup used for BMR experiments.

Source: Adapted from [6].

The mixture exiting the reactor during each experiment passed through a condenser (stainless steel heat exchanger consisting on a bundle of tubes) and an ice-cooled trap using a Dewar, to condense the unreacted water in order to quantify it (direct method). The composition of the outgoing off-gas stream was determined with a gas chromatograph (GC 1000, Dani Chromatographs) equipped with an on-line multiport 16-valve system for sample injection (Valco Instruments Company Inc.), a capillary column (Carboxen 1010 Plot, Supelco), and a thermal conductivity detector. The liquid unreacted water was periodically collected in the ice-cooled trap and separately quantified. In addition, the water conversion was also estimated via the measured amounts of CO formed during reaction (indirect method), according to the global BRM equation stoichiometry (Eq. (3)): 4 mol of CO are formed if 2 mol of water are consumed.

At this point, it must be stressed that the accurate amount of water conversion cannot be calculated through the stoichiometry as several reactions are involved in the overall BRM process. Therefore, it must be kept in mind that only if SRM would occur alone all over the measured temperature range then it would be possible to calculate accurately the conversion. In this case, the  $R_{H_2/CO}$  would also be constant and equal to 3. Since in the higher temperature range the  $R_{H_2/CO}$  value approximates 2, the DRM reaction becomes also dominant, and only an estimate of the amounts of water produced can be obtained by stoichiometric calculation when using the overall BRM (Eq. (1)). The analysis of the mixtures was done at normal temperature and pressure (NTP) conditions, i.e. 293.15 K and 101.325 kPa.

Conversions of the reactants ( $CH_4$ ,  $CO_2$  and  $H_2O$ ) were calculated as described in Eq. (4):

$$X (\%) = \frac{\dot{n}_{i,0} - \dot{n}_i}{\dot{n}_{i,0}} \cdot 100\% \quad (4)$$

where  $\dot{n}_{i,0}$  represents the molar flowrates of  $CH_4$ ,  $CO_2$  and  $H_2O$  in the feed, respectively; and  $\dot{n}_i$  are the outlet molar flowrates of the same reactants. The molar fractions  $y_i$  (or partial pressures) were calculated for all species present in the outlet gas stream according to Eq. (5):

$$y_i = \frac{\dot{n}_i}{\sum \dot{n}_i} = \frac{p_i}{p_{total}} \quad (5)$$

where  $\dot{n}_i$  represents the molar flowrate of one species, and  $\sum \dot{n}_i$  represents the total molar flowrate of the species in the outlet stream. Equilibrium conversions and reactant/product composition are provided in a previous work [4].

### 3. Results and discussion

The most relevant features of the catalyst used are shown in Table 1. The catalyst is composed mainly of nickel (15.4 wt.%) and alumina (84.6 wt.%), corresponding to a relatively high nickel loading. The results obtained are in good agreement with the nominal value indicated by the catalyst supplier. The BET surface area of the catalyst,  $S_{BET} = 250 \text{ m}^2/\text{g}$ , is relatively high and within the range of reported values for this type of catalyst [9].

**Table 1.** Properties of catalyst used.

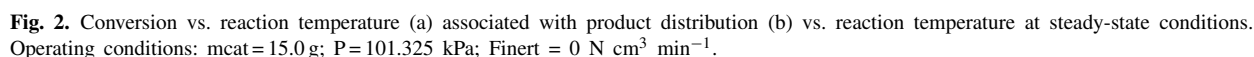
Catalyst	Ni (wt%)	$Al_2O_3$ (wt%)	$S_{BET}$ ( $\text{m}^2/\text{g}$ )
Octolyst	15.4	84.6	250

SEM analyses (not shown in this paper) performed in a glance of the fresh catalyst revealed that the support ( $Al_2O_3$ ) is covered with nickel clusters, with dimensions ranging from 170 to 3720 nm. This is an indication of a poor metal dispersion during catalyst preparation, which will probably lead to relatively low carbon dioxide conversions.

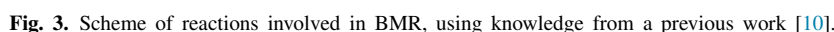
The  $CH_4$ ,  $H_2O$  and  $CO_2$  conversions versus space time were obtained at different temperatures, for the catalytic vapor phase reaction (Fig. 2a). Partial pressures of  $CH_4$ ,  $H_2O$  and  $CO_2$ , CO and  $H_2$  were also obtained (Fig. 2b).

The results show that, although the reactions occur simultaneously, different conversions relative to each of the 3 reactants were reached under different operating conditions, being the  $CO_2$  conversion the lowest one. This shows that the DRM is the limiting step, in particular at lower temperatures.

As expected for endothermal reversible reactions, increasing temperatures and space time lead to larger conversions of the reactants. At temperatures higher than 873 K, higher amount of  $CH_4$  is easily converted, while  $H_2O$  and especially  $CO_2$  require higher reaction temperatures. At a reaction temperature of 1123 K almost all  $CH_4$



The product distribution, depicted as partial pressure of reactants and products vs. reaction temperature during BRM in presence of the catalytic material used, shows also that the hydrogen-to-carbon monoxide ratio ( $R_{H_2/CO}$ ) of



2:1 is only reached for very high temperatures ( $R_{H_2/CO}$  in Fig. 2b). The reason for that is the previously discussed conversion of  $CO_2$  in DRM, as well as other side-reactions involved that influence the final product distribution, as shown in Fig. 3, which shows a possible reaction pathway. Depending on the catalysts used, the reactions involved can differ considerably. Nonetheless, the reactions involved consider the nature of Ni based catalysts due to its suitable electronic configuration as active phases (10th group of the periodic table), and widespread use. It is important to remember that the conversion of the reactants used (methane, water and carbon dioxide) to produce syngas with a hydrogen-to-carbon monoxide ratio of two (product distribution) is strongly dependent on the nature of catalysts (active phase, promoters and support material), and of course the reaction conditions such as the reaction temperature which will strongly influence the reaction rate obtained.

The experimental results confirm that BRM requires high energy input to operate the reaction system. As it can be seen, reaction temperatures of at least 798 K are required for a reasonable reaction conversion of both methane and water, while carbon dioxide does not react at that temperature. Moreover, since in this work the reaction has been conducted at atmospheric pressure, a volume increase was observed, as expected, and this is reflected in the product distribution and partial pressure increase of products, where a starting expansion of carbon monoxide and especially hydrogen amount was observed. Thus, at a lower range of reaction temperature of 798–898 K, the SRM reaction is the dominant one. This is supported also by the partial pressures of carbon dioxide that are close to the feed conditions (Fig. 2b), with almost no carbon dioxide conversion (Fig. 2a). The almost dominance of SRM reaction at this temperature range is also confirmed by analyzing the hydrogen-to-carbon monoxide ratio, which decreases with increasing temperature.

In the middle temperature range of 923–1023 K the carbon dioxide starts to be converted. Nevertheless, the conversion is in low levels and approximately constant, while the decrease of methane and especially water is more pronounced. This behavior can be explained with the enhancement of the SRM reaction with increasing reaction rates. Van Hook [11] demonstrated that normal SRM is conducted at temperatures of 1073–1223 K and pressures of 0.5–4.0 MPa using nickel-based catalyst in industrial units. On the other hand, the decrease in carbon dioxide partial pressure (Fig. 2b) and relatively low carbon dioxide conversion is most probably a result of a moderate increase in DRM reaction. However, carbon dioxide can also be consumed by hydrogen formed in a reverse water gas shift reaction (WGS) [7]. Finally, thermodynamic analysis indicates that the BMR process must be operated at temperatures higher than 998 K. At those thermal reaction conditions the Gibbs free energy starts to enter into the negative zone for DRM, while all other reactions involved are already in the negative zone (except the synthesis of methanol and the Boudouard reaction, which are unfavorable at these conditions). The relatively low activity of the catalyst for BMR in this temperature range, especially at the previously referred lower reaction temperatures, and the product distribution obtained are also a consequence of the catalytic material used. The presence of nickel clusters located on top of the porous  $\gamma$ -alumina support (SEM micrographs not shown) is the expected reason for low activities due to low surface exposure [6].

Finally, in the higher temperature range (1048–1123 K) the partial pressures of the reactants methane and water tend to zero, showing that almost all of those reactants are converted. On the other hand, the partial pressure of carbon dioxide remains relatively high (Fig. 2b), even if carbon dioxide is increasingly more converted with increasing temperature, the highest possible conversion being about 40% at 1123 K. These results suggest that at this temperature SRM is almost complete, while DRM remains with low reaction rates that can be most probably attributed to the nature of the catalytic material used, as mentioned in the previous paragraph.

From the thermodynamic point of view, it is expected that in the temperature range 973–1373 K the carbon dioxide conversion is lower than the methane conversion. Nevertheless, increasing the reaction temperature helps to approximate the conversions of the reactants involved (thermodynamic results at 1073 K;  $X_{CO_2} \sim 85\%$  together with  $X_{CH_4} \sim 95\%$ ).

#### 4. Conclusions and future work

The behavior for BRM over nickel-based catalysts between 798 and 1123 K was studied in this work with a carbon-to-water mole ratio of 2 in the feed. The main goal of this study was to show that it is possible to ennobles carbon dioxide with a conventional nickel-reformer catalysis process, and to produce syngas that can be used for methanol production. In a future work it is intended to develop a simple kinetic model that replaces the conventionally used power rate law model, describing the catalytic BRM reaction on Ni-based catalysts in a fixed-bed reactor for a large temperature range. Most probably the decomposition of carbon dioxide is the rate limiting step when SRM, DRM, WGS, CMD, BD, CG and BRM are considered.



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