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

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Abstract

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. The objective is to study the methane yield of a mixture made up of CO_2 (such as that present in a biogas) and renewable hydrogen; that is, the production of *Synthetic Natural Gas* (SNG) or *Renewable Gas* (RNG). This product is also known as *Biomethane*.

Introduction

One of the biggest problems today is the production of fuel without affecting the environment. 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]. This hydrogen can be obtained from the electrolysis of water, using as an electrical energy source like solar cells or wind turbines, among other renewable sources. 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.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_r^0 = -165 \text{kJ/mol} \quad \text{(r.1)}$$

This reaction (r.1) is highly exothermic, what leads to the appearance of *hot spots* that favor 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

A bimetallic catalyst with a mass composition of 7.5%Ni-2.5%Fe/γ-Al_2O_3 and zeolite 13X was used as a filler-adsorbent. The experiments were carried out in a temperature range between 250 and 400 °C and atmospheric pressure.

The experimental sequence was as follows: activation of the catalyst (A); three cycles of methanation (M), alternating with periods of inerting (I); oxidation (O), purging (P) and catalyst reactivation; three cycles of M, alternating with periods of I. The composition of the input gas mixture in A was 50 ^{v}% H_2, 45 ^{v}% Ar, 5 ^{v}% N_2; in each stage M, it was 72 ^{v}% H_2, 18 ^{v}% CO_2, 5 ^{v}% Ar and 5 ^{v}% N_2; in each stage I it was 95 ^{v}% Ar and 5 ^{v}% N_2; in O it was 95 ^{v}% Ar, 3 ^{v}% N_2, 2 ^{v}% O_2; in P it was 95 ^{v} % Ar, 5 ^{v}% N_2.

The minimum fluidization flow of the solids bed with the gas mixture was previously obtained for each temperature, performing the corresponding fluidization tests to ensure fluidization after the volumetric contraction that occurs in the reaction. A reduced velocity of 1.3 times the minimum fluidization velocity was used.

Results

Figure 1 shows the evolution of CO_2 and H_2 conversion over time during the sequence M+I+M+I+M at T = 350 °C and ambient pressure, with a molar ratio H_2:CO_2 = 4:1. Previously, the catalyst was activated at T= 500 °C for 2 hours. A ratio of 0.002 $g_{catalyst} \cdot min \cdot NmL^{-1}$ was maintained for all runs. Figure 2 shows the temperature profiles achieved at three axial positions of the bed at 5, 3 and 1 cm from the distribution plate.

Relatively high conversions were obtained in the first moments of reaction, starting from 90% for H_2 and

95% 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*).

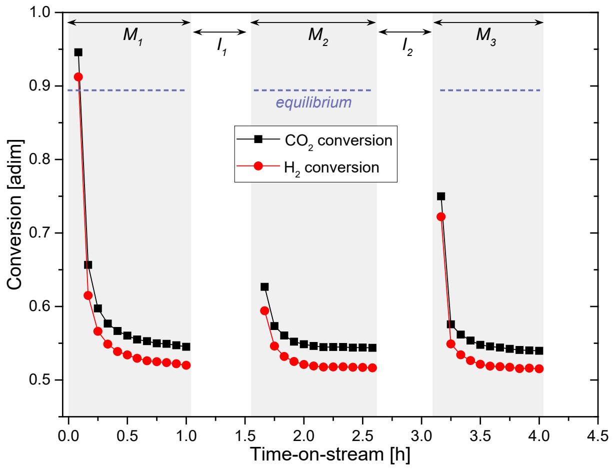

Figure 1. CO_2 methanation at 350 ºC: conversions of reactants against time.

Additionally, 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.

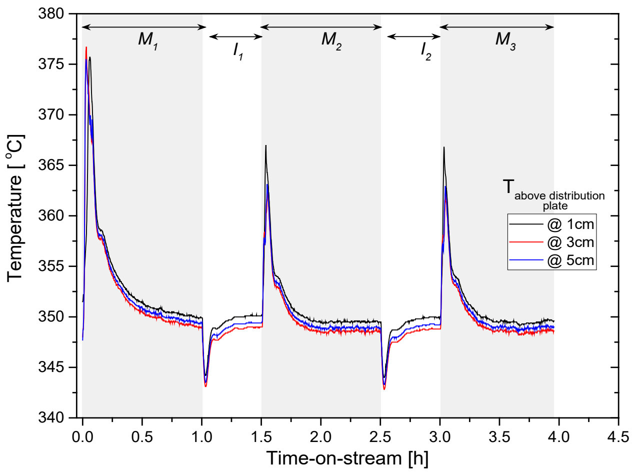

Figure 2. CO_2 methanation at 350 ºC: temporal evolution of temperature.

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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