Catalytic Structures for CO_2 Conversion to Methanol using Structure-Resolved CFD Simulations

Kuldeep Singh[1], Ankita Kumari[1], Olaf Hinrichsen[2] and Vivek V. Buwa[1]*

1 Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, 110016, India
2 Institute of Chemical Technology I, Department of Chemistry, Technical University of Munich, 85748 Garching, Germany
**Corresponding author: vvbuwa@iitd.ac.in*

Highlights

- Effect of catalytic structure on heat transfer and reaction performance for methanol synthesis
- Comparison of reaction performance of simple monolithic vs. complex catalytic structures
- Effect of reactant concentration and operating conditions on methanol conversion

1. Introduction

In recent times, considerable research efforts have been directed towards the capture and conversion of CO_2 into lower hydrocarbons (e.g. CH_4, CH_3OH, etc.), which can be used as secondary energy sources. Among the established methods for carbon utilization, the conversion of CO_2 into methanol has gained widespread importance. Typically, the synthesis of methanol from CO_2 is carried out in packed bed reactors operating under high-pressure and low-temperature conditions. However, the reaction performance of these packed beds is significantly influenced by the heat and mass transfer limitations. In recent years, monolithic structures have emerged as a promising alternative to conventional catalytic pellets (such as spheres, cylinders, trilobes, etc), as they offer higher surface area to volume ratio, lower pressure drop, and improved heat and mass transfer characteristics [1]. Therefore, the focus of this work is to overcome the heat and mass transfer limitations associated with pellets by introducing complex catalytic structured beds for CO_2 conversion to methanol. In view of this, the objectives of the present work are (a) to investigate the reaction performance of complex catalytic structures for CO_2 conversion to methanol, and (b) to investigate the effect of reactant concentration and operating conditions on CO_2 conversion using structure-resolved CFD simulations.

2. Methodology

To evaluate the reaction performance of different catalytic structures, a rectangular computational domain with a square (48x48 mm^2) cross-section consisting of structured packing (simple hexagonal opening, TPMS-based strut, sheet, and gyroid structures with equal solid volume) is considered in the present work [as shown in Figure 1 (a)]. The computational domain is meshed using polyhedral elements which consist of ~15-40 million elements. The Reynolds-averaged continuity, momentum (Navier-Stokes equation), energy, and species transport equations are solved to simulate flow, heat, and species transfer, respectively using commercial solver Ansys Fluent v2021 R1. CO_2, CO, H_2, CH_3OH, and H_2O are modeled as the reactant and product species in the gas phase, Alumina was considered as the solid material. The simulations are performed at a tube Reynolds number of 50,000. The SST k-ω turbulence model is used to simulate the turbulent flow. All simulations are performed using a high-performance computing facility of IIT Delhi with 160-240 cores in parallel. Further details of geometry, computational domain, and models will be provided in the full manuscript.

3. Results and discussion

Preliminary flow and heat transfer simulations (without reactions) are performed to understand the velocity, pressure, and temperature distribution without any reactions in beds packed with structures of hexagonal, primitive strut, primitive sheet, and gyroid structures. In these simulations, air was used as the working fluid. A constant wall heat flux was applied to the tube wall and a volumetric heat sink (equivalent to the heat supplied from the wall in Watts) was applied in the solid domain to mimic endothermic reaction conditions. The simulations were performed at a pressure of 21 bar and ~824 K. A typical velocity distribution in the catalytic structures at a cross-section plane 10 mm before the bed outlet is shown in Figure 1 (i). The strut and sheet structures showed relatively higher velocity regions compared to gyroid and hexagonal shapes. Specifically, the sheet, strut, and gyroid structures offered enhanced intermixing of fluid elements due to their specific structural features, whereas hexagonal structure prohibits fluid mixing due to the presence of straight channels. This results in a higher pressure drop (ΔP) of 2586, 3384, and 3154 Pa for the strut, sheet, and gyroid structures, respectively, compared to ΔP of 169 Pa for the hexagonal shape.

Further, a qualitative comparison of temperature distribution in catalytic structures on a cross-section plane 10 mm before bed outlet is shown in Figure 1 (ii). The enhanced mixing capabilities of the strut, sheet, and gyroid structures resulted in a relatively uniform temperature distribution. Whereas, the hexagonal structure exhibited significant temperature gradients between the solid and fluid domains due to its limited mixing characteristics. A comprehensive analysis of the velocity, pressure, and temperature distribution will be presented in the full-length manuscript.

Further, study was conducted to investigate the reaction performance of these aforementioned catalytic structures for CO_2 conversion to methanol. In these simulations, the solid-particle model is incorporated to perform reactions in the solid domain. The species transport in the solid domain is modeled through the UDS transport equation, and the multicomponent actual diffusivities, reaction mass, and energy source terms are incorporated through UDFs. The

kinetic model developed by Graaf et al. [2] for methanol synthesis is considered in the present work. The walls are considered adiabatic, and the reactor is operated at a pressure of 50 bar and an inlet temperature of 523 K. The velocity distribution is relatively comparable for hexagonal and primitive strut structures, however, significant differences in ΔP are found. The pressure drop for the hexagonal and primitive strut structures is 43 and 809 Pa, respectively, owing to their shape features.

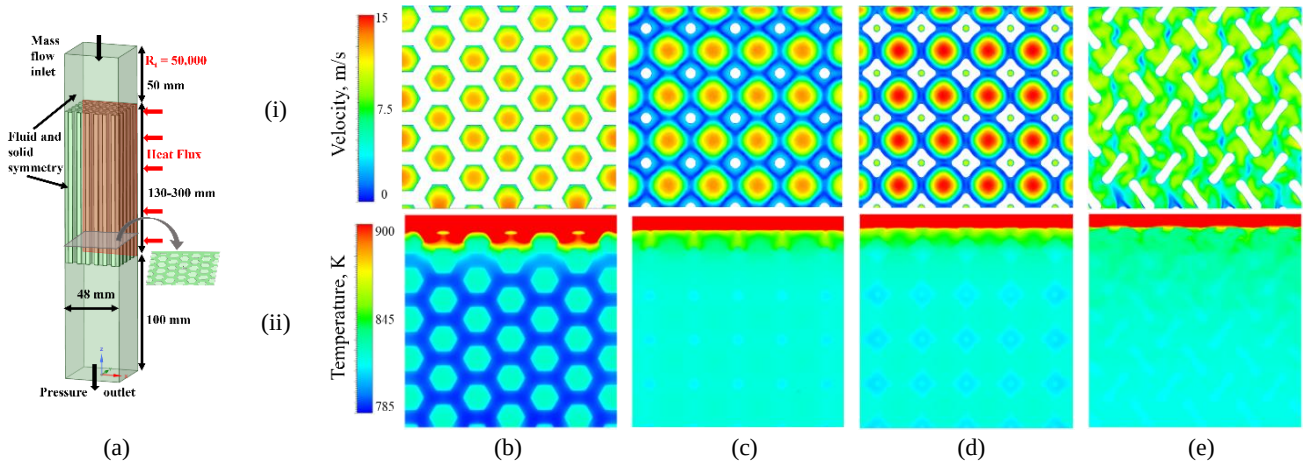

Figure 1. (a) Computational domain with boundary conditions and effect of catalytic structures on (i) velocity and (ii) temperature distribution for (b) hexagonal, (c) primitive strut, (d) primitive sheet, and (e) gyroid structures, respectively.

In addition, the temperature and concentration distribution resulting from reaction simulations for these structures are shown in Figure 2. A qualitative analysis shows that primitive strut exhibits lower temperature and methanol concentrations compared to the hexagonal structure. Further, quantitative comparison of the area-averaged surface temperature $< T_s >$ and volume-averaged temperature $< T_v >$ indicated that the hexagon and primitive strut have $< T_s >$ values of 528.6 K and 525.4 K, and $< T_v >$ values of 529.2 K, and 526.3 K, respectively. This marginal increase in temperature results from the slightly higher conversion of CO_2 in the hexagonal structure (0.22 %) compared to the primitive strut (0.19 %). From the preliminary results, it can be inferred that complex structures such as primitive strut show enhanced performance in severe endothermic conditions. However, at moderate reaction conditions such as the CO_2 conversion to methanol, the performance of hexagon and primitive strut is relatively comparable. These combined results indicate that the reaction performance of catalytic structures is significantly influenced by the reaction types and operating conditions. Therefore, it is important to optimize the design of catalytic structures depending on the given reaction conditions (kinetics and operating conditions). A detailed discussion of reaction performance for different catalytic structures will be presented in the full-length manuscript.

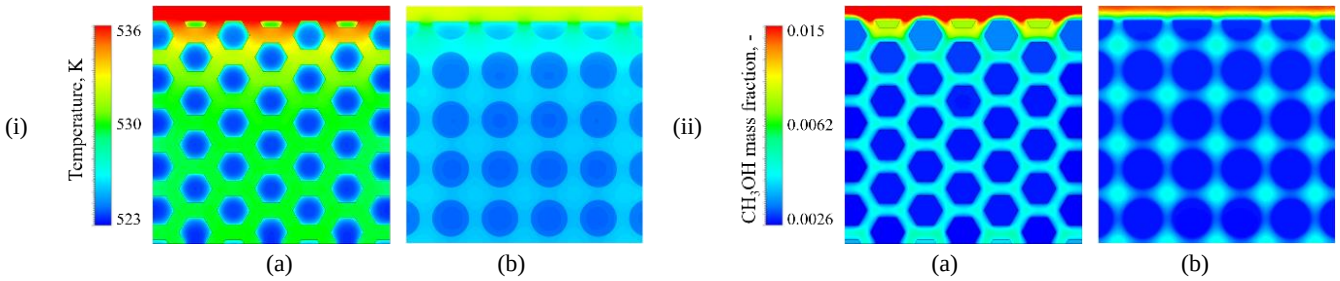

Figure 2. Effect of catalytic structures on (i) temperature and (ii) concentration distribution for (a) hexagonal, and (b) primitive strut structure for CO_2 conversion to methanol.

4. Conclusions

In the present work, structure-resolved simulations are performed to investigate the flow, heat, and mass transfer performance of catalytic structures. The preliminary (endothermic conditions) study suggests that the performance of complex catalytic structures is better compared to hexagonal structures in terms of velocity and temperature distribution. However, incorporating methanol synthesis reaction (mild exothermic conditions), the performance of both the hexagon and primitive strut shows comparable temperature and concentration distribution. These findings highlight the necessity of considering specific reaction conditions and their influence on the overall performance of catalytic structures.

References

[1] K. Gopal Manoharan and V. V. Buwa, "Structure-Resolved CFD Simulations of Different Catalytic Structures in a Packed Bed," *Ind. Eng. Chem. Res.*, vol. 58, no. 49, pp. 22363–22375, 2019, doi: 10.1021/acs.iecr.9b03537.

[2] G. H. Graaf, H. Scholtens, E. J. Stamhuis, and A. A. C. M. Beenackers, "Intra-particle diffusion limitations in low-pressure methanol synthesis," *Chem. Eng. Sci.*, vol. 45, no. 4, pp. 773–783, 1990, doi: 10.1016/0009-2509(90)85001-T.

Keywords: CFD, Catalytic Structures, Reaction Simulation, Heat Transfer