Sorption-enhanced CO_2 methanation to SNG: optimizing conditions in a Ni-Fe/Al_2O_3 fixed bed reactor

P. Aragüés-Aldea*, P. Durán, V. Mercader, A. Sanz-Martínez, E. Francés, J. Herguido, J.A. Peña
Grupo de Catálisis, Separaciones Moleculares e Ingeniería de Reactores (CREG)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Contact e-mail: 735393@unizar.es

CREG Catalysis, Molecular Separations and Reactor Engineering Group

Instituto Universitario de Investigación en Ingeniería de Aragón Universidad Zaragoza

Departamento de Ingeniería Química y Tecnologías del Medio Ambiente Universidad Zaragoza

INTRODUCTION

There is a great concern about finding feasible low CO_2 emission energy sources. While renewable sources, like wind and solar power, are increasing their capacity and share in electricity generation [1] [2], most of them depend on weather conditions and cannot provide a reliable supply of energy.

Thus, the *Power to Gas* strategy (PtG or P2G) uses temporary energy surpluses to split water by electrolysis and generate hydrogen, which later reacts with CO_2 to obtain methane (CH_4).

The resulting *Synthetic Natural Gas* (SNG) can be used as an energy source when other alternatives are not available.

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O \qquad [r.1]$$

It is possible to modify the equilibrium through use of zeolites as an adsorbent solid, removing water from the reaction atmosphere as soon as it is generated [3]. Hence, a very important matter is in which conditions the *Sorption Enhanced Sabatier Reaction* (SESaR) is carried out.

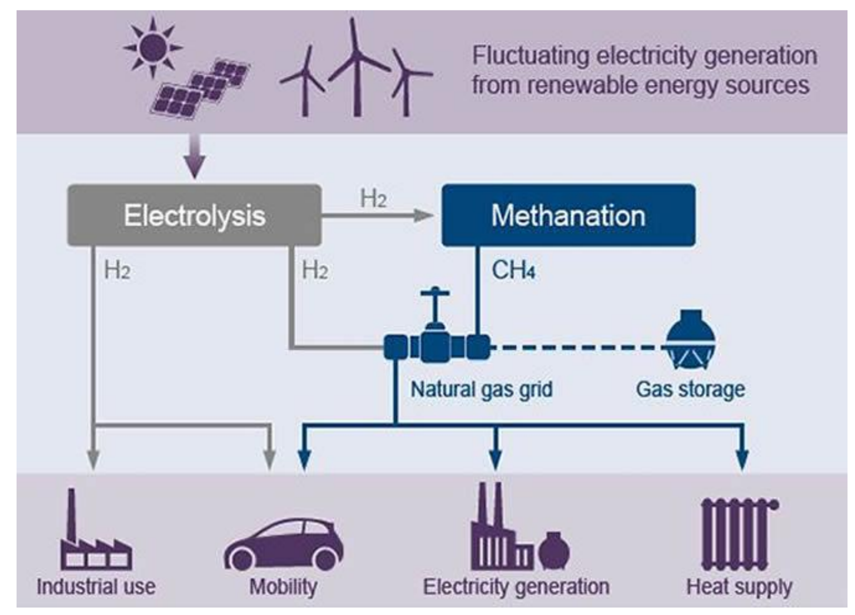

Figure 1. *Power to Gas* strategy: process and applications

EXPERIMENTAL

Catalyst: Ni-Fe (7.5 wt.%-2.5 wt.%) with γ-Al_2O_3 as support material
Adsorbent solid: LTA zeolite, 5Å
Reactor: fixed bed. 5 thermocouples, located at 1, 3, 6, 9 and 12 cm. Atmospheric pressure
Analyzed parameters:

- Catalyst weight (W)
- Reactants flowrate (q_0)
- Reaction temperature (T)
- Feeding gas (biogas, H_2/CO_2 mixtures)
- $H_2:CO_2$ proportion

Reaction conditions

W = 0.125, 0.25, 0.5, 0.75 and **1** g.
q_0 = **250** mL(STP)/min.
T = 250, 300, **350** and 400 °C.
$CH_4:CO_2$ = 7:3 (when feeding biogas).
Stages: 3 methanation stages (M_1, M_2, and M_3) lasting 1 hour, with 2 desorption process (D_1 and D_2) lasting 30 and 10 minutes, respectively. D_1 takes place at the same temperature as M_1, M_2 and M_3, while D_2 is carried out at 500 °C.
There is a previous activation, lasting 2 hours, at 500 °C, with 50 v% H_2 and 50 v% inert.
5 v% N_2 and 5 v% Ar were always introduced as an internal standard and as a dilutant, respectively.

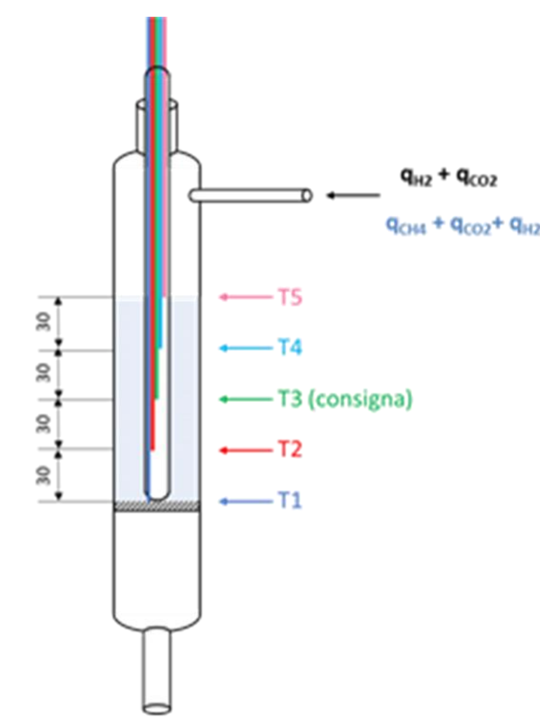

Figure 2. Fixed bed reactor layout

RESULTS

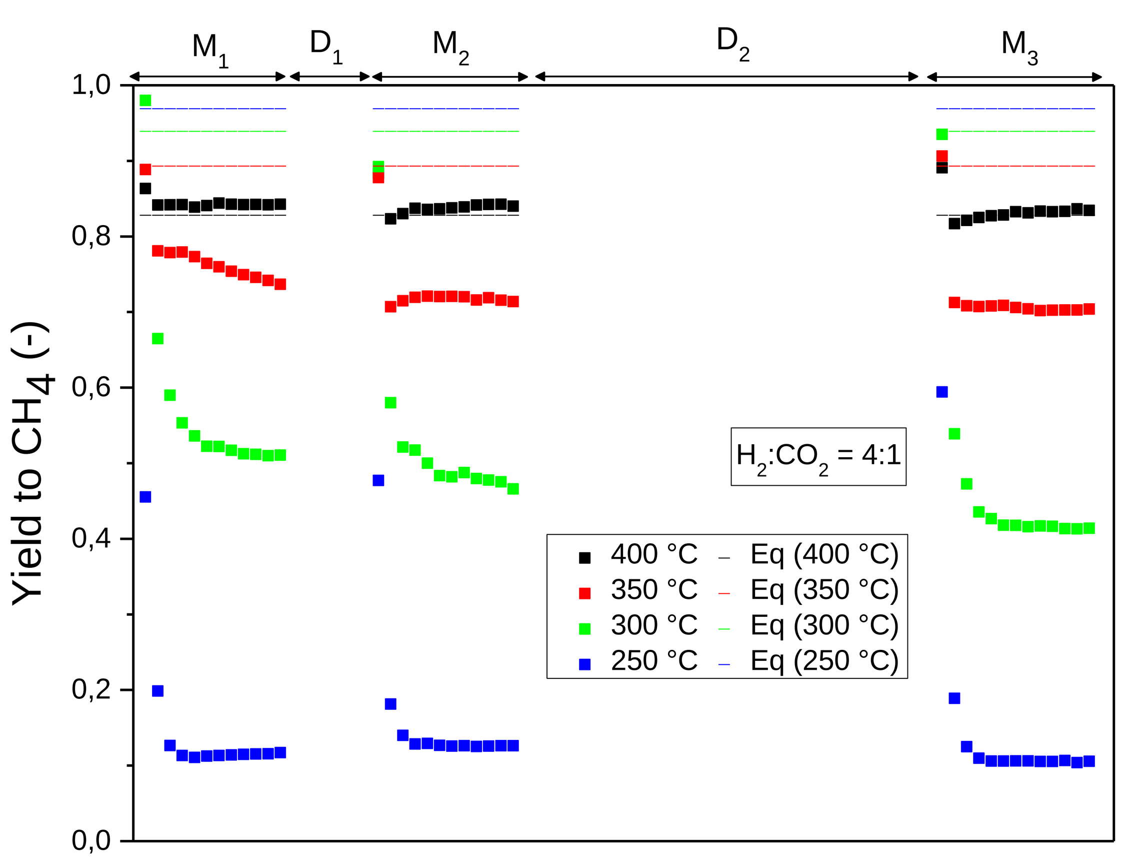

Figure 3. Yields to methane (from CO_2) as a function of temperature. $H_2:CO_2$ = 4:1. Dashed lines: theoretical equilibrium values

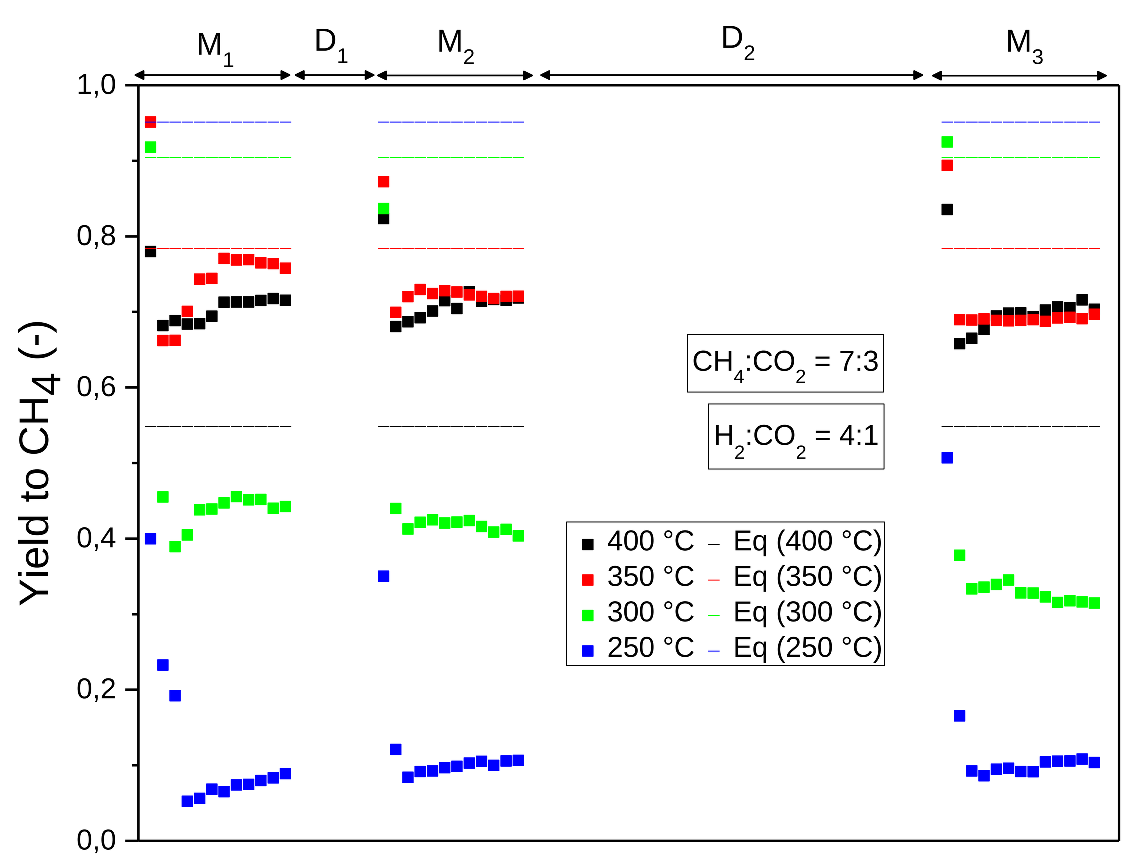

Figure 4. Yields to methane (from CO_2) as a function of temperature (biogas). $CH_4:CO_2$ = 7:3. Dashed lines: theoretical equilibrium values

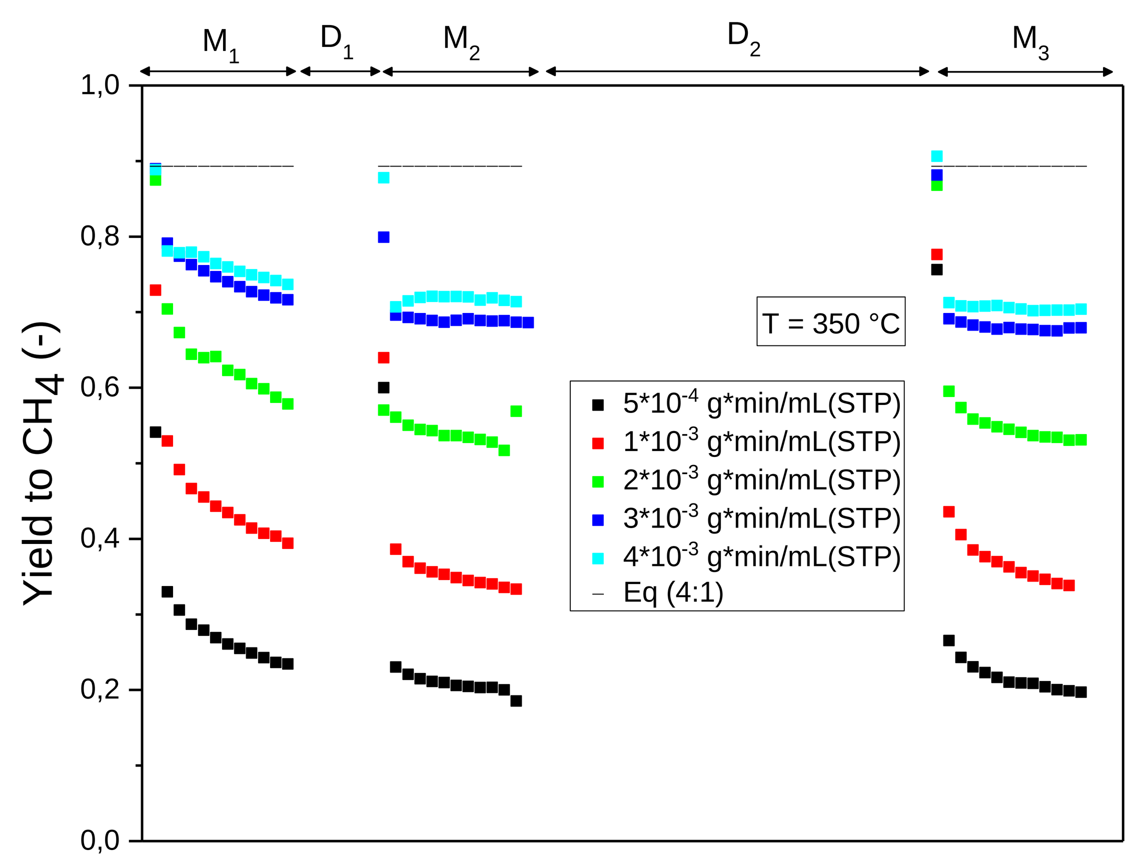

Figure 5. Yields to methane (from CO_2) as a function of W/q_0. $H_2:CO_2$ = 4:1. Dashed lines: theoretical equilibrium values

Table 1. Intensification for the methanation process (ratio $H_2:CO_2$ = 4:1) quantified as relative amount of water adsorbed (mol H_2O/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. Intensification for the methanation process when using biogas (ratio $CH_4:CO_2$ = 7:3) as mol H_2O/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

- Figures 3, 4, and 5 show yields to methane as a function of temperature when using a CO_2 and H_2 mixture, as a function of temperature when using biogas, and as a function of W/q_0, respectively.
- Tables 1 and 2 show intensifications, quantified as amounts of water adsorbed into the zeolite, when analyzing the effect of temperature (using only H_2 and CO_2, in Table 1, and biogas in Table 2).
- Equilibrium values are depicted as broken lines. Experimental results, on the other hand, appear as coloured squared points.
- The five stages that form an experiment appear on the top of the three Figures.

CONCLUSIONS

- With a $W/q_0 = 4{*}10^{-3}$ g catalyst*min*mL(STP)$^{-1}$, the greatest yields to methane are achieved.
- When using this W/q_0 ratio, the maximal intensifications are met at 250 °C in the M_1 stage when using biogas and at 300 °C in the M_2 and M_3 stages. When no methane is fed, 300 °C is the optimal temperature for any methanation stage (M_1, M_2 and M_3).
- Similar results are achieved while supplying biogas and when using mixtures of only H_2 and CO_2, except when working at 400 °C (due to reaching equilibrium). At this temperature, yields reduce considerably if methane is part of the feeding mixture.
- Finally, deactivation was proven to exist. Its causes are coke formation and, in a lesser degree, sintering.

REFERENCES

[1].REN21 (2021). Renewables 2021. Global Status Report. ISBN: 978-3-948393-03-8.
[2].INTERNATIONAL ENERGY AGENCY (2021). Renewable Power. Available from: https://www.iea.org/reports/renewable-power
[3].RINCÓN, M. Metanación de CO_2 en reactor de lecho fijo con catalizador basado en Ni-Fe mejorada por adsorción selectiva de agua con zeolitas LTA (*Sorption Enhanced Sabatier Reaction* – SESaR). (Degree's Thesis). Universidad de Zaragoza.

ACKNOWLEDGEMENTS

This work has been carried with financing of the project PID2019-104866RB-I00 by MCIN/ AEI /10.13039/501100011033.CREG research group (T43-20R) has been financed by Gobierno de Aragón through FEDER.