Exploring carbon dioxide methanation: experimental insights and simulation strategies

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Highlights
- Experimental synthesis and tests of Ni-based catalyst at ambient and high pressure.
- Simulation of the methanation plant with Aspen Plus and Aspen Adsorber.
- PSA dehydration unit to meet CH_4 grid entry specifications.
- 4 stage to yield over 75% CO_2 conversion.

1. Introduction

Over the past few decades, the significant release of carbon dioxide resulting from fossil fuel consumption has evolved into a formidable challenge. Despite the increasing traction of renewable energies, they face the inherent issue of intermittency. The surplus energy generated from renewable sources, like solar and wind power, is now being harnessed and stored in the guise of green hydrogen, produced through the process of water electrolysis [1]. Unfortunately, the current state of technology lacks the necessary infrastructure for the transportation and distribution of hydrogen. Chemical carriers that can be distributed using existing technologies and infrastructure are therefore of great interest. Methane in particular presents, in addition to a widely present distribution network, a clear and well-defined regulatory framework which makes it a promising candidate.

This Carbon Capture and Utilization (CCU) technology works by converting CO_2, extracted from biogas produced in an anaerobic digester, to generate methane [2]. Anaerobic digesters represent a well-known, grown-up, and relatively common technology that allow the valorization of agricultural and municipal waste, creating biogas composed of both CH_4 and CO_2 [3]. In this study the methanation of carbon dioxide, specifically coming from biogas streams, using green hydrogen is approached both from the experimental and the simulation side.

2. Methods

Catalysts have been synthetized using Nickel as active phase and different support, such as ZSM-5, Al_2O_3, TiO_2, CeO_2, ZrO_2 and SiO_2. A wide spectrum of loadings has been synthetized and tested. Tests were carried out using two different setups. The first, consisting of a reactor made of Inconel 600 and operating at atmospheric pressure was used for initial screening of the catalysts. The latter reactor, a FR-50 produced by PID and Micromeritics, equipped with a high-pressure unit and a continuous G/L separator, has been used for high pressure tests and GHSV screening. In both cases, a mixture of CO_2 and H_2, together with He used as diluent and N_2 used as internal standard have been used as reactant mixture. Tests were carried out within a Gas Hourly Space Velocity (GHSV) range of 3000 h^{-1} to 400000 h^{-1}. The two reactors were equipped respectively with an Agilent GC 7890 and with an Agilent GC 8860. Process design was carried out with the Aspen Plus and Aspen Adsorption simulation tools. Simulations were conducted on a small scale, resembling a standard biogas plant. Green hydrogen was employed, and pre-treatment of the biogas flow was taken into account to prevent catalyst poisoning caused by sulphides. Both the direct hydrogenation of the biogas stream and the hydrogenation of a previously separated CO_2 portion were considered.

3. Results and discussion

Experimental results over Ni/Al_2O_3 and Ni/ZSM-5 showed that these catalysts offer good performances, which, combined with the relatively low cost, makes them very attractive potential candidates for CO_2 methanation.

The simulation flowsheet [4], reported in Figure 1, can be divided into three sections: a reactive one, the recycle section and third one concerning the PSA purification. The ENRTL model was employed to calculate activity coefficients with electrolytes. When determining vapor-liquid equilibria (VLE), the Redlich-Kwong equation of state (EOS) was chosen in conjunction with the ENRTL model. Gas solubility in the liquid phase was represented using the Henry equation. The multistage reactor was simulated using multiple multitubular plug-flow reactor blocks, with adjustments made to catalyst density and particle size to achieve reasonable pressure drops. The design incorporates four stages aimed at converting 75% of the CO_2. Cooling of the product occurs after each stage, and the reactive bed itself is represented as a bundle of tubes filled with the catalyst, cooled by the feed flowing on the shell side. Two condensers, operating at different pressures, with the second capable of working up to 17 bar, are employed to eliminate water from the stream exiting the reactor. The CO_2 adsorption process using the potassium method is flexible in terms of pressure. Although lower total pressures could be used, maintaining the gas pressurized is advantageous for the Pressure Swing Adsorption (PSA) section. Following reboiling, a portion of the process water is directly injected into the reactor as LP steam to mitigate coke deposition and buffer the exothermic nature of the reaction. The PSA section is simulated with two solid beds switched by a four-step cycle, utilizing Zeolite 13-X as the adsorbent material.
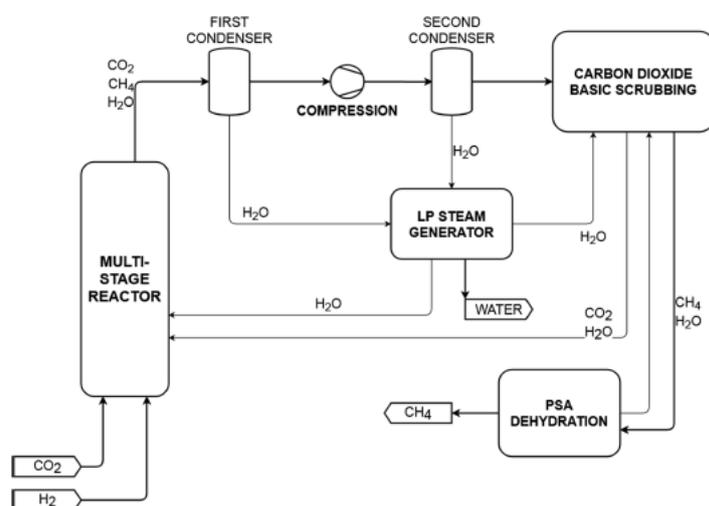
Figure 1. Block scheme of the simulated methanation process

4. Conclusions

Despite the relatively high loading, the catalyst with 36% w/w Ni showed the best performance, proving to be the potential and suitable candidate for this process, posed an effective a priori desulfurization step so as to avoid deactivation of the active phase.
The simulation performed over 10^5 Nm^3/day of synthetic methane showed that to achieve a conversion of more than 75%, at least four stages are required. Adiabatic fixed bed reactors and cooled catalytic beds have been compared, both operated at atmospheric pressure and below 400°C.

References

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