Enhancing methanol synthesis by continuous in-situ adsorption of reaction products

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Highlights

- Enhancing methanol conversion through selective in-situ removal of products.
- Continuous sorbent entrainment from bubbling fluidized bed of catalyst pellets.
- Water adsorption capacity trends are crucial for validating the Langmuir model.
- Cold flow setup demonstrates the feasibility of the new reactor concept.

1. Introduction

Decentralized methanol synthesis offers a valuable means to convert carbonaceous waste, biomass, and hydrogen into a versatile liquid energy carrier, enabling storage, transport, and use within the chemical industry. Traditionally, state-of-the-art methanol reactors use fixed-bed configurations with copper/zinc oxide/alumina (CZA) catalysts operating at temperatures around 250°C and pressures ranging from 50 bar to >100 bar [1]. The reason is equilibrium limitation resulting in low per-pass conversion, mainly when CO_2 is used as the feed, with high recycling rates of unreacted species. High-pressure equipment and associated compression costs further hinder economic viability on a small scale [2]. To tackle these challenges, in-situ removal of reaction products has been explored, either via membrane integration [3] or by introducing sorbents with batch-wise regeneration [4] in fixed-bed reactors.

An alternative approach presented here involves continuously adding and removing sorbents, avoiding the issues associated with sealing and material stability in membrane reactors. This method allows for smaller reactors than fixed-bed configurations with sorbents, ensuring continuous operation with the regeneration of spent sorbent in a separate vessel. The continuous sorbent circulation requires vertical entrainment of particles through the catalyst bed, maintained in a bubbling fluidization state by selecting sufficiently larger catalyst particles. This presentation compares the potential of this reactor concept with fixed-bed sorption-enhanced (SE) methanol synthesis from CO_2.

2. Methods

The feasibility of this new reactor concept, displayed in Figure 1, is being experimentally investigated on a TRL 2-3 at a low constant pressure of 3 bar and temperature ranging from 200 to 300°C (hot flow setup). So far, a commercial CZA catalyst and three zeolites specifically chosen for water and methanol adsorption have been characterized in a fixed-bed reactor of 21 mL volume with varying temperature, feed gas composition, and space velocity. A mass spectrometer and in-reactor thermocouples enabled real-time gas composition and temperature monitoring. The following experiments with a 1:1 sorbent-to-catalyst ratio explore operation constraints of an SE fixed-bed methanol reactor to validate the model for adsorption used in simulations. In parallel, a fluidized-entrained flow system was studied with a cold-flow setup involving a transparent test section (in Figure 1) filled with dense black sand particles (mimicking the CZA catalyst) and lighter, smaller γ-alumina particles (mimicking the sorbent).

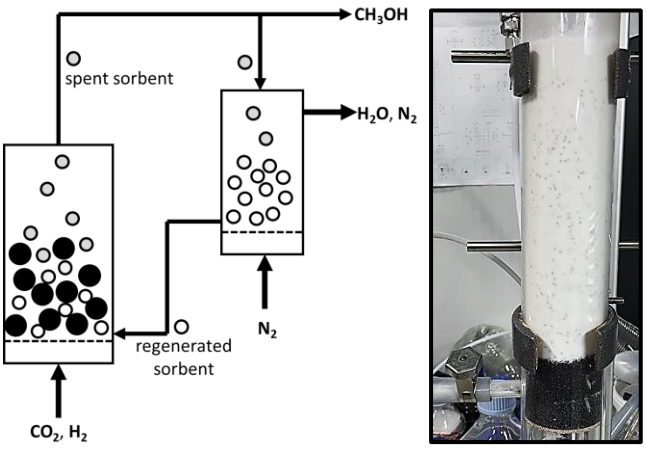

Figure 1 Reactor concept (left) and cold flow setup (right).

3. Results and discussion

The cold-flow setup proved the feasibility of maintaining one type of particle in the bubbling fluidization state while the second particle type was entrained in and out of the test section, with uninterrupted operation for several hours. The sufficiently large difference in fluidization velocity of the two-particle types and thorough control of pressure drop within the stand-pipe in the return leg compared to the pressure drop over the inlet duct to the reactor was crucial.

The water adsorption capacity results obtained from breakthrough experiments on molecular sieves 3A, 4A, and sodium mordenite comply with previous studies. Specifically, their water uptake was always lower than 10 weight-% and showed a significant decrease for reactor temperatures higher than 250°C. No significant change of capacity upon increasing gas space velocities was observed, but a non-linear increase with water partial pressure. This latter effect is represented by the saturation curve of molecular sieve 3A in Figure 2, highlighting no further increase of water adsorption capacity above 40% of water content. This trend will be used for the validation of a Langmuir water adsorption model integrated with a kinetic model for methanol synthesis.

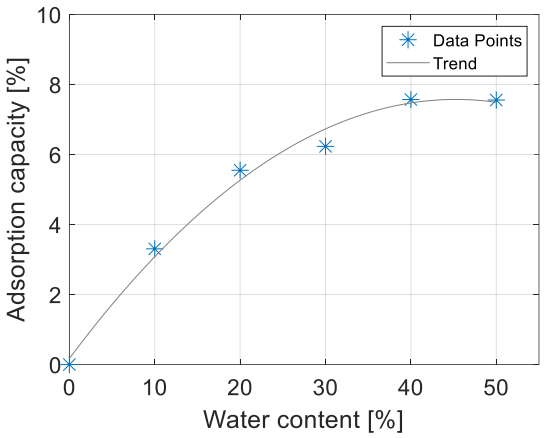

Figure 2 Adsorption capacity of 3A vs water content.

In methanol synthesis experiments conducted without sorbents, the CO_2 conversion to methanol reached around 4% at 3 bar and reactor temperature of 250°C, accompanied by CO formation. Reducing the reactor temperature to 200°C enhanced CO_2 conversion with lower CO production. Based on the results achieved so far, combining methanol synthesis with continuous sorbent transport anticipates improved methanol conversion in future experiments. The measured adsorption selectivity of the sorbents allows for process optimization concerning CO production (in scenarios where only water is removed) or anticipating upgrading units (when methanol is co-adsorbed, leading to an additional enhancement of the methanol synthesis reaction).

4. Conclusions

The use of entrained-bubbling fluidized beds with two different particle types, here CZA catalyst and sorbents, combines the advantages of sorption enhancement, overcoming the equilibrium limitation in methanol synthesis, and improved temperature control in smaller reactor volumes. Further to improving methanol yield, this can be achieved with continuous, thus facilitated, operation. Offering promising insights on sustainable energy carriers, the presentation will showcase experimental results of SE methanol synthesis, which open the door to upscale the reactor to TRL 4, supported by reactor modeling.

References

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Keywords

Sustainable energy carriers; sorption-enhancement (SE); methanol synthesis; bubbling fluidized-bed reactors.