Experimental insights on the scaling of single pellet string reactors based on the CO_2 methanation

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Highlights

- Experimental approaches for demonstrating heat and mass transfer limitations.
- Introduction of different methods to compare various reactor configurations.
- Assessment of single pellet string lengths on reactor performance.

1. Introduction

The single pellet string reactor (SPSR) has garnered increased attention for testing new catalysts in a scaled-down version of a fixed-bed reactor under the same operating conditions as employed in the industrial process. As the space velocity is typically maintained at a constant level, resulting in lower velocities in the small-sized reactor, mass transfer rate becomes the limiting step compared to the reaction rate, particularly for fast exothermic reactions such as the CO_2 methanation. The SPSR as a new reactor geometry was developed to intensify heat and mass transport. This reactor has a diameter that closely matches the one of the catalyst particles, featuring a high length-to-diameter ratio. The main goal of this study is to examine the scalability of different single pellet string lengths and to evaluate their comparability with a small fixed-bed or a powder-bed reactor. The highly exothermic CO_2 methanation served as a model reaction with Ni-based catalysts used for activity measurements. The findings from the experimental investigations are extended by simulative studies based on a multi-region model using computational fluid dynamics (CFD).

2. Experimental and methodology

Spherical catalyst pellets (d = 3.6 mm) were prepared by impregnating Al_2O_3 pellets with a nickel-nitrate solution, resulting in a nickel loading of 20 wt.-%. The catalysts were calcined, activated, and the catalytic activity was determined in a single-pass setup equipped with a gas chromatograph as described elsewhere [1]. The setup was extended with an infrared thermal imaging camera to examine heat development and hotspot formation within the catalyst bed. For all reactions, a stoichiometric feed gas ratio of H_2/CO_2 = 4/1 was used. Different reactor configurations (6 and 12 pellets in a SPSR, a 20-pellet and a powder fixed-bed) were investigated under different conditions: (I) constant gas hourly space velocity (*GHSV)* and (II) constant total volume flow. The experimental results contributed on setting up a detailed multi-region CFD model, which considers heat and mass transport within the pellets and CO_2 methanation reaction kinetics.

3. Results and discussion

Activity measurements of SiC-diluted Ni/Al_2O_3 powder fixed-beds revealed no indication of heat and mass transport limitations. Therefore, these measurements can be seen as a reference for ideal plug flow conversion. The most common way of comparing different reactor configurations is keeping the *GHSV* constant over all measurements, as shown in Fig. 1A. The CO_2 conversion curves indicate that increasing the length of the SPS leads to a more pronounced plug flow conversion, aligning with the findings proposed by Fernengel et al. [1]. However, operating under constant *GHSV* leads to higher total volume flows when increasing the SPS lengths. Owing to a rapid reaction rate, the catalyst efficiently transforms incoming reactants, even with a shorter residence time in the reactor, leading to an elevation in reactor temperature. Especially in the case of highly exothermic reactions, elevated volume flows consequently

result in noticeable hotspots, as observed through thermal imaging, along with significant CO formation. In the 20-pellet fixed bed, the emergence of hotspots coupled with inefficient heat dissipation shifts the CO_2 conversion curve towards lower temperatures. Hence, comparing different reactor types at constant *GHSV* suffers from the drastic change in volume flow over all measurements. To circumvent this issue, a new method is developed: the total volume flow is kept constant while adapting the mass flow of CO_2 and H_2 to the respective catalyst volume. To achieve this, the feed gas is diluted with varying amounts of argon. As the partial pressures of the reactive gases are now affected and inconsistent over the measurements, the overall pressure in the reactor is adjusted maintaining the partial pressures of the reactive gases in order to exclude effects originating from the thermodynamics of the reaction. The results are depicted in Fig. 1B. At the chosen conditions, no hotspots were formed allowing for an improved comparability of the analyzed reactor configurations. We aim to demonstrate methods for comparing different reactor configurations, recognizing that the most effective approach is highly contingent on the specific reaction and chosen reaction conditions.

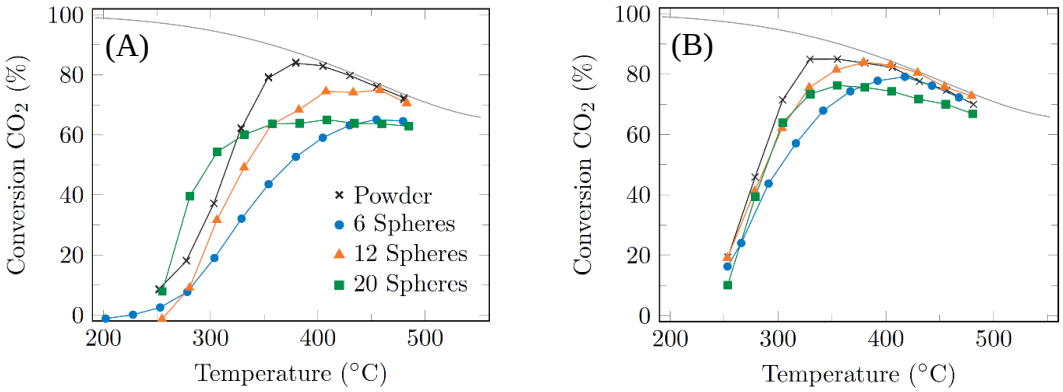

Figure 1. Comparison of the CO_2 conversion of a powder catalyst, a 6- and a 12-sphere long single pellet string and a 20-pellet fixed-bed at (A) *GHSV* = $1.1 \cdot 10^5$ 1/h and (B) $\dot{V}_{\text{total}} = 86$ sccm.

4. Conclusions

In conclusion, SiC-diluted Ni/Al_2O_3 powder fixed-beds exhibit no heat and mass transport limitations, serving as a reference for ideal plug flow conversion. The practice of maintaining a constant *GHSV* for comparing different reactor configurations, while prevalent, introduces challenges in the face of highly exothermic reactions. This is evident in the emergence of hotspots and significant CO formation with increasing total volume flows. To address this issue, a novel method is introduced, wherein the total volume flow is kept constant, and the mass flow of CO_2 and H_2 is adjusted by diluting the feed gas with varying amounts of inert gas. This approach minimizes the effect the heat development has on the catalytic activity and therefore enhances comparability among different reactor types. However, the most effective method for comparing reactor configurations remains context-dependent, considering the specific reaction and chosen conditions.

References

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Keywords
Single pellet string reactor, CO_2 methanation, heat and mass transfer limitations