Enabling small-scale methanol synthesis reactors through the adoption of highly conductive structured catalysts

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Introduction

The low T-low P MeOH synthesis is a mature and well-developed process and many large industrial plants are in operation. Due both to thermodynamic equilibrium and to the high exothermicity, CO conversion per pass in commercial multi-tubular packed-bed (PB) reactors is limited to 60-80% [1] and high syngas stoichiometric numbers \( M_f \) must be used to boost the CO conversion per pass and to obtain high gas thermal conductivity. Industrially, large recycles of unconverted gas are necessary to ensure high overall syngas conversions in commercial plants. This inevitably results in high operating costs and large pressure drop.

PB reactors suffer from poor radial heat transfer across the reactor tubes. Heat conduction in the packed-bed is in fact practically negligible, since only point contacts exist between catalyst pellets. So, obeying to a convective mechanism, high mass flow rate must be employed to grant acceptable radial heat transfer rates and avoid marked hot-spots (\( T < 300^\circ C \) to prevent catalyst sintering). This typically involves the adoption of long (i.e. several meters) reactor tubes and rules out the possibility of developing compact configurations.

Thanks to low pressure drop, negligible intraporous diffusion limitations and efficient heat removal (i.e. effective conduction within the metallic matrix of the structured support), highly conductive structured catalysts are promising for the intensification of several catalytic processes, especially for those involving highly exo-/endothermic gas/solid reactions in which large T-grads should be avoided to control selectivity and/or catalyst deactivation [2] [3].

We herein assess the potential of highly conductive structured reactors (SR) for the methanol synthesis by detailed mathematical modeling of metallic honeycomb monolith (HM) and open-cell foam (OF) reactors, and we discuss their performances in comparison to the behaviour of a commercial PB reactor.

Materials and Methods

For each externally-cooled multi-tubular reactor configuration we have developed a 2-D steady-state heterogeneous pseudo-continuous model, describing concentration and temperature gradients along axial and radial coordinates of one representative tube. The model includes also the mathematical description of the intraporous concentration profiles according to isothermal-isobaric intraporous reaction-diffusion model. Kinetics published by Graaf et al. [4] has been implemented. For SR, we have considered the same high catalyst load and reactor geometry of PB. Copper has been selected as substrate material due to its very high intrinsic thermal conductivity. Each reactor model has been then included in a simplified process loop model assuming i) an ideal condenser separating all water and methanol in the reactor effluents from the rest, ii) a constant fresh feed flow to catalyst volume ratio and iii) variable recycle and purge ratios. Mathematical models have been implemented in gPROMS® commercial software.

Results and Discussion

After validating the full scale (FS) PB reactor model against industrial data, we have investigated the reactors behaviour upon changing: i) the fresh syngas composition (i.e. the stoichiometric number \( M_f = (H_2-CO_2)/(CO+CO_2) \) at constant CO/CO₂ molar ratio and inert content, and ii) the bed length (i.e. FS/4 and FS/8) at constant fresh feed flow to catalyst volume ratio.

Our analysis points out that PB reactors outperform SR when long (FS) tubes are adopted due to the high mass flow rate, which results in high overall heat transfer coefficients \( U \) (Fig. 1a).

![Figure 1. a) Overall heat transfer coefficient U as a function of M_f for FS and FS/4 reactors and b) solid axial temperature profiles at center line (M_f=2.109) for FS/4 reactors.](image)

Conversely, being associated with a conductive heat transfer mechanism, compact (FS/4) SR performances remain unaffected by the mass flow rate and thus grant higher \( U \) than PB reactors, where convection is the dominating mechanism (Fig. 1a). This enables more limited hot-spot temperatures (Fig. 1b) and lower recycle ratios (3.1 for SR Vs. 3.7 for PB reactor).

Significance

The present study shows that compact SR reactors grant enhanced heat transfer performances over PB reactors. This opens new scenarios for the development of small-scale methanol synthesis processes, particularly appealing for the exploitation of feedstocks available in limited amounts, like e.g. syngas from biomass or stranded/associated NG reservoirs.

References