CO_2 methanation in a Ni-Fe based catalyst fixed bed reactor enhanced by selective water adsorption with LTA zeolites (*Sorption Enhanced Sabatier Reaction* – **SESaR**)

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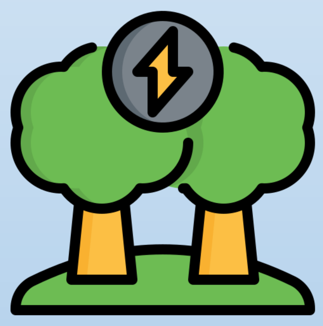
INTRODUCTION

Problem

Nowadays, the need of finding low CO_2 emission sources of energy is more critical than ever. Apparently, how to produce the electricity is solved by renewable sources as solar energy and wind turbines, but an efficient energy storage is still missing.



Possible solution

Power to Gas technologies (PtG).

PtG is based on combining renewable H_2 with high CO_2 concentration streams into methane [1]. At the same time, PtG is bringing an opportunity to decrease the CO_2 emissions of new energy sources such as biogas, since CO_2 from biogas (ca. 30%^{v} CO_2+70%^{v} CH_4) can be trapped and transformed into methane through the *Sabatier* reaction (r.1) [2]. As a result, the upgraded biogas after the methanation process would have a concentration in methane close to 100%.

$$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O \quad \text{(r.1)}$$

Intensification

Sorption Enhanced Sabatier Reactor (**SESaR**) with zeolites.

SESaR technologies incorporate the use of water adsorbent solids in order to *in situ* remove the water produced by (r.1) trying to push up its thermodynamical equilibrium. Removing the water from the products, a behavior of reaction shift appears as result of *Le Chatelier*'s principle [3]. Thus, reaction shift to products, increases the CO_2 conversion and warily the selectivity to CH_4.

EXPERIMENTAL

Set-up

Reactor: The reactor consists in a fixed bed, 12 cm length (catalyst bed) and 13 mm inner diameter.

Catalyst: A lab-made Ni-Fe based catalyst supported on alumina (7.5 %^{wt} Ni, 2.5 %^{wt} Fe).

Catalyst synthesis method: Incipient wetness impregnation from $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3) \cdot 9H_2O$, both from *Sigma Aldrich*

Support material: γ-Al_2O_3 (200 m^2/g, *Puralox, SASOL)*

Water absorbent: LTA zeolite (5A).

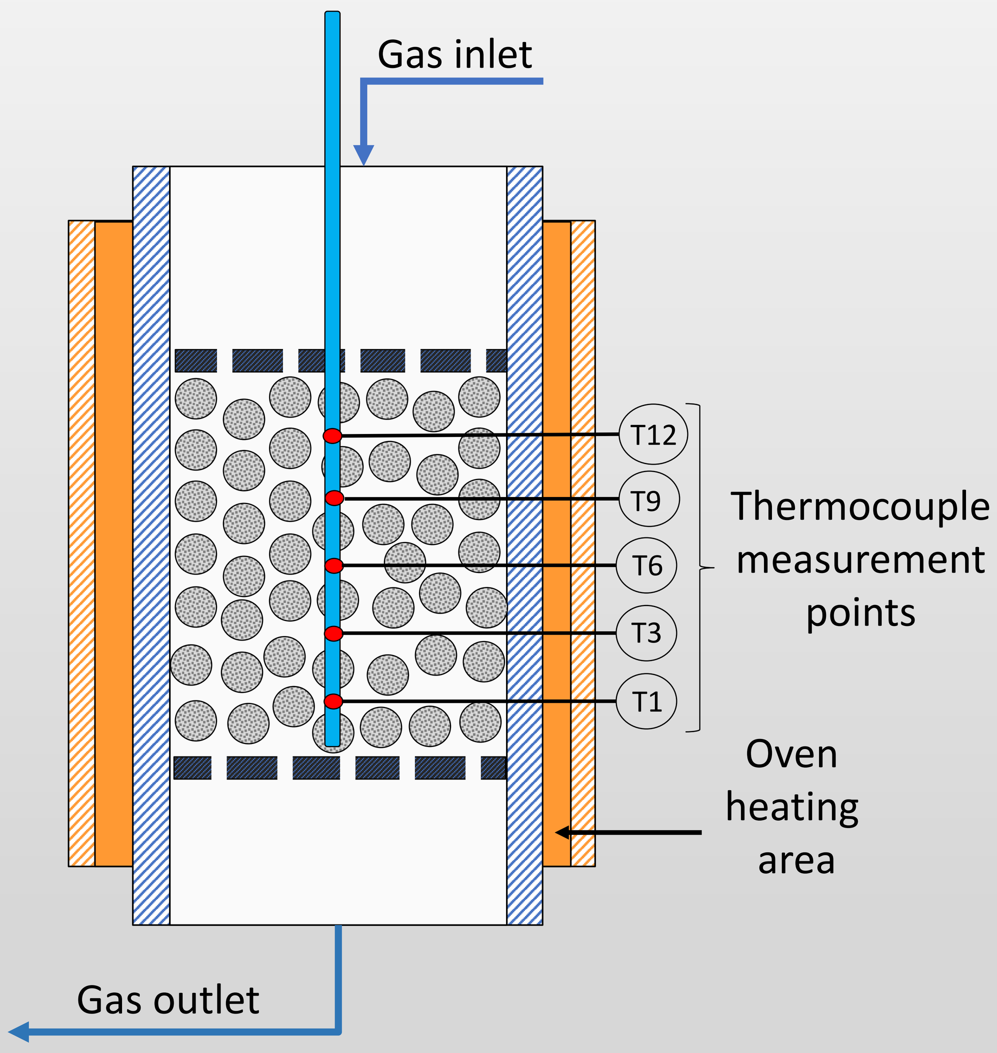


Figure 1. Schematic representation of the SESaR used for carrying out the experiments. The thermocouple label indicates the height (cm) of the measurement point in the fixed bed .

Experimental steps

1. **Charge of solids in the column (pre-mixed):** 0.25 g of catalyst and 10.25 g of 5A zeolite.
2. **Catalyst activation**: the catalyst was activated at 500 ºC for 2 hours with a gas flow composition of 50% H_2, 45% Ar and 5% N_2 (%^{v}).
3. **Experiment conditions:**

- **Temperature:** between 450 and 250 ºC.
- **Pressure:** atmospheric.
- **Feed flow:** A total volumetric flow of 250 mL(STP)/min.
  - Methanation of CO_2 : Molar ratios H_2/CO_2 of 2/1, 4/1 and 6/1 diluted with a 5 %^{v} of Ar and 5%^{v} of N_2.
  - Synthetic biogas (CO_2+CH_4) methanation: CH_4/CO_2 molar ratio=7/3 and H_2/CO_2 =4/1 diluted with a 5 %^{v} of Ar and 5 %^{v} of N_2.

RESULTS

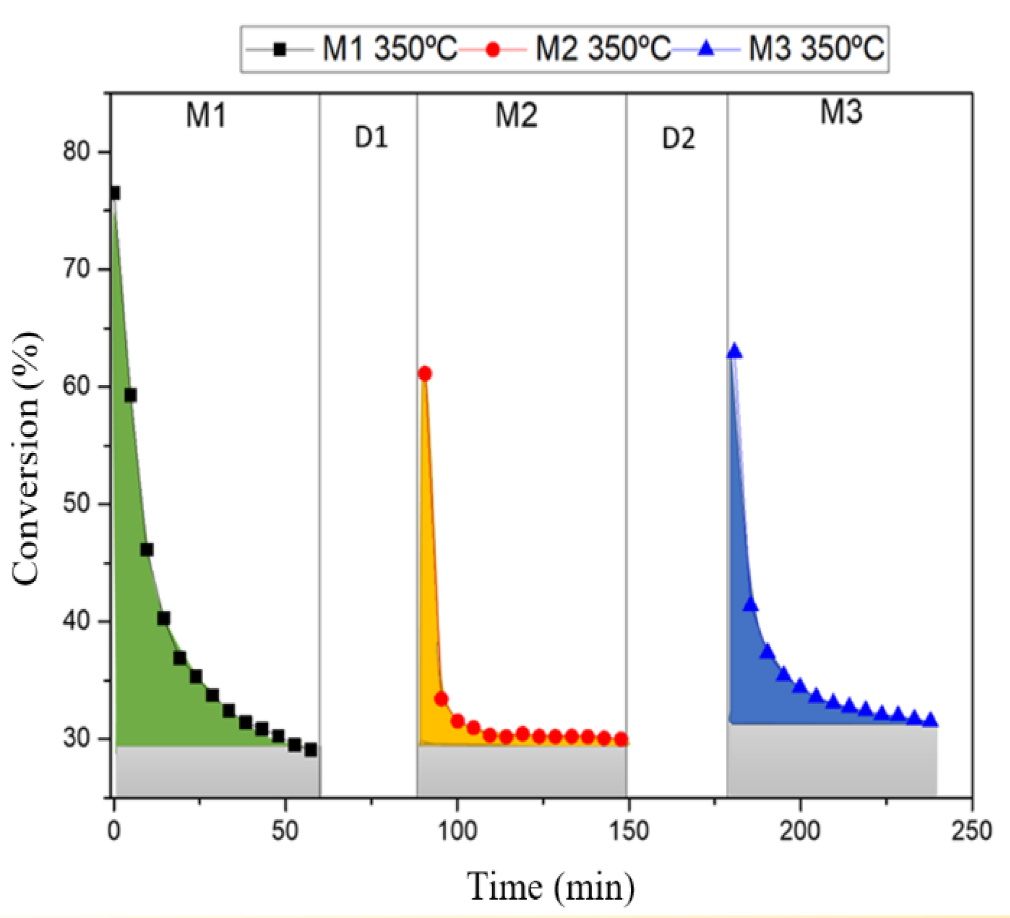


Figure 2. Comparison of SESaR enhanced methanation (colored) vs. conventional (upper grey) methanation. M1, M2, and M3 are the methanation intervals, that were interspersed by D1 and D2 showing the desorption steps. D1 was carried out at 350 ºC and D2 at 500 ºC.

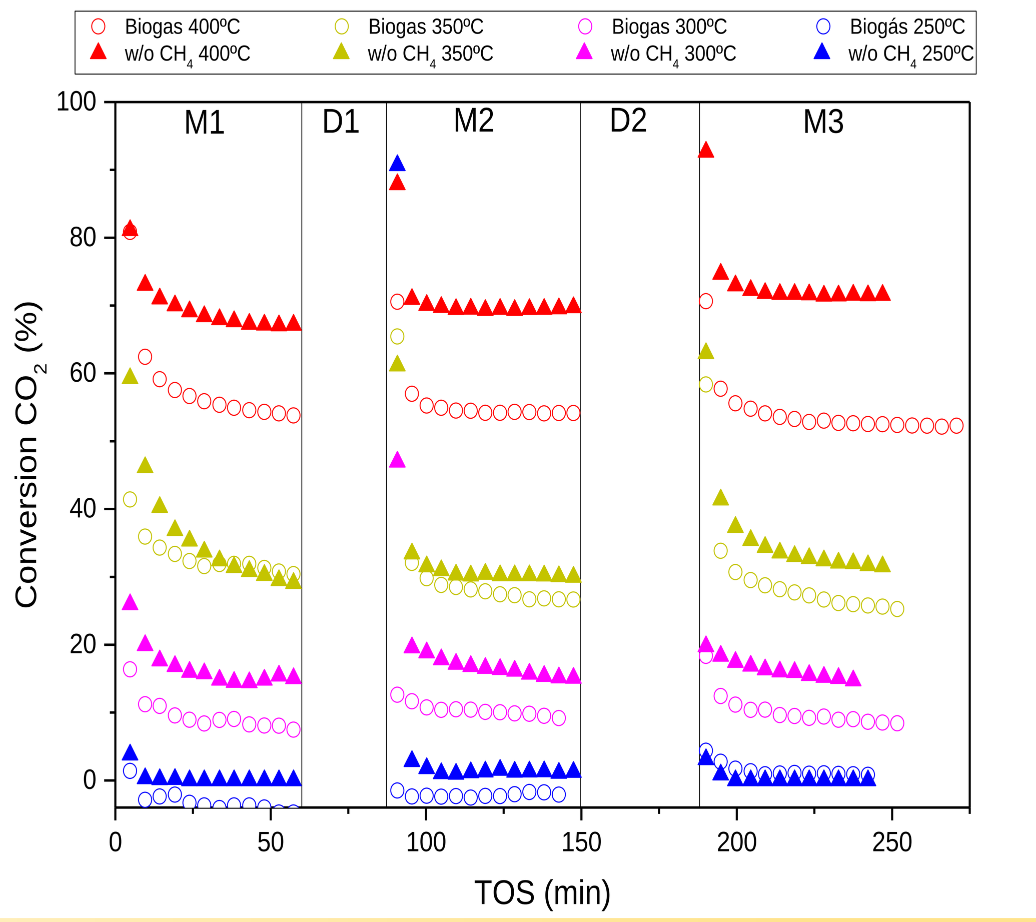


Figure 3. CO_2 conversion for different experiment temperatures and a ratio H_2/CO_2 of 4/1 in the gas inlet. Circles show the experiments fed with biogas and triangles the experiments without methane in the feed.

CONCLUSIONS

- The Ni-Fe catalyst showed a good conversion to CH_4 allowing to decrease the operational cost in comparison with a conventional nickel catalyst.
- An important improvement in the CO_2 conversion has been shown by replacing the inert solid in the packed bed with 5A LTA zeolite.
- Increasing temperature on the desorption steps (e.g., D2) has been observed as a feasible way in the recovery of the adsorption capacity of the zeolite.
- The conversion enhancing effect is also observed when methane is fed simulating biogas upgrading experiments.

[1] ANGELIDAKI, I., TREU, L., TSAPEKOS, P., LUO, G., CAMPANARO, S., WENZEL, H., and KOUGIAS, P.G. Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances.* 2018, 36(2), 452-466. Available from: doi:10.1016/j.biotechadv.2018.01.011.

[2] SABATIER, P., and SENDERENS, J.B. New Synthesis of Methane. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* 1902, 134, 514-516. Available from: doi:10.1039/CA9028200333.

[3] VAN KAMPEN, J., BOON, J., VAN BERKEL, F., VENTE, J., and VAN SINT ANNALAND, M. Steam Separation Enhanced Reactions: Review and Outlook. *Chemical Engineering Journal.* 2019, 374, 1286-1303. Available from: doi:10.1016/j.cej.2019.06.031.

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