Intensified methanation (SESaR) with Ni-Fe based catalysts for biogas upgrading

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ENERGY CHALLENGE

Reducing carbon emissions is more critical than ever, but at same time **renewable energies** are still strongly limited by the difficulties of ensuring the capacity of supplying the **energy demand,** or how to store the surplus electricity to solve the **intermittence of renewables**. Moreover, it is been shown the need of reducing the European energy model **dependency** of **international providers** (e.g., natural gas).

ALTERNATIVES

Power to Gas technologies (PtG) can transform into methane, renewable H_2 using surplus electricity from renewable origin [1]. Through methanation reaction (*Sabatier* reaction, r.1), a high purity synthetic natural gas (close to 100%) can be obtained from concentrated CO_2 streams (i.e., biogas -ca. 30%v CO_2+70%v CH_4-). The upgraded biogas could fulfill all the regulatory parameters imposed by codes and normative. Moreover, methane (**Synthetic Natural Gas, SNG**) is an energy vector easier to transport and storage than hydrogen. In fact, the technology required to adapt the preexisting natural gas network to SNG is relatively simple, being an interesting substitute of natural gas. On the contrary, H_2 admissible for preexisting natural gas is limited to a maximum concentration of 10%v in the total flow [2].

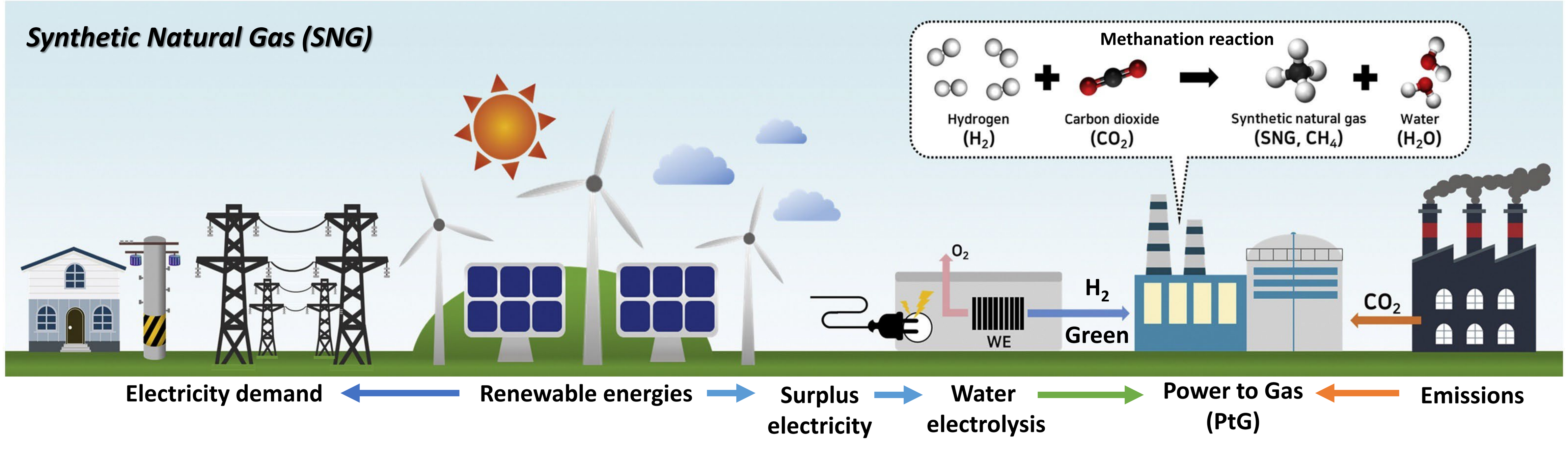
$$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O \quad \text{(r.1)}$$

INTENSIFICATION

Sorption Enhanced Sabatier Reactor (**SESaR**) with zeolites incorporates 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** (*Le Chatelier*'s principle). Thus, reaction shift to products, **increases the CO_2 conversion** and warily the selectivity to **CH_4**.

FEASIBILITY CASE STUDY

CREG group has developed a feasibility case study for methanation technology of the **resulting biogas** from a **waste management plant** for ca. 84000 inhabitants [3]. The study was based on **CAPEX/OPEX** analyses in order to obtain the **breakeven point price** of the **synthetic natural gas** produced. Simulation shown a breakeven point of **69 €/MWh** in 2021. In October 2021, the average price for importing natural gas in the Iberian gas market was 89.25 €/MWh [4], and during the first trimester of 2022, natural gas in the **Iberian gas market exceeded 100 €/MWh.**



Adapted from Boreum Lee, Hyunjun Lee et al. *Journal of Energy Storage, 24, 8 2019*

EXPERIMENTAL

Set-up

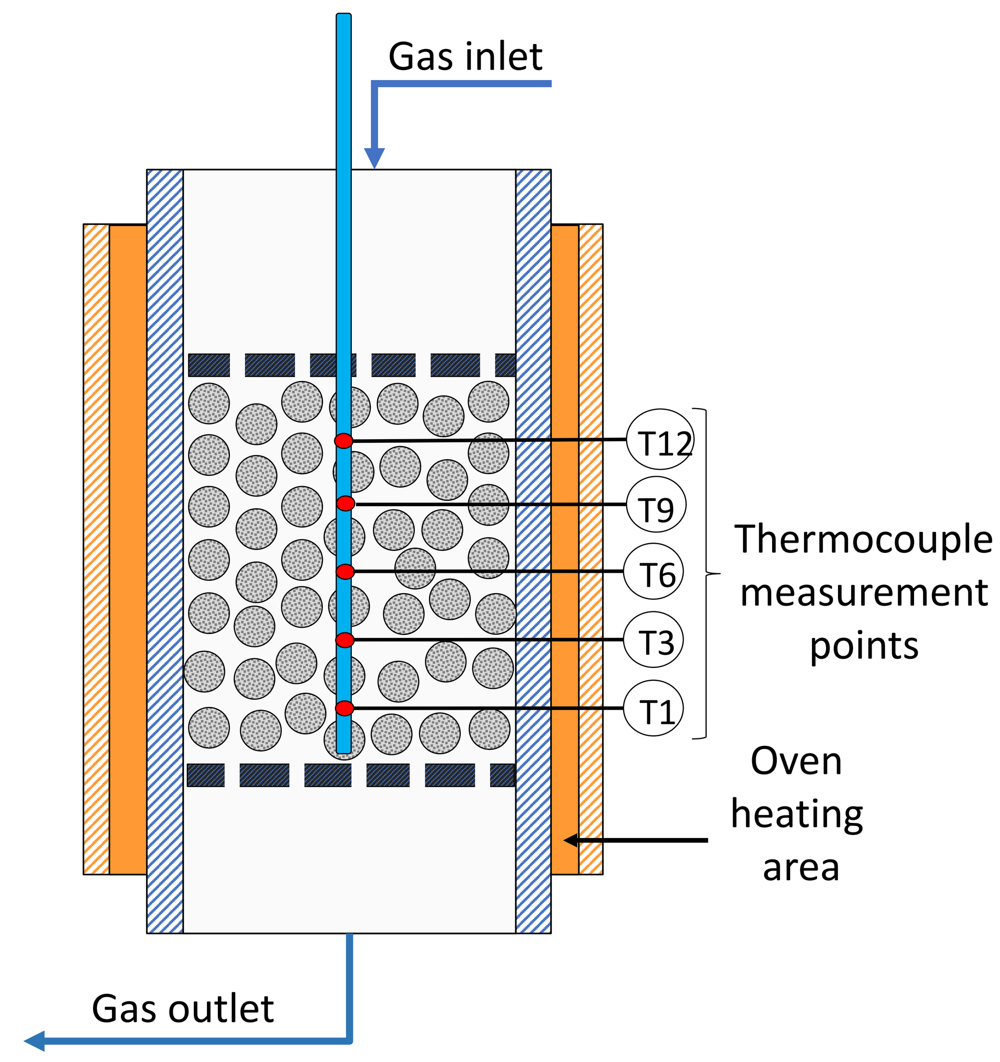


Figure 1. Schematic representation of the SESaR set-up used for carrying out the experiments. The thermocouple label indicates the height (cm) of the measurement point in the fixed bed .

Steps

1. **Charge of solids** in the column (pre-mixed)
2. **Catalyst activation:** 500 ºC for 2 hours with a gas flow composition of 50% H_2, 45% Ar and 5% N_2 (%v).
3. **Methanation** (M1, M2, M3): 1h at same temperature.
4. **Desorption** (D1 ,D2):
   - D1→30' at same temperature as in the methanation step.
   - D2→140', increasing the temperature up 500 ºC (20 ')
5. **Experiment conditions:**

Catalyst load	0.25 g
Zeolite (5A) load	10.25 g
Particle diameter	100-200 µm
Bed height	12 cm
Reactor inner diameter	13 mm
Temperature	250 - 450 ºC
Volumetric flow	250 mL(STP)/min
H_2:CO_2 molar ratio (feed)	2:1, 4:1 & 6:1
CH_4:CO_2 ratio (biogas feed)	7:3
Pressure	1 bar
Thermocouple height	1/3/6/9/12 cm

RESULTS AND DISCUSSION

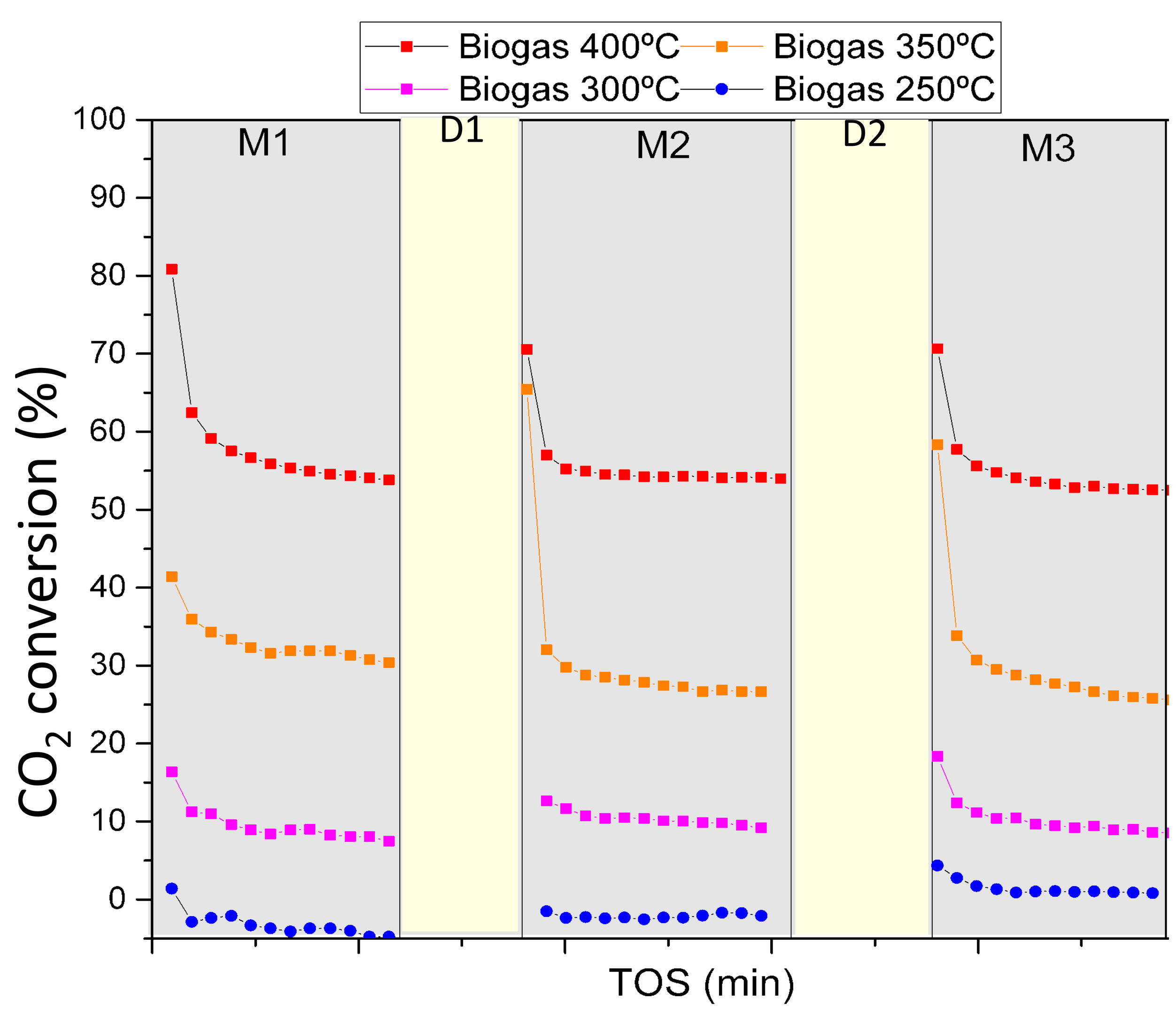


Figure 2. Methanation+adsorption (M1, M2, M3) - desorption (D1, D2) cycles for different temperatures H_2:CO_2 ratio 4:1 ; CH_4:CO_2 ratio 7:3

- 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 **highest conversion** enhancing effect is observed at **400 ºC**.
- Feasibility case study showed a **breakeven point 69 €/MWh** when the **importing natural gas price** market for the same time period **was 89.25 €/MWh**

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[2] Altfeld, K., Pinchbeck, D. Reprint: gas for energy 03/2013: *Admissible hydrogen concentrations in natural gas systems.* ISSN 2192-158X. Available from: https://gerg.eu/g21/wp-content/uploads/2019/10/HIPS_Final-Report.pdf
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