A multifunctional reactor for CO_2 capture and conversion to CH_4 – Effect of Pressure and sorbent/catalyst ratio

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Highlights

- A sorptive reactive unit was tested for CO_2 capture and methanation.
- The performance was assessed under different total pressures and sorbent/catalyst ratios.
- Pressure increase was beneficial for the CH_4 productivity and purity.

1. Introduction

In Power-to-Methane processes, green H_2 and CO_2 are converted into CH_4 (or synthetic natural gas - an easily stored and distributed energy vector), through the Sabatier (or methanation) reaction (Eq. 1) [1].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H^{298K} = -165\ \mathrm{kJ\cdot mol^{-1}} \qquad (1)$$

The CO_2 can arise from several sources. For instance, flue gas, which is a post-combustion stream generated at power plants, is essentially composed of CO_2 (typically below 15 %) and N_2 (apart from other minor impurities) [1]. Other manufacturing activities, such as cement, petrochemicals, iron, and steel production, generate similar streams, though with distinct CO_2 concentrations [1]. Biogas is another source of CO_2, which results from the degradation of organic waste. It is composed essentially of CH_4 (50-70 %) and CO_2 (30-50 %) [1]. In this work, an innovative sorptive reactive unit is operated to simultaneously capture CO_2 from synthetic flue gas and biogas streams and convert it to CH_4 [2]. The performance of the cyclic system was studied at different operating conditions.

2. Methods

One sorptive reactor was filled with two commercial materials: a K-promoted hydrotalcite (CO_2 sorbent), and a Ru/Al_2O_3 methanation catalyst – *cf.* Fig. 1.

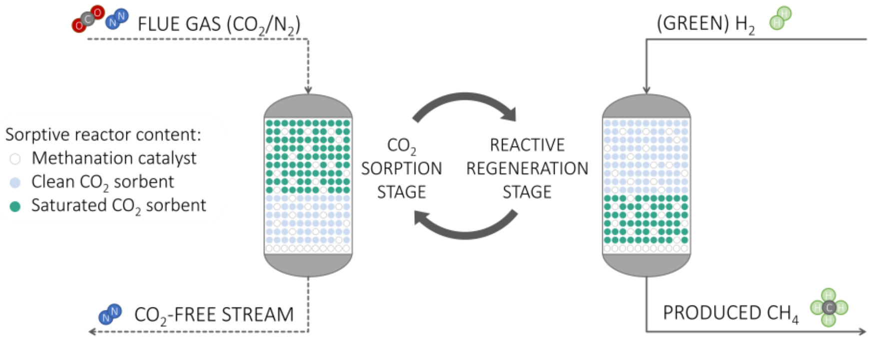

Figure 1. Scheme of the sorptive reactor cyclic operation, using flue gas as the CO_2 source stream.

As can be observed in Fig. 1 (which depicts, as an example, a flue gas stream as the source of CO_2), the operation of the reactor comprises two stages, carried out cyclically: the CO_2 sorption stage and the reactive regeneration stage. During the sorption stage (*cf.* Fig.1 – left side), the flue gas (CO_2/N_2 mixture) is fed to the column, and the CO_2 is captured by the sorbent, which becomes progressively saturated. The outlet stream is mostly composed of N_2. After nearly complete sorbent stage, one switches to the reactive regeneration stage (*cf.* Fig.1 – right side), wherein the inlet is H_2, and, at the catalyst active sites, it reacts with the previously captured CO_2 simultaneously regenerating the sorbent and producing CH_4 (which composes most of the outlet stream during this stage). After the reactive regeneration, the column is in condition to undergo again a new CO_2 sorption stage.

The inlet of the sorptive reactor was switched every 20 minutes, creating multiple sorption/reactive regeneration cycles, which was carried out until a cyclic steady state was achieved. The inlet flow rate during the sorption stage was 100 $mL_N \cdot min^{-1}$ (15 % of CO_2), and during the reactive regeneration stage, it was 60 $mL_N \cdot min^{-1}$ (of H_2). The experiments were carried out at 300 °C and 350 °C. This study evaluated the effect of the process pressure (1, 4, and 7 bar) and sorbent/catalyst mass ratio inside the column (1, 5, and 10). Several indicators were calculated to assess the performance of the column under different conditions, namely: CO_2 sorption capacity, CO_2 conversion, the ratio of H_2 fed per CH_4 produced, and CH_4 purity and productivity [2].

3. Results and discussion

For brevity reasons, this discussion will focus on the effect of pressure variation, using a sorbent/catalyst ratio of 10, at 350 °C, and with flue gas as the source of CO_2. The top graph of Fig. 2 shows that the increase in the total pressure was favorable for the CH_4 productivity ($Prod_{CH4}$ - the amount of CH_4 produced per catalyst mass and time unit). This is because this increment is beneficial both for the sorption process (due to the increased partial pressure of CO_2 and improved sorption kinetics) and for the methanation reaction (which is favored by high pressures, both kinetically and thermodynamically) [3].

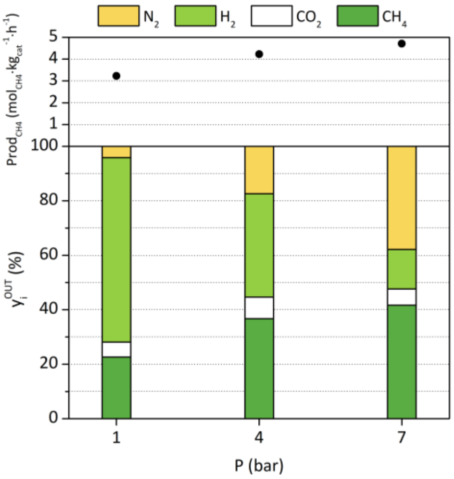

Figure 2. Effect of pressure on CH_4 productivity and on average outlet fraction of CH_4, CO_2, H_2, and N_2.

On the bottom graph of Fig. 2, it is shown that the average outlet fraction of CH_4 during the reactive regeneration stages, *i.e.*, the CH_4 purity (represented by the dark green column) was also improved by working at higher total pressure. The reason is that, since more CH_4 was produced (at higher pressure), more H_2 was consumed, and so the amount of H_2 that exited the column unreacted was reduced, and so was the average fraction of H_2 in the outlet (*cf.* smaller light green column in Fig. 2). However, the average outlet fraction of N_2 increased with the rise of total pressure (*cf.* yellow columns in Fig. 2). This N_2 was present in the flue gas feed, but only exited the reactor at the beginning of the reactive regeneration stage, decreasing CH_4 purity. A way to minimize such negative effect is to discard the outlet stream generated at the start of the reactive regeneration stage, when it is mostly composed of N_2. When this approach was considered, the CH_4 purity was increased from 41.7 to 62.6 % at 7 bar, though at the cost of CH_4 productivity (due to the presence of some CH_4 in the discarded stream), which was slightly reduced from 4.71 to 4.37 $mol \cdot kg_{cat}^{-1} \cdot h^{-1}$.

4. Conclusions

The increase of total pressure was overall beneficial for the sorptive reactive method presented. The study of this and other parameters (such as sorbent/catalyst ratio) will allow the optimization of the process for both the flue gas and biogas feed cases.

Acknowledgments

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Keywords

Multifunctional reactor, CO_2 Methanation, Carbon Capture and Utilization, Power-to-Methane