Modeling of Fischer-Tropsch fixed-bed reactors: A comparison between pseudo-homogeneous and heterogeneous approaches

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Highlights

- Pseudo-homogeneous and heterogeneous models showed minor concentration profile differences. Smaller particles yielded a higher conversion;
- The heterogeneous model was more sensitive to temperature changes, showing central hotspots in smaller particles due to higher energy release and conversion rates;
- C5+ hydrocarbon selectivity varied, especially in smaller particles, due to temperature fluctuations influencing chain growth probability;

1. Introduction

The Fischer-Tropsch synthesis focuses on producing hydrocarbons and chemicals from organic byproducts or synthesis gas. Companies like Sasol and Shell have implemented this process industrially using fixed-bed reactors, known for their scalability and economic viability [1,2]. The reaction, however, is complex due to its multiple mechanisms and high exothermicity, which requires tools such as detailed mathematical models for achieving optimal operation [3]. These models, either pseudo-homogeneous or heterogeneous, differ in their assumptions, by considering or not the gradients between the fluid and solid phases. Furthermore, recent literature reviews highlight different modeling approaches, but also show that there is a lack of comparative studies between these [2]. This study aims to bridge this gap by examining differences regarding both types of models through a sensitivity analysis focusing on the effect of catalyst size on concentration profile, thermal stability, CO conversion, selectivity towards heavier hydrocarbons, and bed pressure drop.

2. Methods

In the present study, the model proposed for a Fischer-Tropsch fixed-bed catalytic reactor, consisted of a 2-D axisymmetric tubular configuration. The assumptions used for the model were: 1. Stationary regime; 2. Solid-gas model; 3. The tube wall is maintained at constant temperature due to the fast flow of saturated water in the coolant side; 4. Formation of alcohols or aromatics was neglected; 5. Constant reaction enthalpy, bed porosity and radial diffusion coefficient; 6. Formation of paraffins and olefins was considered up to a chain length of 20 carbons; 7. Water-gas shift reaction, coal deposition at catalyst surface and catalyst deactivation were not considered; 8. Catalyst pores are assumed to be filled with liquid products [4]; 9. Intraparticle diffusion effects are assumed to be well represented by the adoption of an effectiveness factor [2]. Within these hypothesis, mass and energy balances as well as the Ergun pressure drop correlation were implemented in Aspen Custom Modeler® v12 interface, giving rise to a system of partial differential algebraic equations. The system was solved using the method of lines, employing the central finite differentiation technique to discretize the radial direction and Implicit Euler as the integration method for the axial direction. Once a stable solution was reached, a sensitivity analysis considering particle sizes from 3 mm to 5 mm could be performed in order to compare the obtained results for both models.

3. Results and discussion

The results revealed minor differences in concentration and axial pressure profiles across the models. However, the heterogeneous model shows a higher sensitivity to temperature variations, particularly in smaller catalyst particles, leading to the formation of central hotspots and negatively affecting C_{5+} hydrocarbon selectivity due to the tendency of the process to produce lighter hydrocarbons. Also, these pronounced temperature fluctuations, especially in 3 mm particles, impacted syngas conversion and energy release, since the temperature increase due to the higher reaction rate in a smaller particle also tend to increase the system's conversion. While both models produce similar outcomes under stable

temperature conditions, the heterogeneous approach showed to be more suited to scenarios with greater temperature variation, emphasizing the importance of selecting an appropriate model based on the specific characteristics of the system under study.

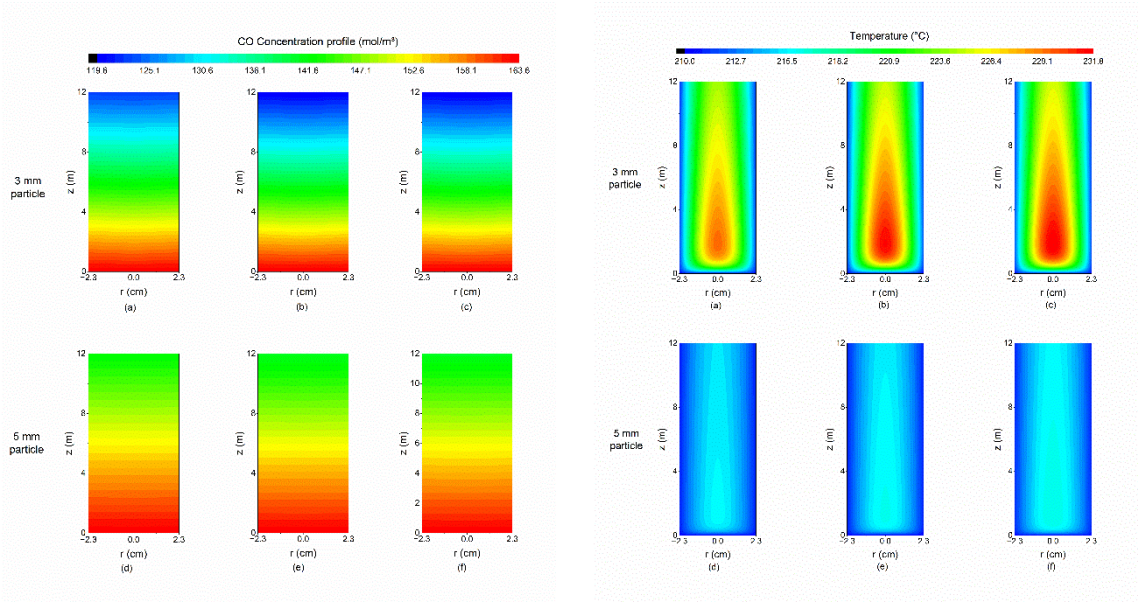

Figure 1. Concentration (left) and Temperature profile (right) for the 3 mm and 5 mm particles. Subscripts (a) and (d) refer to the results of the pseudohomogeneous model, while (b) and (e) refer to the profile in the bulk fluid for the heterogeneous model and (c) and (f) to the profile at the solid surface for the heterogeneous model.

4. Conclusions

The comparative study between pseudo-homogeneous and heterogeneous models revealed distinct sensitivities and advantages. The heterogeneous model displayed higher sensitivity to temperature fluctuations, resulting in slightly elevated temperatures within the reactor compared to the pseudo-homogeneous model when temperature rise was more prominent. As a general matter, an increase in catalyst size, although responsible for decreasing pressure drop and increasing the temperature stability, also proved to dimmish carbon monoxide conversion. Ultimately, these findings underscore the nuanced trade-offs between different modeling approaches, highlighting the potential benefits associated with different catalyst sizes.

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Keywords

Fischer-Tropsch; Fixed-bed; Mathematical Modeling; Biofuels.