Mechanical Mixture (MM) Materials for Cyclic CO_2 Power-to-Methane: Filler Influence and Stability

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Power to Methane (PtM)

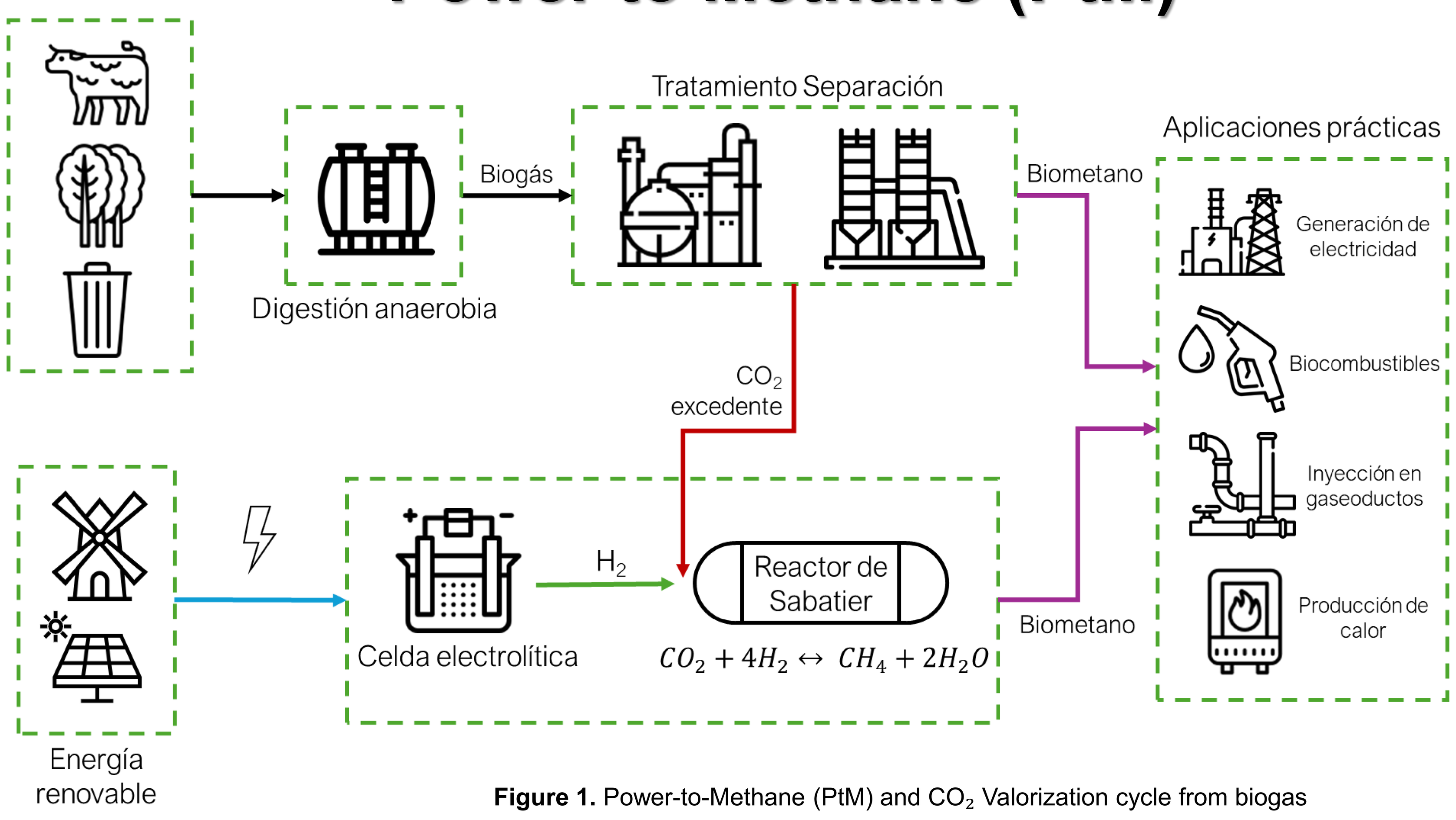


Figure 1. Power-to-Methane (PtM) and CO_2 Valorization cycle from biogas

Mechanical Mixture Materials (MM)

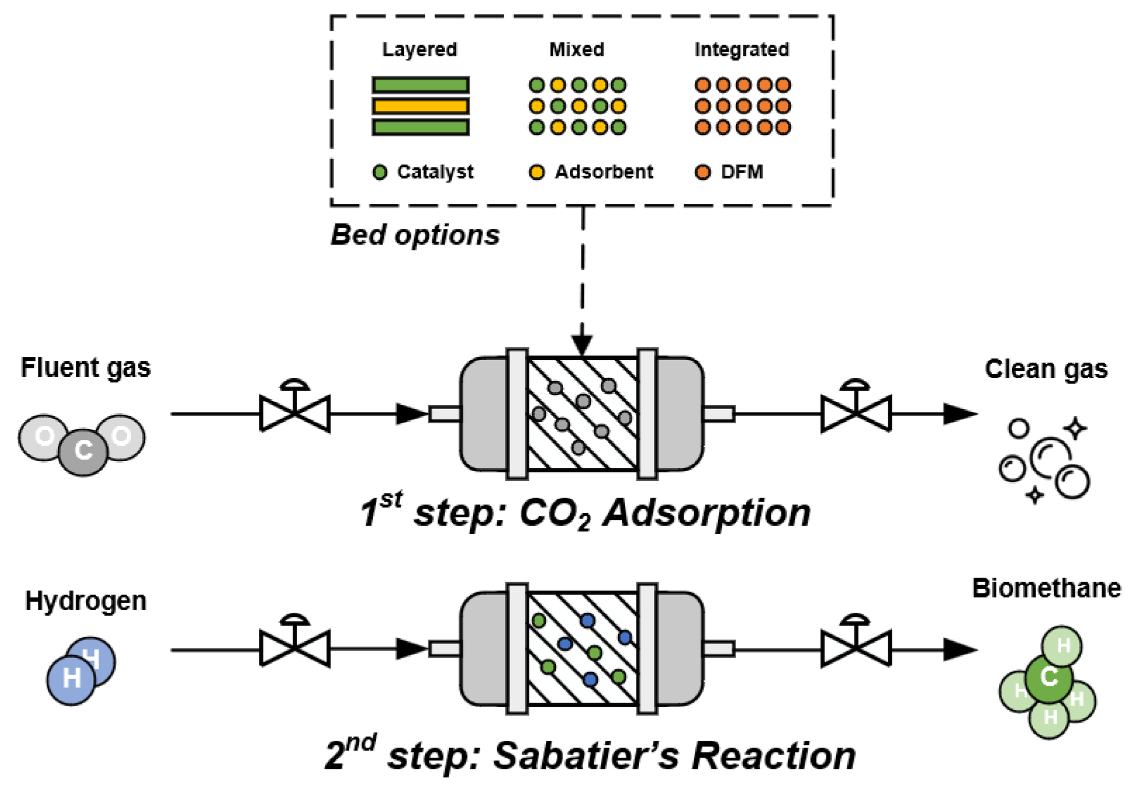


Figure 2. Functional solids and catalyst configurations

1. **Mechanical Mixture** (**MM**) materials are proposed as an alternative for **cyclic CO_2 adsorption-assisted methanation** processes
2. **MMs** physically **separate** the **adsorption** and **catalysis** functions, thereby **avoiding competition** for active sites, unlike **Dual-Function Materials (DFMs)**.
3. This technology falls within the scope of **Carbon Capture, Utilization and Storage** (**CCUS**) technologies

CHARACTERIZATION

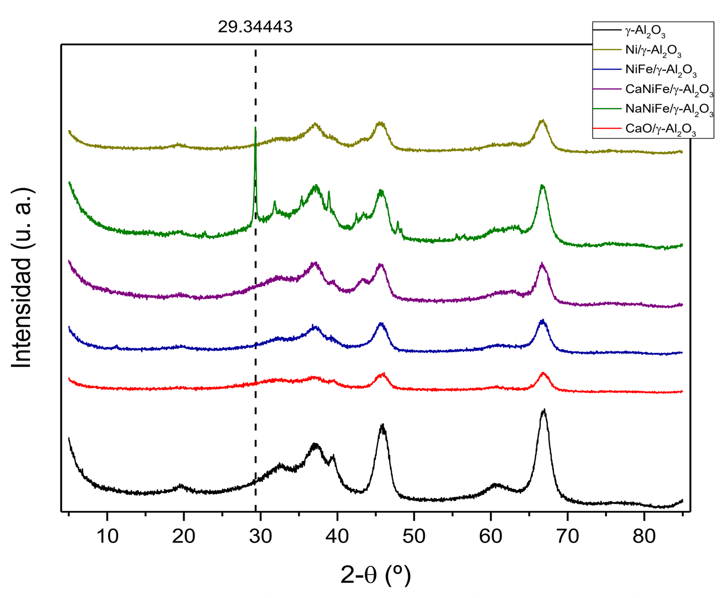


Figure 3. X-ray Refractometry (XRD)

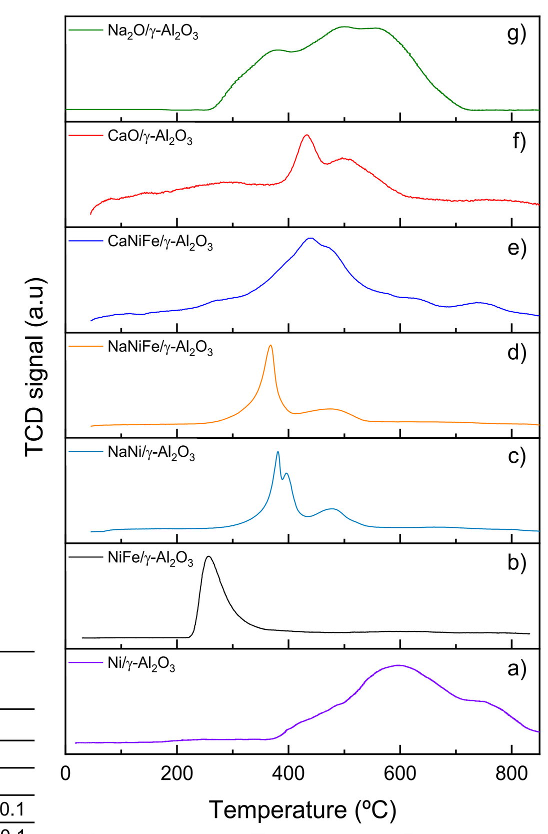


Figure 4. Temperature-Programmed Reduction with H_2 (TPR-H_2)

Table 1 . X-ray Fluorescence (XRF) and BET

Solid	BET area ($m^2 \cdot g^{-1}$)	XRF ($\%^{wt}$)				
		Ni	Fe	Al	Ca	Na
7.5Ni-2.5Fe	167.4 ± 0.4	7.4 ± 0.1	2.1 ± 0.1	46.9 ± 0.3	-	-
10Ca-7.5Ni-2.5Fe	89.3 ± 0.4	9.6 ± 0.1	3.4 ± 0.1	35.1 ± 0.1	11.3 ± 0.1	
10Na_2O-7.5Ni-2.5Fe	113.6 ± 0.4	8.5 ± 0.1	2.6 ± 0.1	36.6 ± 0.1	-	11.44 ± 0.1
10Na-10Ni	82.2 ± 0.4	6.75± 0.1	-	42.3 ± 0.1	-	10.23 ± 0.1
10CaO	98.3 ± 0.4		-	44.0 ± 0.1	11.7 ± 0.1	-
10Na_2O	100.5 ± 0.4	-	-	42.5 ± 0.1	-	14.01 ± 0.3

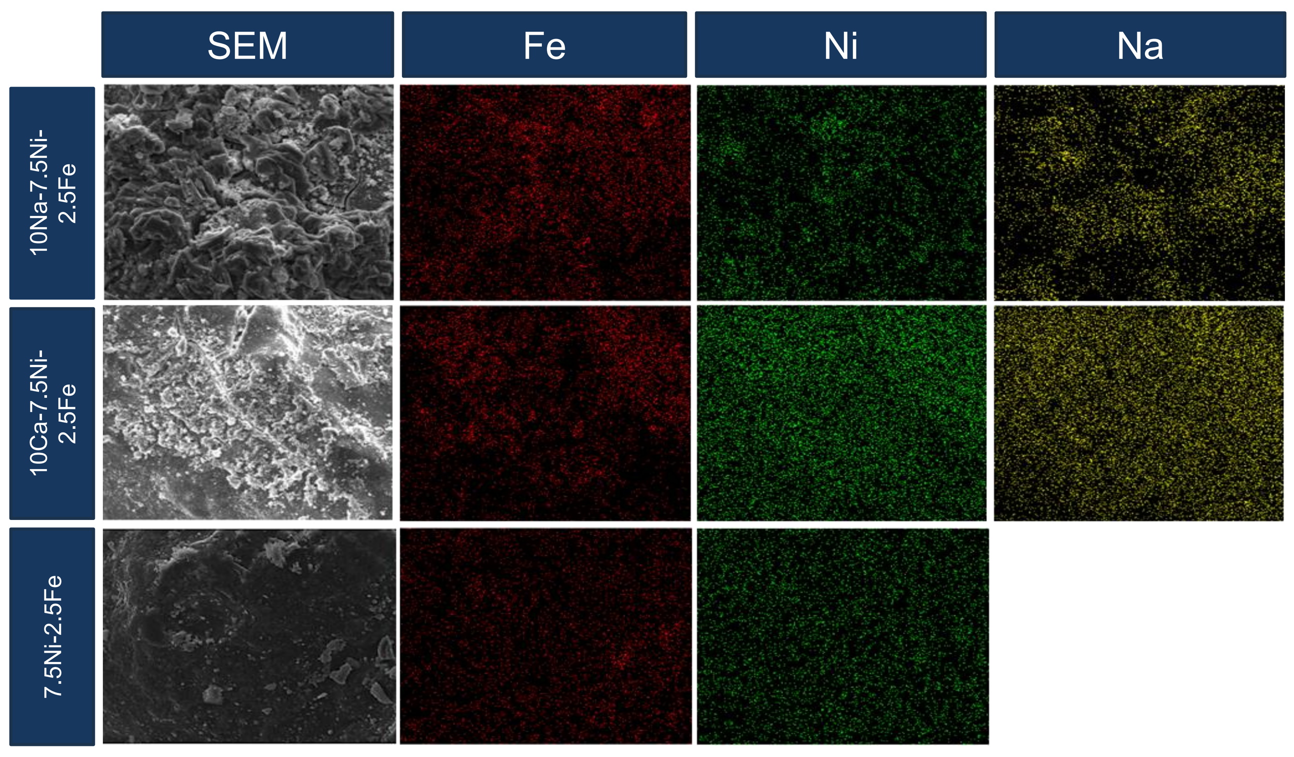
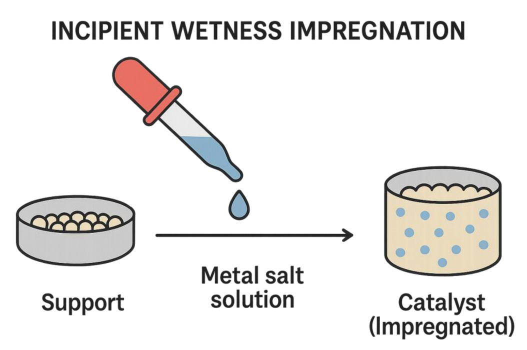


Figure 5. FESEM Images – Dispersion of Active Phases

EXPERIMENTAL

1. The **solids** used in this study were synthesized by **incipient wetness impregnation** using nitrate (Ni and Fe) or carbonate (Na and Ca) precursors. They were subsequently dried at 90 °C for 12 hours and calcined at 500 °C



2. The experiments were carried out in a **fixed-bed reactor** with the specifications shown in Table 2. The reported results were obtained using gas **chromatography** and an infrared (**IR**) **gas analyzer**

Table 2. Experimental conditions

Parameter/Property	Conventional methanation	Cyclic Adsorption-methanation
Catalyst mass	0.25 g	2 g
Adsorbent mass	-	2 g
Mass filler (γ-Al_2O_3, 5A,13X)	10.25 g	6.5 g
Volumetric flow	250 mL (SATP) / min	150 mL (SATP) / min
CO_2 concentration (adsorption step)	18 %^{v}	12/40 %^{v}
WHSV (STPmL·gcat^{-1}·h^{-1})	60000	4500
H_2 concentration (methanation step)	72 %^{v}	5 %^{v}
N_2 concentration (Internal Standard)	5 %^{v}	5 %^{v}
Inert gas	Ar	Ar
Pressure	1 bar	1 bar
Temperature	200 - 400 °C	200 - 400 °C
Duration of the Adsorption Step	-	30 min
Duration of the Methanation Step	1h	1h 30 min
Thermocouple Height	1, 3, 6, 9 and 12 cm	1, 3, 6, 9 and 12 cm

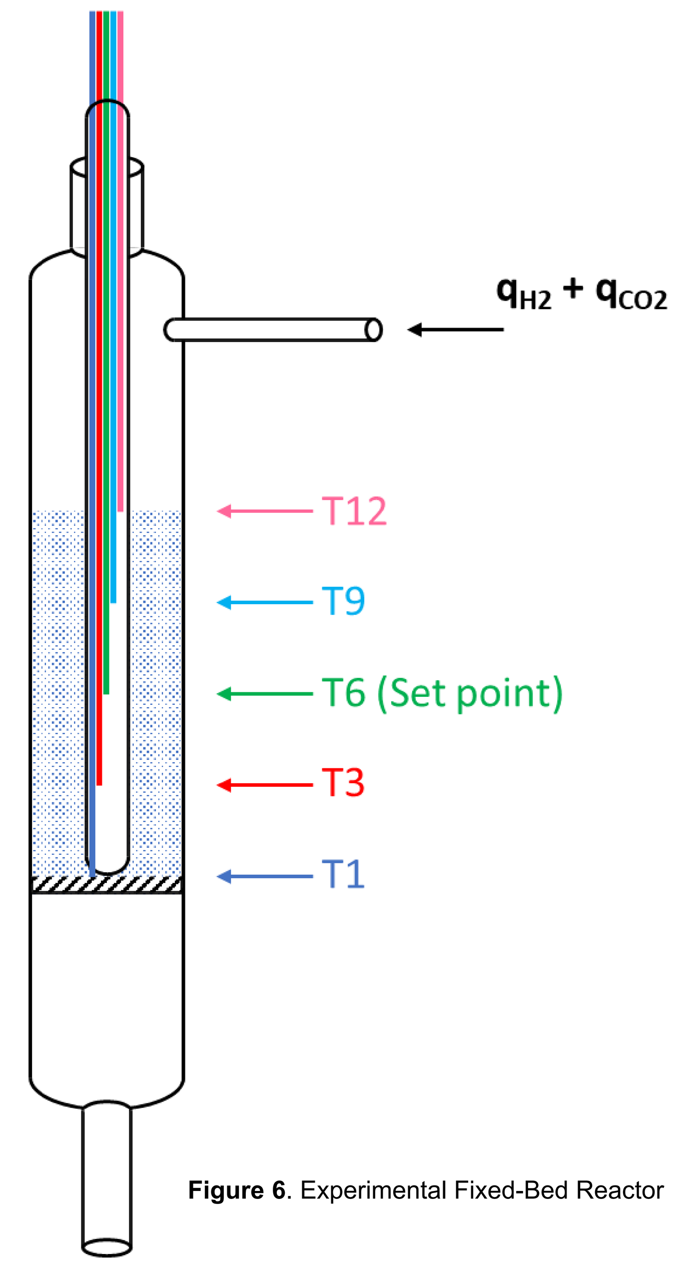


Figure 6. Experimental Fixed-Bed Reactor

RESULTS

Conventional methanation

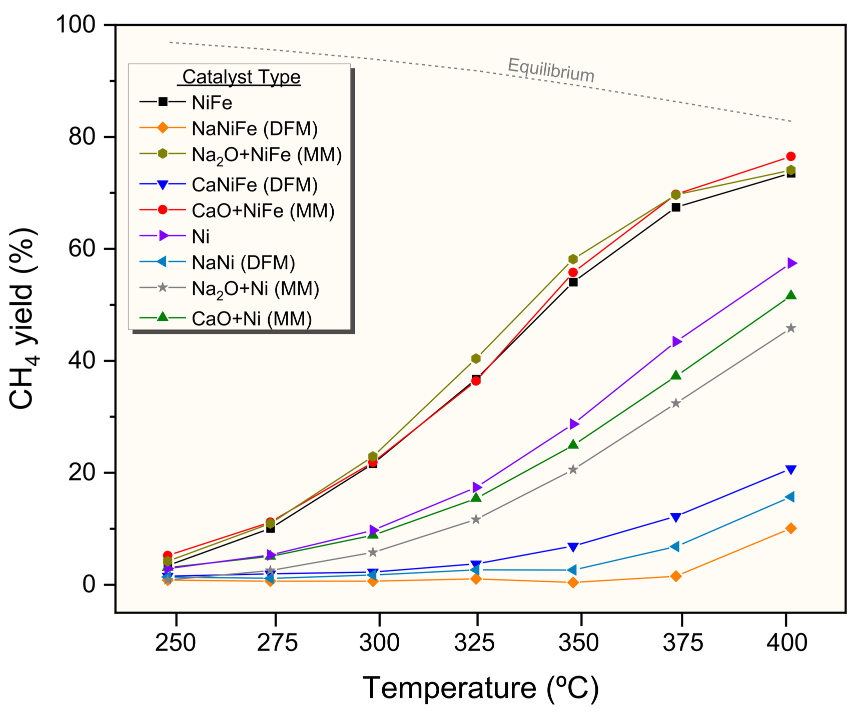


Figure 7. DFM vs. MM in conventional methanation

Cyclic Adsorption-methanation

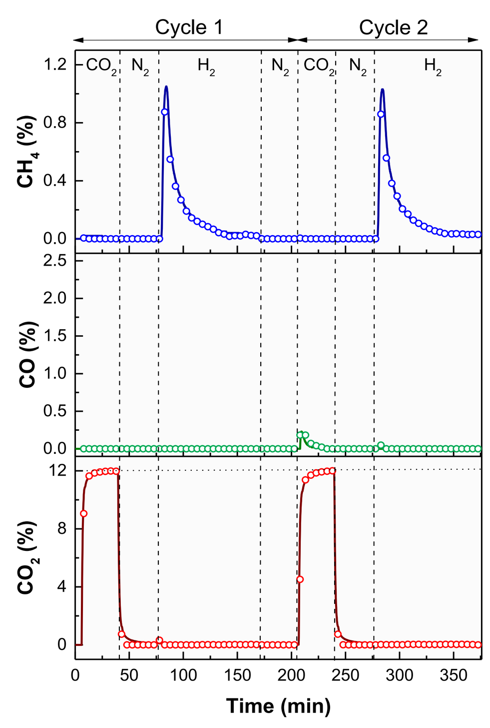


Figure 8. Diagram of Cyclic Adsorption–Methanation Operation

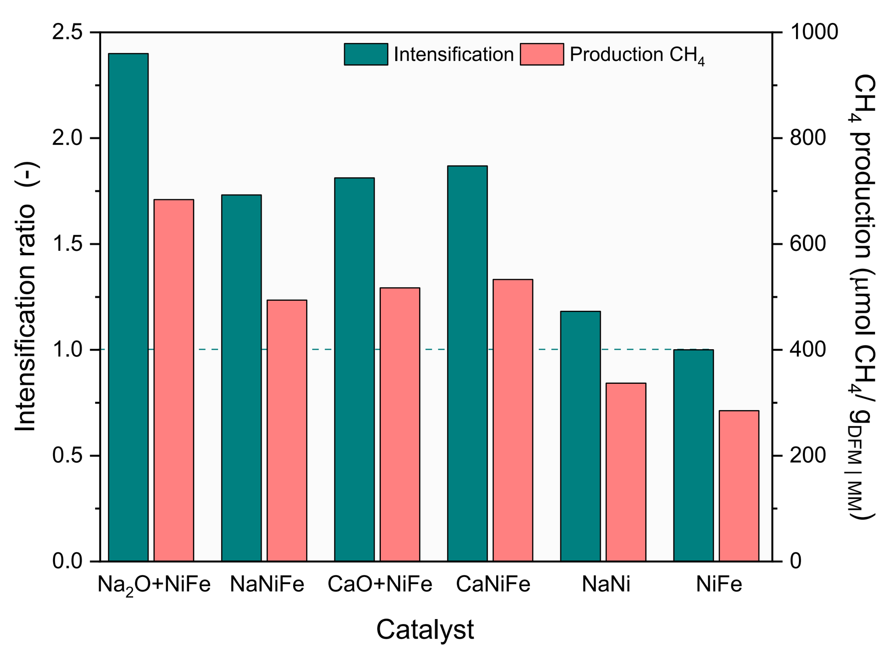


Figure 9. DFM vs. MM in Cyclic Adsorption–Methanation

Intensification and Stability

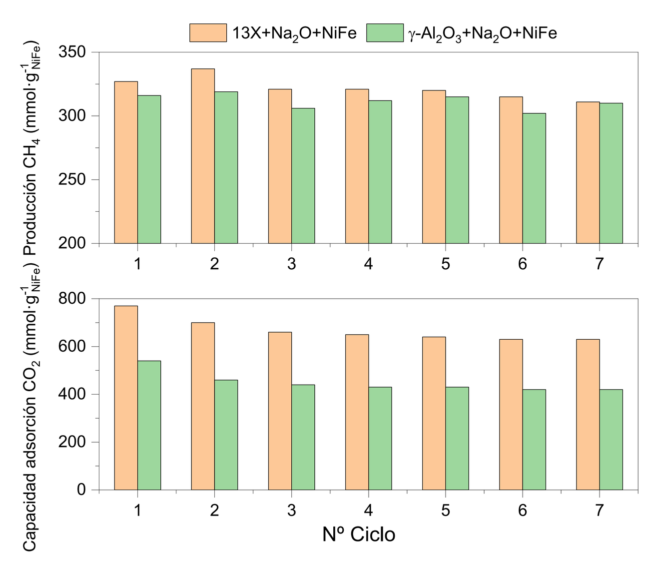


Figure 10. Influence of Temperature on CH_4 Production and CO_2 Adsorption Capacity

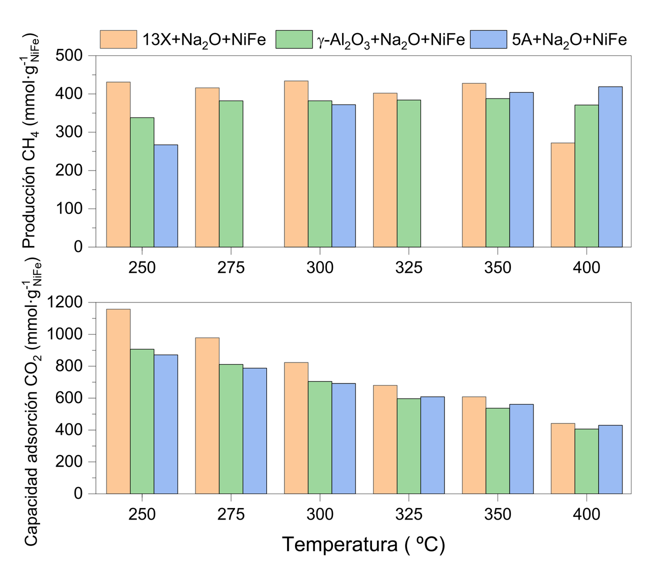


Figure 11. Stability of CH_4 Production and CO_2 Adsorption Over Consecutive Cycles

Acknowledgments and References

Al MICIU (proyecto **PID2022-136947OB-I00**, Plan Complementario del Hidrógeno (PC-H2) Unión Europea Next Generation **PRTR-C17.I1** Task LA4.A1, y contrato **PRE2020-095679** concedido a V. D. Mercader), el Gobierno de Aragón por financiación al grupo CREG (T43-23R) vía FEDER y la beca predoctoral concedida a P. Aragüés-Aldea.

[1] Bermejo-López, A. et al. *Journal of Environmental. Sciences.* (2023), 140, 292-305.
[2] X. Su, L. Shen, *Carbon Capture Science & Technology* 13 (2024) 100278.

CONCLUSIONS

MM vs DFM

MMs offer greater flexibility in operating conditions, avoiding competition between the active phase and the CO_2 adsorbent

Thermal Regime

The optimal balance between CO_2 adsorption capacity and methane production was found at 300 °C for the MM combined with Zeolite 13X

Stability

The MM combined with Zeolite 13X shows higher methane production and relative stability under cyclic methanation conditions