Development of a sorption-enhanced methanation (SEM) process for the production of synthetic natural gas

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Objectives and novelty

The development of a sustainable energy system based on the efficient use of natural resources and a minimal carbon footprint has gained significant attention in recent years. This approach aims to replace fossil-based technologies with renewable material alternatives. In this context, the production of methane or synthetic natural gas (SNG) from renewable resources offers a viable alternative for energy storage while reducing emissions associated with fossil fuels. This thesis investigates the technological feasibility of a Sorption Enhanced Methanation (SEM) process for the production of high quality SNG. In the SEM process, the water produced as a by-product of the methanation reaction is removed from the reaction medium using porous materials such as zeolites, shifting the reaction equilibrium towards CH_4 production ($CO + 3 \cdot H_2 \leftrightarrow CH_4 + H_2O$ and/or $CO_2 + 4 \cdot H_2 \leftrightarrow CH_4 + 2 \cdot H_2O$). When the adsorbent material becomes saturated and unable to adsorb further water, it is regenerated by variations in pressure and/or temperature for cyclic use. This method enables high CH_4 purity under milder temperature and pressure conditions and in a smaller number of stages than conventional methanation, simplifying the process and increasing overall efficiency. These features make the SEM process highly effective for SNG production, which could be stored without restriction in the current natural gas transportation network.

The objective of this thesis was to develop, investigate, optimise and scale up the SEM process using commercial catalysts and zeolites for different applications. Due to its versatility, the work explores the SEM process in two scenarios, investigating different feed gas mixtures: (i) $H_2/CO/CO_2$ mixtures simulating syngas from biomass gasification process, representing a biomass-to-SNG pathway; and (ii) H_2/CO_2 mixtures obtained from renewable H_2 via water electrolysis and CO_2 captured from industrial processes or air, representing an e-SNG production pathway. The SEM process was examined through two distinct technological developments: initial investigations were conducted in a micro fixed-bed reactor at lab scale (2 gr of material) coupled to a mass spectrometer [1], followed by testing in a pressurised TRL-3 fixed-bed reactor (100 gr of material), where the gas was analysed using a micro-chromatograph [2].

Results

Firstly, various catalysts and zeolites, as functional materials, were independently evaluated under relevant conditions for the SEM process to identify those with optimal. Ni, Rh and Ru-based catalysts were evaluated in a fixed bed microreactor at a laboratory scale on methanation activity over a temperature range of 200-300 ºC for CO and CO_2 methanation at different gas space velocities. Ni-based catalyst demonstrated the highest activity achieving 80.1% of CO_2 conversion (X_{CO_2}) and 23.3 %vol. CH_4 purity at 250 ºC with a gas space velocity of 1 $kg_{CO_2}/kg_{cat} \cdot h$. Concerning zeolites, zeolites 3A, 4A, 5A and 13X were texturally and physico-chemically characterised to evaluate their H_2O adsorption performance by thermogravimetric analysis (TGA). All the zeolites showed a higher affinity for H_2O than for CO_2 due to their hydrophilic nature. Zeolite 4A demonstrated the highest H_2O adsorption capacities (0.12 $g_{H_2O}/g_{zeolite}$ at 250 °C), which was attributed to its larger specific surface (S_{BET}) and micropore volume ($V_{micropore}$) [1].

Based on this study, different zeolite/catalyst mixtures were evaluated under SEM conditions in a micro-fixed bed reactor. The SEM process was initially demonstrated using a commercial Rh-based catalyst combined with zeolite 5A in a 1/5 mass ratio (catalyst/zeolite). While the Rh catalyst showed good activity under conventional methanation, its performance improved significantly under SEM conditions for H_2/CO, H_2/CO_2 and $H_2/CO/CO_2$ feed gas mixtures. The best outcomes were obtained for a H_2/CO_2 mixture at 275 ºC and 0.58 $kg_{CO_2}/kg_{cat} \cdot h$. Under these conditions, during the pre-breakthrough period, as the zeolite adsorbed the H_2O produced, complete conversion of H_2 and CO_2 was achieved, producing CH_4 with 100 vol%. purity compared to 22.9 vol%. for conventional methanation. The zeolite adsorbed 0.14 $g_{H_2O}/g_{zeolite}$ during this stage. Once the zeolite was saturated, the gas composition attained in the post-breakthrough period was the same as under pure methanation conditions. In addition, the performance of the SEM was tested using a $H_2/CO_2/CO$ mixture as feed gas, a novel approach in the literature. At 250 ºC and 1.1 $kg_{cx}/kg_{cat} \cdot h \cdot$, the CH_4 content achieved during the pre-breakthrough period was 59.4 vol%, with H_2 being the main product impurity [3].

After demonstrating the potential of the SEM process, the performance of the most extensively studied zeolites in the literature (i.e. 3A, 4A, 5A and 13X) was assessed under SEM conditions using a Rh-based catalyst under CO_2 SEM conditions at 275 ºC and 0.58 $kg_{CO_2}/kg_{cat} \cdot h$. The result showed a

significant improvement in CH4 purity from 8.3 vol%. under conventional methanation to around 70 vol%. under SEM conditions, with XCO2 increasing from 38.4 % to 90.2 %. However, the duration of the pre-breakthrough period varied significantly between the zeolites: 2.8 min, 17.3 min, 6 min and 16.2 min for the zeolites 3A, 4A, 5A and 13X respectively, with 3A and 5A exhibiting the shortest durations. In order to identify the optimum combination, Rh/4A and Rh/13X were tested at 275 ºC and 0.45 kg_{CO_2}/kg_{cat}·h. Under these conditions the Rh/4A combination presented higher X_{CO_2} (94.5 %), CH_4 content (85 %) and H_2O uptake capacity (0.142 $g_{H_2O}/g_{zeolite}$) than the Rh/13X combination. These differences were attributed due to CO_2 adsorption on the zeolite 13X. Finally, long-term stability tests confirmed consistent Rh/4A performance over multiple SEM/ regeneration cycles, with effective regeneration achieved by heating until 400 ºC [1].

In parallel, the reaction mechanisms for three commercial catalysts (Ru, Rh and Ni as active phases) were investigated under conventional methanation and SEM conditions using *in-situ* Fourier Transform Infrared (FTIR) technique. This analysis confirmed the superior catalytic activity of the Ni-based catalyst compared to Rh and Ru catalysts during CO_2 conventional methanation. Based on the detected surface intermediates, a reaction mechanism involving formate and CO as precursors for CH_4 formation was proposed. With Ni identified as the most active catalyst, SEM tests were carried out with Ni/4A and Ni/13X combinations. For Ni/4A, CH_4 and a small proportion of CO_2 were detected in the gas phase at the beginning of the SEM reaction, while H_2O appeared at a later event indicating its initial adsorption on the zeolite. In contrast, for Ni/13X, these phases were indistinguishable due to the chemisorption of CO_2 on zeolite 13X before the reaction started. This CO_2 adsorption on 13X was further confirmed during the regeneration stage by raising the temperature to 400 ºC [4].

Based on the results obtained at the laboratory scale, the combination of zeolite 4A and Ni-based catalyst was identified as the most appropriate for evaluating the performance of the SEM process in a lab-scale TRL-3 fixed bed reactor. A comprehensive optimisation of the different process stages was carried out to maximise CH_4 productivity and purity and the H_2O adsorption capacity of the zeolite under moderate pressure and temperature conditions. Operating at 250 ºC, 10 bar and 1.4 kg_C/kg_{cat}·h with a $H_2/CO/CO_2$ mixture, the process achieved pure CH_4 during 25 min. Different zeolite regeneration methods were evaluated to facilitate cyclic operation, with Pressure Swing Adsorption (PSA) selected as the most suitable and efficient method in terms of energy saving, allowing successive SEM/regeneration cycles to be performed [2]. In addition, a parametric study of the SEM process was carried out using both $H_2/CO/CO_2$ and H_2/CO_2 feed gas mixtures. In both cases, the influence of several process variables was determined, such as the effect of th

e $H_2/CO/CO_2$ and/or H_2/CO_2 ratio, pressure, temperature and the addition of light hydrocarbons such as CH_4 and C_2H_4. Finally, a synthetic syngas was used as a feed gas (including hydrocarbons up to C7). In this scenario, pure CH_4 streams were obtained for 16 minutes at 10 bar, 200°C and a gas space velocity of 1.4 kg_C/kg_{cat}·h [5].

Finally, a comparative study was carried out to evaluate the performance of the SEM process and the conventional methanation process using $H_2/CO/CO_2$ mixtures as feed gas. Both studies were carried out in the same experimental setup, i.e. a TRL-3 scale fixed bed reactor. The results showed that under SEM conditions it was possible to obtain pure CH_4 operating at moderate pressure and temperature conditions. However, in the case of conventional methanation, the maximum CH_4 purity achieved was 78%vol. (dry basis) using a two cascade reactors scheme. Therefore, this work demonstrates the feasibility and versatility of the SEM process to produce high quality SNG under different feed gas scenarios [6].

Conclusions

This thesis demonstrates the potential of the SEM process for CH_4 production by combining zeolites as adsorbent materials with methanation catalysts to remove the H_2O from the gas phase, thereby achieving high CH_4 purities. The study started with a micro-fixed bed reactor and was scaled up to a TRL-3 fixed bed reactor based on the promising results obtained. Different catalysts (Rh-, Ru- and Ni-based) and zeolites (3A, 4A, 5A and 13X) were evaluated, demonstrating the flexibility of the process under different feed gas scenarios. The research focused mainly on two feed gas compositions: $H_2/CO/CO_2$ mixtures from sorption enhanced gasification and H_2/CO_2 mixtures where H_2 is produced from water electrolysis and CO_2 is sourced from industrial processes or direct air capture. By operating all stages at a uniform temperature, the SEM process reduces the need for high temperatures to enhance catalytic activity and low temperatures for H_2O condensation, offering significant reductions in both investment and operating costs. In conclusion, this work highlights the versatility and economic advantages of the SEM process for SNG production from diverse feed gas scenarios.

Related Publications

[1] Gomez L, Martínez I, Navarro MV, Murillo R. Selection and optimisation of a zeolite / catalyst mixture for sorption-enhanced CO_2 methanation (SEM) process. J CO_2 Util 2023;77.

[2] Gómez L, Martínez I, Grasa G, Murillo R. Experimental demonstration of a sorption-enhanced methanation (SEM) cyclic process on a lab-scale TRL-3 fixed bed reactor. Chem Eng J 2024;491.

[3] Gómez L, Martínez I, Navarro M V., García T, Murillo R. Sorption-enhanced CO and CO_2 methanation (SEM) for the production of high purity methane. Chem Eng J

[4] Goméz L, Nguyen-Quang M, Azzolina-Jury F, Martínez I, Murillo R. In-situ FTIR analysis on conventional and sorption-enhanced methanation (SEM) processes over Ni, Rh, and Ru-based catalyst systems. Appl Catal A Gen 2024;678.

[5] Laura G, Mart I, Grasa G. Different Feed Mixtures for the Sorption-Enhanced Methanation (SEM) Process on a Lab-Scale TRL - 3 Fixed-Bed Reactor. Energy and Fuels 2024.

[6] Gómez L, Grasa G, Martínez I, Murillo R. Performance study of a methanation process for a syngas obtained from a Sorption Enhanced Gasification process. Chem Eng Sci 2022;267:118291.

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