

Sorption-enhanced CO₂ methanation to SNG: optimizing conditions in a Ni-Fe/Al₂O₃ fixed bed reactor

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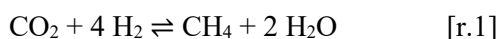
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Abstract

This research sought to determine the optimal conditions to carry out the SESaR (*Sorption Enhanced Sabatier Reaction*) process, which can be used in order to intensify Synthetic Natural Gas (SNG) production through CO₂ methanation. The analyzed parameters were: reaction temperature, reactants proportion, and the ratio [catalyst weight / gas flowrate]. Additionally, its upgrading feasibility has been also proven by cofeeding biogas.

Introduction

Currently, there is a great concern about finding low CO₂ emission energy sources. While renewable sources -such as wind and solar power- are experiencing a constant increase in terms of both capacity and share in global electricity generation [1] [2], most of them are highly dependent on weather conditions and thus are unable to provide a reliable supply of energy. In this context, the *Power to Gas* strategy (PtG or P2G) addresses these shortcomings by using temporary energy surpluses to split water and generate hydrogen, which would react with carbon dioxide to obtain methane (CH₄). This *Synthetic Natural Gas* (SNG) might be easily used in those periods with no energy source available.



The *Sabatier* reaction to produce methane [r.1] is an exothermal and reversible one. A possibility to modify the equilibrium, obtaining higher yields to methane, is to use adsorbent solids, such as zeolites. They would remove water from the reaction atmosphere as soon as it is generated, thus modifying the equilibrium -in accordance with the *Le Châtelier* principle- and leading to greater conversions and selectivities towards methane. This *Sorption Enhanced Sabatier Reaction* (SESaR) is a case of *process intensification*. Once it has been

successfully proven that zeolites are useful for retaining water during reaction [3], a very important matter is in which conditions the process is carried out. This way, parameters such as catalyst weight (W), reactants flowrate (q₀), and reaction temperature (T) –both while feeding only carbon dioxide or biogas-, were tested in an experimental fixed bed reactor in order to optimize the process performance. Additionally, some other factors were analyzed, such as: the reactants ratio (H₂:CO₂), the sweeping gas used in the desorption stages, the temperature gradients in the bed, and the effect and causes of deactivation, which was proven by long-term experiments.

Experimental

Both the catalyst and the adsorbent were used in preliminary tests made by our research group [3]. The catalyst (Ni 7.5 wt.%, Fe 2.5 wt.%) was synthesized by incipient wetness impregnation, γ -Al₂O₃ (~200 m²/g) being selected as support material. The catalyst was then crushed and sieved, obtaining a final particle diameter of 100-200 μm , and later activated at 500 °C for 2 hours with a gas flow composed of 50 % H₂ and -depending on the experiment- either 45 % N₂ and 5 % Ar, or vice versa. The zeolite was a commercial one: *LTA 5A* (*Alfa Aesar*).

The applied techniques to characterize both the catalyst and the zeolite were: adsorption-desorption isotherm by nitrogen adsorption (BET) to determine the specific surface, X-ray fluorescence (XRF) for elemental quantification, and X-ray diffraction (XRD) to identify crystalline structures. Lastly, temperature programmed reduction (TPR) was used for the catalyst reducibility analysis. The effect of diffusional constraints was also experimentally tested: flowrates of 125 mL (STP)/min and a particle diameter of < 250 μm were enough to avoid control of effects other than reaction kinetics.

Experiments were carried out in a fixed bed reactor, at atmospheric pressure. The mass of solids loaded in the reactor (pre-mixed) ranged from 0.125 to 1 g of catalyst and from 9.5 to 10.375 g of zeolite. As described above, before the experiment the catalyst was activated at 500 °C for 2 hours. Once the system was heated to the reaction temperature (ranging from 400 to 250 °C, with steps of -50 °C between them), the reactor was usually fed with a total volumetric flow of 250 mL(STP)/min (a value of 125 was also tested). Different molar ratios H₂:CO₂ (2:1, 3:1, 4:1, 5:1 and 6:1) were analyzed. On the other hand, for synthetic biogas methanation the feed included a 7:3 CH₄:CO₂ molar ratio and a 4:1 H₂:CO₂ ratio. In any case, these mixtures were diluted with a 5 % of Ar and 5 % of N₂. The experiments consisted of three one-hour methanation stages (M₁, M₂, and M₃), with a half-hour desorption process (only Ar and N₂) at the same temperature between the first and second intervals (D₁) and another one at 500 °C between the second and third intervals (D₂).

Results

This work tries to determine the best conditions to conduct the SESaR process as well as to quantify the water adsorption by zeolite, in the proposed reactor configuration. Maximal intensifications and process enhancement being the criteria for setting the operation parameters. It is proven that for a $W/q_0 = 1 \text{ g}_{\text{catalyst}} / 250 \text{ mL(STP)/min}$, high yields to methane close to thermochemical equilibrium, and therefore to water, are achieved. As such, using a higher W/q_0 ratio would not give a much higher performance. Moreover, using a lower volumetric flow (125 mL(STP)/min) smaller quantities of water are generated, so the results would be less sensitive to any change of other factors. As such, once this $W/q_0 = 1/250 \text{ g}_{\text{catalyst}} \cdot \text{min} \cdot \text{mL(STP)}^{-1}$ was established, the reaction temperature was tested, finding an optimal yield at 300 °C for every methanation intervals (M₁, M₂, and M₃), as shown in Figure 1 and Table 1. However, this changes when biogas is fed: while 300 °C remains as the optimal temperature for M₂, and M₃, for fresh catalyst -i.e., for M₁-, the highest intensification took place at 250 °C.

Additionally, it is proven that at 250, 300 and 350 °C, similar results are met while feeding biogas and

when using H₂ and CO₂ mixtures. However, yields to methane decrease at 400 °C when biogas is supplied, as a result of being close to equilibrium.

Lastly, it was found that the catalyst suffered some type of deactivation, conversions and yields being lower at M₃ than at M₁ –even when the zeolite was saturated. Long-term experiments at 300 °C –with both CO₂ and biogas feedings- confirmed the loss of activity with time-on-stream. Hence, after these experiments the bed was oxidized, at 500 °C. CO_x release proved that deactivation was due to coke formation as a side product. Nevertheless, this is not the only reason for deactivation, as shown when using silicon carbide (SiC) instead of zeolite. While performances were much more similar between methanation stages M₁ to M₃, it was confirmed that they were a bit lower at the third one, demonstrating that another causes, such as sinterization, were present.

Conclusions

The operation conditions for the SESaR process have been experimentally tested. As such, it is confirmed an optimal $W/q_0 = 1/250 \text{ g}_{\text{catalyst}} \cdot \text{min} \cdot \text{mL(STP)}^{-1}$ ratio in terms of process enhancement. When this W/q_0 ratio is used, the optimal temperature is 250 °C during the first methanation (M₁ stage) when feeding biogas and 300 °C otherwise. Similar results are achieved when methane is fed into the reactor and when only H₂ and CO₂ are supplied, except when working at 400 °C, which proves biogas upgrading feasibility. Finally, deactivation was proven to exist, its causes being coke formation and sinterization to a lesser degree.

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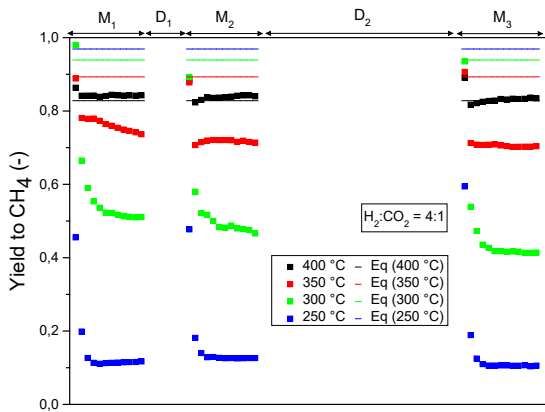


Figure 1. Yields to methane (from CO₂) as a function of temperature. H₂:CO₂ = 4:1. Dashed lines: theoretical equilibrium values.

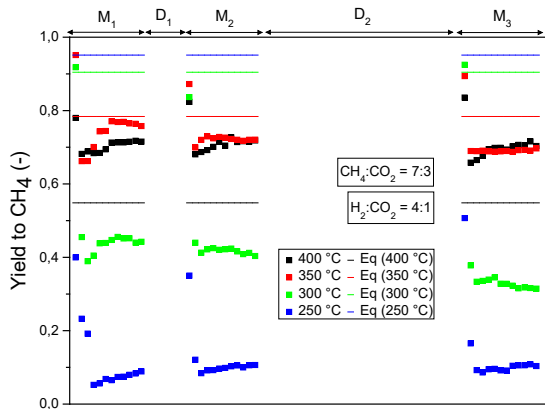


Figure 2. Yields to methane (from CO₂) as a function of temperature (biogas). CH₄:CO₂ = 7:3. Dashed lines: theoretical equilibrium values.

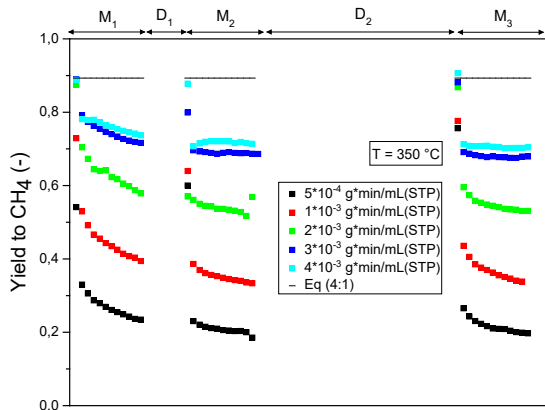


Figure 3. Yields to methane (from CO₂) as a function of W/q₀. H₂:CO₂ = 4:1. Dashed lines: theoretical equilibrium values.

Table 1. Process intensification for the methanation process ratio H₂:CO₂ = 4:1, quantified as relative amount of water adsorbed (mol H₂O/g zeolite)

	Temperature (°C)			
	400	350	300	250
M ₁	2.18E-07	1.29E-04	2.20E-04	9.04E-05
M ₂	-4.44E-06	4.50E-05	2.16E-04	9.57E-05
M ₃	-1.27E-05	4.73E-05	1.91E-04	1.36E-04

Table 2. Process intensification for the methanation process (biogas) ratio CH₄:CO₂ = 7:3, quantified as relative amount of water adsorbed (mol H₂O/g zeolite)

	Temperature (°C)			
	400	350	300	250
M ₁	-4.49E-05	-5.18E-05	7.19E-05	9.58E-05
M ₂	-3.02E-05	2.89E-05	1.48E-04	2.17E-05
M ₃	-2.21E-05	7.43E-06	1.96E-04	7.89E-05