Thermocatalytic production of Synthetic Natural Gas from renewable carbon dioxide and hydrogen in a fluidized bed reactor with bifunctional solids

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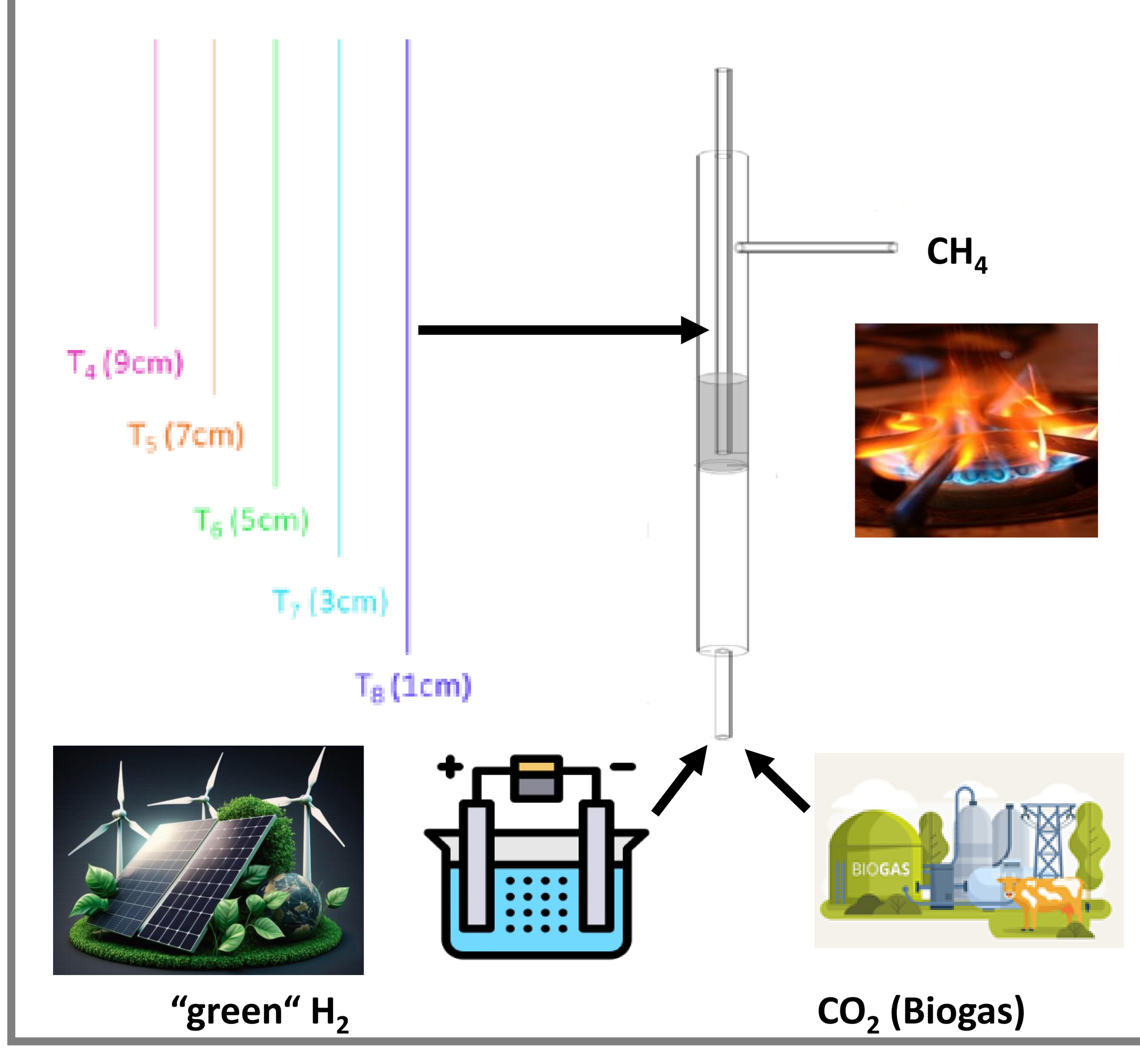
INTRODUCTION

In a fluidized bed reactor, the Sabatier reaction was carried out, using a bimetallic Ni/Fe catalyst supported by γ-Al_2O_3 and zeolite 13X as water adsorbent.



Through the methanation process (based on Sabatier reaction (r.1)) [1], synthetic natural gas (SNG) can be obtained, using "green" hydrogen and CO_2 [2].

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O \quad ; \quad \Delta H_r^0 = -165.1 \text{ kJ/mol} \quad \text{(r.1)}$$

- CO_2 is obtained from biogas resulting from the anaerobic decomposition of organic matter [3]. Since CO_2 is one of the main gases that cause the greenhouse effect, its use as reactant is a good way to take advantage of it without being released into the atmosphere (constituting a good example of circular economy)
- Synthetic natural gas, like fossil gas, has multiple advantages; among them, its easy transport, relatively low reactivity and existence of an already stable infrastructure for gas distribution.
- (r.1) is highly exothermic, what leads to the appearance of hot spots that favour the rapid deactivation of the catalyst by sintering.
- To reduce the occurrence of such hot zones, the use of a fluidized bed reactor is proposed as an alternative to traditional fixed-bed reactors. This reactor configuration ensures that the bed is isothermal.

MATERIALS/METHODOLOGY

Reactor diameter (cm)	3.0
Catalyst composition (%^{w})	7.5%Ni-2.5%Fe/ϒ-Al_2O_3
Water adsorbent	Zeolite 13X (diameter: 200-250µm)
Temperature range(ºC)	250-400
Pressure (atm)	1.0
molar ratio H_2:CO_2 (adim.)	4:1
Ratio W/Q (g min mL^{-1}(SATP))	0.002
Bed height (cm)	7.0
Experimental sequence	
Activation of the catalyst (A)	50 ^{v}% H_2, 45 ^{v}% Ar, 5 ^{v}% N_2, T=500 ºC
Methanation (M)	72 ^{v}% H_2, 18 ^{v}% CO_2, 5 ^{v}% Ar, 5 ^{v}% N_2, 250≤T≤400 ºC
Inerting (I)	95 ^{v}% Ar, 5 ^{v}% N_2, 250≤T≤400 ºC
Oxidation (O)	95 ^{v}% Ar, 3^v% N_2, 2 ^{v}% O_2, T=500 ºC
Purging (P)	95^v% Ar, 5^v% N_2 , T=500 ºC
Catalyst reactivation	50 ^{v}% H_2, 45 ^{v}% Ar, 5 ^{v}% N_2, T=500 ºC

RESULTS

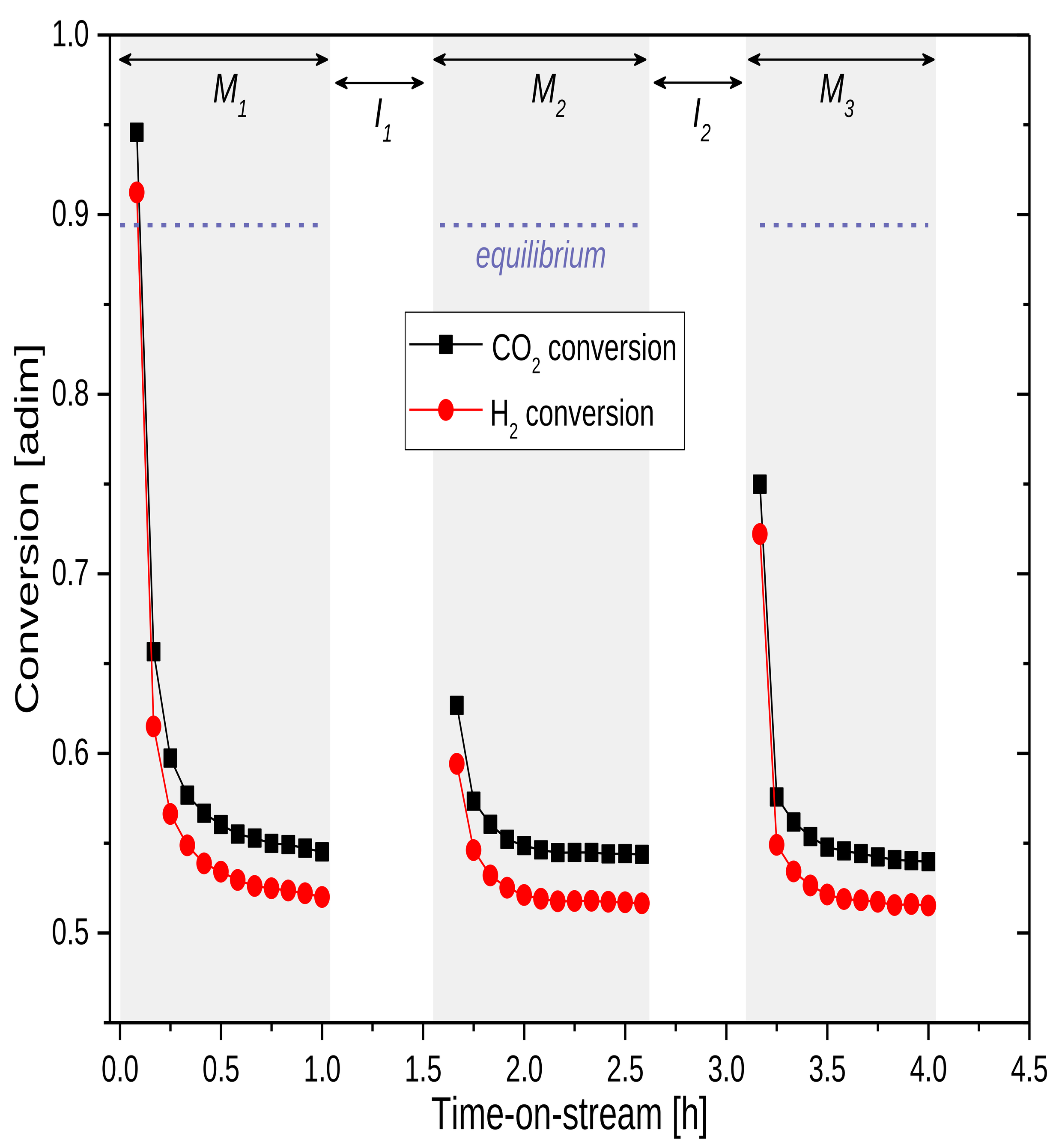


Figure 1. CO_2 methanation at 350 ºC: conversions of reactants vs TOS.

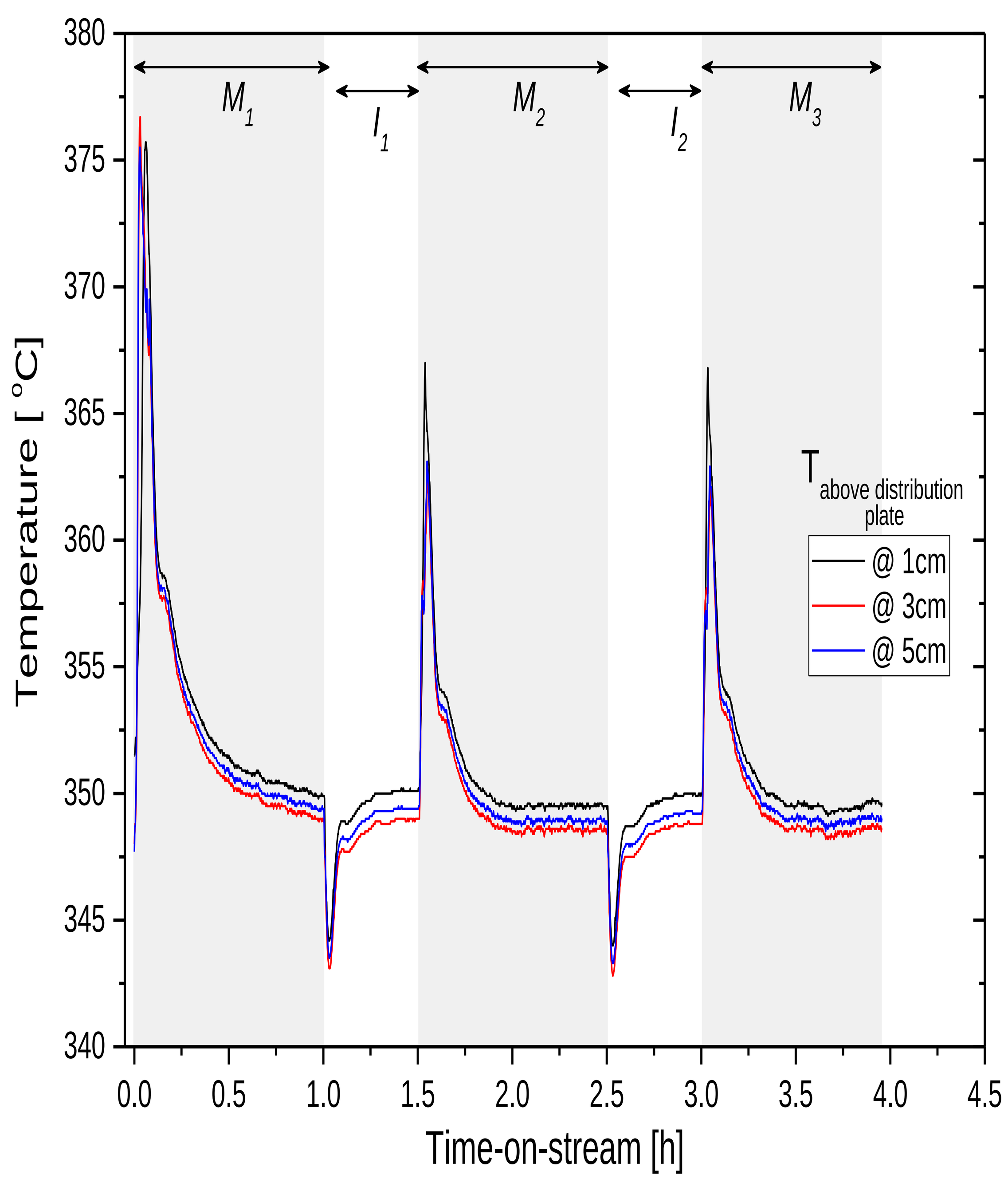


Figure 2. CO_2 methanation at 350 ºC : temporal evolution of temperature.

Figure 1. Relatively high conversions were obtained in the first moments of reaction, starting from 90%^{v} for H_2 and 95%^{v} for CO_2 and with a stabilization value of 51% for H_2 and 55% for CO_2. This behaviour is largely attributed to the intensification of the reaction due to the adsorption effect of water by the 13X zeolite, favouring the shift of the equilibrium towards the products (*Le Châtelier*).

Figure 2. Due to the fact that the reaction is very exothermic, there is evidence of an increase in temperature at the beginning of each methanation cycle, but later it decreases to the set temperature, observing that the temperature marked by each thermocouple tends to equalize, confirming the isothermicity of a fluidized bed.

CONCLUSIONS

Fluidized bed reactors ensure that thermal homogeneity is maintained for the methanation reaction (*Sabatier*) of CO_2 streams, such as those from a sweetened biogas, which prevents the appearance of hot spots. The use of 13X zeolite increases the conversion of reactants and therefore the amount of methane obtained. Logically, water vapor saturation of zeolites requires alternating methanation stages (M) along with regeneration stages (I) and optimizing them to maximize synthetic natural gas production.

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