

# CO<sub>2</sub> Rich Streams Methanization Intensified by Steam Adsorption with LTA Zeolites in Fluidized Bed Reactor

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## Abstract

The *Sabatier* reaction enhanced by selective water sorption (SESaR process), was evaluated in a fluidized bed reactor. This constitutes a configuration alternative to the traditional fixed bed one. A Ni-Fe bimetallic catalyst (Al<sub>2</sub>O<sub>3</sub> as support) and zeolite 5A as adsorbent were used.

## Introduction

It is known that CO<sub>2</sub> plays an important role on greenhouse effect, and that up to 412.5 ppm had been measured by 2020 as the highest concentration registered to date. That is the main reason why nowadays the production of renewable fuels that recycle CO<sub>2</sub> had become relevant. CH<sub>4</sub> is a H<sub>2</sub>-rich energy-carrier fuel with a higher energy density compared to H<sub>2</sub>. Furthermore, a mature and wide gas infrastructure and underground storage are placed all over the world (1).

Surplus renewable energy can be transformed into H<sub>2</sub> by electrolysis. Electrolytic H<sub>2</sub> can react with CO<sub>2</sub> e.g., from biogas obtained as a result of the anaerobic decomposition of organic matter) favouring the methanations process through the so called *Sabatier* reaction, as it is detailed in (r.1) (2):



This reaction is highly exothermic and typical conditions include pressures of up to 60 bar and a temperature range between 250 and 450°C. Its high exothermicity may lead to hot spots formation, concluding that the reactor type becomes very relevant. Traditionally fixed bed reactor has been selected to operate in a system where a cascade of adiabatic reactors are placed. Between them intermediate cooling and recirculation are present. On the other side, sorption enhanced methanation might shift the balance towards methane formation, enhancing conversions and allowing lower operating

pressures and/or higher temperatures. To carry out this task, dehydration consists of removing steam from the reaction media while methanation is carried out. For that purpose an adsorbent material is mechanically mixed with the catalyst allowing reaction and adsorption to occur simultaneously. On this way, a CH<sub>4</sub> rich gas stream can be obtained.

Taking all the above considerations into account, it has been established to operate with a single fluidized bed reactor to improve isothermicity. The bed is comprised of zeolite 5A as adsorbent and Ni-Fe/Al<sub>2</sub>O<sub>3</sub> as a bifunctional catalyst supported on alumina. Prior to methanation experiments, fluidizing tests were carried out to determining the appropriate flow rate to guarantee the fluidization of the bed.

## Experimental

The 250-400°C temperature range and different partial pressures (molar ratios H<sub>2</sub>:CO<sub>2</sub> as 2:1, 4:1 and 6:1) were considered. The experiments take place at atmospheric pressure in a quartz fluidized bed reactor (i.d. 26 mm). When the zeolite becomes saturated with water, conversion rates decrease and tend to stabilize. Due to this fact, desorption/drying steps are required after every methanation to recover catalyst activity for the following methanation. Each experiment consisted of six methanation stages (M1 to M6) and their subsequent desorptions (D1 to D6) after each one.

Fluidization flowrate was established in 570 mL(STP)/min considering a factor of 1.4 times the minimum fluidization velocity (3) to ensure complete fluidization. Experiments were conducted considering temperatures within the reaction range and diverse zeolite/alumina ratios. Alumina promotes the fluidization behaviour since zeolite is cohesive and favours aggregation and slugs formation. 67 wt% zeolite and 33 wt% alumina and catalyst was set as reactor's bed composition, in

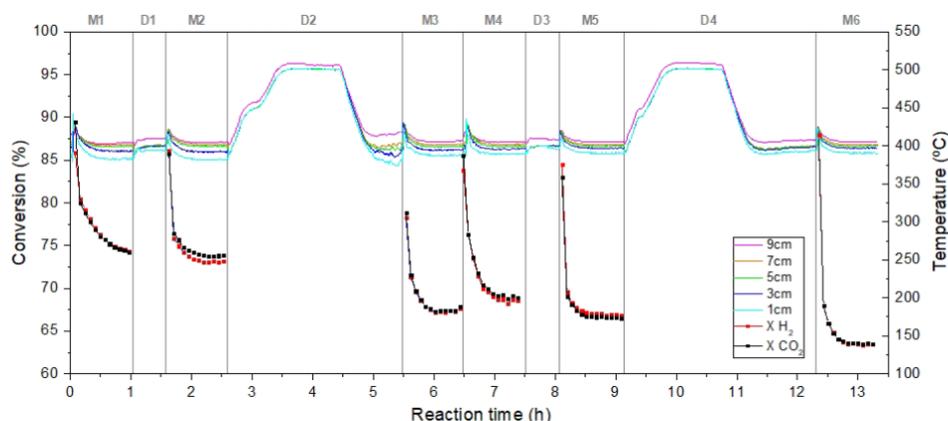
which 1.14 g correspond to the Ni-Fe catalyst, as  $20 \cdot 10^{-4} \text{ g}_{\text{cat}}/\text{mLSTP}$  is the space velocity.

## Results

Fig.1 shows an experiment carried out at 400 °C and ambient pressure, no CH<sub>4</sub> in the feed, a 4:1 ratio as H<sub>2</sub>:CO<sub>2</sub> and a 9:1 molar ratio as reactants versus inerts. Prior catalyst activation was carried out at 500 °C for 2 hours and a feed composition of 50 %H<sub>2</sub>. This repeats also between every three methanation stages (M1 to M3, and M4 to M6)). Outlet composition was monitored by  $\mu\text{GC}$ . A taylormade ANN has been built and deployed to estimate real concentration of species and avoid the marked non-linear behaviour (matrix effect) observed.

High conversions were obtained for M1, starting from 90% approximately and stabilizing on 75 %. Intensification is observed at the beginning of each methanation since H<sub>2</sub>O is adsorbed into the zeolite surface. Later, when the adsorbent gets saturated, conversion stabilizes. It is also noted that desorption stages (D1 through D4) recover almost complete catalyst activity. Nevertheless, smooth but progressive deactivation and loss of CH<sub>4</sub> selectivity take place as conversion decline on every methanation, even when the adsorbent is saturated. This may be the result of coke deposits on the solid particles favored by steam removing; sintering, enhanced by steam presence and high temperatures (above 500 °C in D2 and D4); or attrition caused by particles movement while fluidizing.

As a result of the exothermicity of the reaction, a sudden cascade of temperature increments is observed from the closest thermocouple to the entrance of the reactor towards the exit. M1 and M4 methanation stages (Fig. 1) registered increments as high as 40 °C, coincidentally taking place after the activation stage.



**Fig. 1:** H<sub>2</sub> and CO<sub>2</sub> conversions and temperature profiles at different heights for Sorption Enhanced Sabatier reaction (SESaR) on a fluidized reactor (M<sub>i</sub>: methanation stages, D<sub>i</sub>: desorption stages). Methanation conditions: 400°C, room pressure, H<sub>2</sub>:CO<sub>2</sub> = 4:1, reactants:inerts = 9:1. Bed composition: 66.7 wt% zeolite LTA 5A, 29.5 wt% alumina, 3.8 wt% Ni-Fe/Al<sub>2</sub>O<sub>3</sub> catalyst.

## Conclusion

As it has been exposed, the sorption enhanced Sabatier process shows its potential, improving efficiency and decreasing the energy requirements as a benefit of low operating pressure. Moreover, it becomes a sustainable and realistic alternative that could reach the challenging objectives established to tackle climate change.

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## FIGURES