From Biogas to SNG in a Fixed Bed Reactor by Alternating Adsorption/Methanation Stages with Multifunctional Solids

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Abstract

This research evaluates the use of catalyst + CO_2-sorbent mechanically mixed (MM) solids for the separation, capture, and valorization of CO_2, through the *Sabatier* reaction, from a desulfurized biogas stream. Furthermore, the effect of CH_4 ready present in the feed stream on CO_2 adsorption and subsequent methanation will be compared with results when CO_2 was fed instead of biogas.

Introduction

This study is integrated into the ***Power to Methane*** concept, which consists of transforming surplus electrical energy from renewable sources into renewable hydrogen to thereafter convert the CO_2 from biogas into Synthetic Natural Gas (SNG) via *Sabatier's* reaction (r.1). This technology is a potential solution to the intermittency of energy generation from renewable sources and the associated storage problems.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H_r^{\circ} = -165.1 \text{kJ mol}^{-1} \qquad (r.1)$$

Mechanically mixed solid (MM) are used in these experiments. They combine a catalyst (NiFe) and a CO_2 adsorbent (Na_2O).

This work investigates the impact of introducing CH_4 as part of a sweetened biogas feed stream in cycles consisting in alternating stages of CO_2 adsorptions followed by methanation with H_2. The CO_2 retention capacity is evaluated during the adsorption step, while CH_4 yield is assessed in the subsequent hydrogenation of the CO_2 adsorbed in the previous stage. The main advantage of this procedure lies in the effective separation of the CO_2 from the CH_4 originally present in the biogas, as well as from that formed along the methanation stage.

Experimental

The experiments were carried out in a fixed-bed reactor (12 cm height, 13 mm inner diameter), with MM particles between 100-200 μm. The solids were synthesized by incipient wetness impregnation. The MM is composed of 2 g of NiFe (7.5%^{wt} Ni-2.5%^{wt} Fe/γ-Al_2O_3) as catalyst and 8.5 g of Na_2O (10%^{wt} Na/γ- Al_2O_3) as CO_2 adsorbent; the precursor of catalyst are nitrates and Na_2CO_3 for the absorbent.

Total feed stream in all experiments was 150 mL(SATP)/min. This flowrate was sufficient to ensure kinetic regime control. Prior to the tests, the solids were activated at 450 °C for 2 hours (50%^{v} H_2, diluted in 5%^{v} N_2 and 45%^{v} Ar).

The experiments consisted of three alternating stages: adsorption + purge + methanation at temperatures between 250 ºC and 400 ºC at intervals of 50 ºC. The purge between adsorption and methanation has been described as a method to increase the CH_4 selectivity by eliminating the weakly adsorbed CO_2 on the catalyst. However, it could also result in a lower CH_4 production, since part of the CO_2 adsorbed on the MM might be unwantedly desorbed.

The experimental conditions tested are shown in Table 1 for the two types of experiments depending on the feeding to the adsorption stage: 1) biogas (CH_4:CO_2 ratio = 7:3) and 2) only CO_2.

Table 1. Experimental conditions.

	Stages	Feed
Biogas Methanation	Adsorption (45 min)	12 %^{v} CO_2 + 28 %^{v} CH_4
	Purge (30 min)	5 %^{v} N_2 + 95 %^{v} Ar
	Hydrogenation (2h)	5 %^{v} H_2
CO_2 Methanation	Adsorption (45 min)	12 %^{v} CO_2
	Purge (30 min)	5 %^{v} N_2 + 95 %^{v} Ar
	Hydrogenation (2h)	5 %^{v} H_2

Blank experiments were carried out using SiC. On-line NDIR and mass spectrometer were utilized to analyse the exhaust gases.

Results

Figure 1 shows the concentration of different species in the exhaust gases along the adsorption and purge stages at different temperatures. The %CO_2 at 400 °C stabilizes at a lower value than that in the blank,

indicating that CO_2 is not only being adsorbed but also reacting. Similar phenomenon occurs with CH_4: biogas in the adsorption stage produces CO, which increases at elevated temperatures (Table 2). On the contrary, when only CO_2 is fed instead of biogas, CO is not produced at all (view Table 3). Consequently, CO generation should be associated with introducing CH_4 in the feed stream.

Table 2. Biogas methanation (CH_4:CO_2 ratio = 7:3); [µmol/min·g_{cat}].

	Adsorption		Hydrogenation			
T ºC	$CO_{2,effective}$	*CO*	CH_4	*CO*	CO_2	Y_{CH_4} (%)
400	1739	2091	1086	70	96	62
350	2100	916	1008	46	103	48
300	2473	215	908	16	60	37
250	2336	0	612	0	32	26

Table 3. CO_2 methanation [µmol/min·g_{cat}].

	Adsorption		Hydrogenation			
T ºC	$CO_{2,effective}$	*CO*	CH_4	*CO*	CO_2	Y_{CH_4}(%)
400	1744	0	1091	106	143	63
350	2077	0	1055	43	128	51
300	2307	0	930	19	74	40
250	2277	0	630	0	45	28

Dry reforming of methane (r.2) seems to be a plausible hypothesis to justify the presence of CO along the adsorption stage; furthermore, when analysing the outlet gases with a mass spectrometer, H_2 production is also observed (not shown).

$$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2 \quad \Delta H_r^{\circ}=247{,}3 kJ\ mol^{-1} \qquad (r.2)$$

Taking this hypothesis into account, the *effective* CO_2 has been determined (Table 2 and 3), which refers to the CO_2 retained in the bed and available for the methanation stage (Figure 2); the *effective* CO_2 and CH_4 production are very similar with no dependence whether CH_4 is present in the feed or not.

During the hydrogenation stages (Figure 2), CH_4 profiles exhibit similar trends, with all curves starting from comparable values and increasing at similar rates, followed by a temperature-dependent maximum and decay. The small amounts of CO_2 and CO detected suggest concurrent dry reforming and/or CO_2 hydrogenation, while the shoulders observed in the CO profiles remain under investigation.

Conclusions

The study validates the use of catalyst + CO_2-sorbent MM materials in alternating adsorption-methanation stages for SNG production from biogas. This approach allows the separation of a SNG stream from biogas while converting the captured CO_2 into additional SNG. CH_4 in the adsorption stage does not act as an inert; however, it does not alter the bed's capacity to adsorb CO_2.

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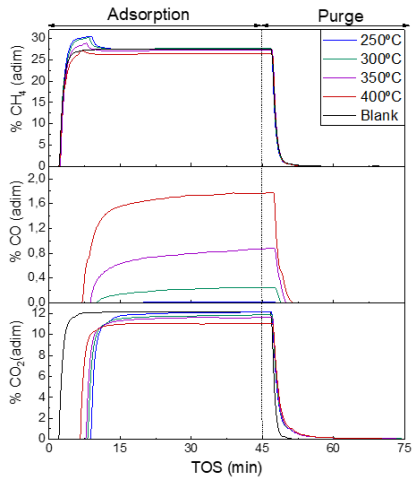

Figure 1. Temporal evolution of the percentages of CH_4, CO, and CO_2 in the adsorption and purge stages, for biogas methanation.

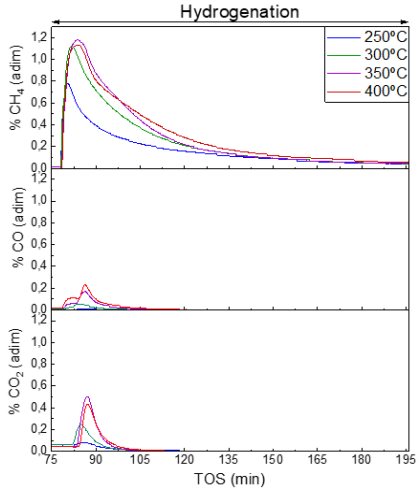

Figure 2. Temporal evolution of the percentages of CH_4, CO, and CO_2 in the hydrogenation stage, for biogas methanation.