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Optimization of compact multitubular fixed-bed reactors for the methanol synthesis loaded with highly conductive structured catalysts

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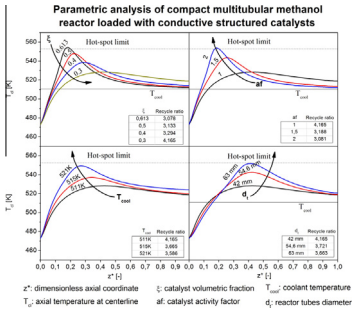
HIGHLIGHTS

- Optimization of compact conductive structured reactors for the methanol synthesis.
- Washcoated honeycomb monolith and open-cell foam based reactors were simulated.
- The synthesis loop model was considered to take into account the effect of recycle.
- Catalysts with enhanced activity and reactors with larger tubes were simulated.
- Compact reactors are promising for small-scale GTL (Gas-To-Liquid) processes.

GRAPHICAL ABSTRACT



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ABSTRACT

By computer simulation, we analyze the performances of a compact (2 meter-long) externally-cooled multitubular reactor for the methanol synthesis loaded with highly conductive structured catalysts, namely washcoated copper honeycomb monoliths and copper open-cell foams. Such a reactor is simulated as inserted in a synthesis loop including an ideal condenser, a recycle and a purge stream.

Parametric analysis of the catalyst volumetric fraction points out that compact methanol structured reactors can be operated even with loadings as low as 0.30 m^3 catalyst/m^3 tube, but they would grant lower CO_x conversions per pass, resulting in higher recycle ratios. The excellent radial heat transfer performances of the structured reactors enable however the catalyst intrinsic activity and/or the coolant temperature to be properly optimized to compensate for the lower catalyst loads, eventually granting lower recycle ratios (i.e. keeping CO_x conversion per pass close to the equilibrium value) as well as limited hot-spot temperatures.

Furthermore, reactor tubes with larger diameters can be adopted in compact conductive structured reactors loaded with limited catalyst volumetric fractions, thus allowing for reduction of investment costs. In particular, we show that, thanks also to the efficient radial heat transfer, the greater thermal loads generated in the configurations with larger tubes can be effectively managed to enhance the reactor performances.

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Notation

af	multiplying activity factor [-]
CPSI	honeycomb monolith cell density [cells/in^2]
$(CO/CO_2)_F$	CO/CO_2 molar ratio in fresh feed [-]
d_t	internal reactor tube diameter [m]
F	fresh feed molar flow rate to the reactor [mol/s]
h_w	wall heat transfer coefficient [W/m^2/K]
L	reactor length [m]
M_F	stoichiometric number in fresh feed [-]
n_{tubes}	number of reactor tubes [-]
PD	foam pore density, espressed in PPI [i.e. pores/in]
P	pressure [Pa]
r	reactor radial coordinate [m]
T	temperature [K]
T_{cool}	coolant temperature [K]
U	1-D length-averaged overall heat transfer coefficient [W/m^2/K]
x_{inerts}	inerts molar fraction at reactor inlet [-]
z	reactor axial coordinate [m]

Greek symbols

ε	bare substrate void fraction [m^3 void/m^3 substrate]
δ_w	washcoat thickness [μm]
λ_{ea}	axial effective thermal conductivity [W/m/K]
λ_{er}	radial effective thermal conductivity [W/m/K]
ξ	catalyst volumetric fraction [m^3 catalyst/m^3 tube]

Superscripts

0	reactor inlet
$*$	dimensionless variable
out	reactor outlet

Subscripts

cl	centerline ($r = 0$)
g	referred to the gas phase

1. Introduction

Methanol is presently one of the top five chemical commodities by volume shipped around the world per year: it is the starting material for the production of a variety of oxygenated chemicals (e.g. formaldehyde, methyl *tert*-butyl ether) and hydrocarbons (e.g. ethene, propene through the so-called Methanol-To-Olefins processes) or a substitute for traditional oil-based fuels for internal combustion engines (ICEs) [1,2].

The modern low temperature-low pressure methanol synthesis is industrially carried out in externally-cooled fixed bed multitubular reactors, from 8 to 12 meter-long, using $H_2/CO/CO_2$ mixtures and $Cu/ZnO/Al_2O_3$ pelletized catalysts [2]. Due to the thermodynamic constraint, CO_x conversions per pass are limited, therefore requiring a large recycle of unconverted gas to ensure high overall syngas conversions [3]. This inevitably results in high investment and operating costs and large pressure drop [4].

In both reactor configurations, the accurate control of the temperature profile in the catalytic bed is a priority, in view of maximizing the syngas conversion per pass and the catalyst lifetime (i.e. minimizing the number of shut-downs per unit time) as well as minimizing the selectivity towards byproducts like dimethyl ether and methyl formate [5,6].

Methanol technology is currently of interest for two completely diverging applications. One is the design and commercialization of larger plants to decrease operating costs according to the economy of scale (see Lurgi's MegaMethanol concept as an example [7]). Externally-cooled multitubular packed-bed (PB) reactors with long reactor tubes are used in this case due to their intrinsic modularity and their effective convective heat transfer mechanism boosted by the high gas flow rates. The opposite application strategy is designed for the exploitation of underutilized and therefore low-cost small gas reservoirs in remote areas, but also of other feedstocks available in limited amounts only, like syngas produced from biomass. In this case, smaller reactor capacities are required. The scale-down of the PB reactor technology, however, cannot result in reactor designs with short tubes, as this would reduce the flow velocity and therefore cause a significant drop in the heat transfer performances of such reactors. There is accordingly a serious limit to the possibility of developing compact configurations of multitubular PB reactors for the methanol synthesis [8].

Thanks to their high thermal efficiency, modularity and reduced sensitivity to flow conditions, microchannel reactors are reported to be promising for converting biomass or stranded/associated gas into methanol. In this respect, Tonkovic et al. [9,10] have proposed an innovative compact modular reactor for the methanol synthesis based on the microchannel technology. In the same field, it is worth mentioning the Printed Circuit Heat Exchanger (PCHE) concept as well, developed and commercialized by Heatric, which finds specific application in the case of highly exothermic catalytic processes [11]. In the academia, Bakhtiary-Davijany et al. [12] and Phan et al. [13] carried out experimental investigations of novel microstructured methanol reactors pointing out their superior heat transfer properties, particularly appealing for the design of small-scale methanol synthesis processes. Nevertheless, microchannel technology is still in an early development stage and technical issues related to the operational complexity can be enumerated, such as managing a number of reactors to handle large overall capacities [14], the high sensitivity to flow distribution, the scarce expertise in operating and maintaining such reactors and the difficulty in loading/unloading the catalytic bed.

Structured catalysts usually consist in a thin catalyst layer (some tens of microns) deposited on a structured substrate, e.g. a honeycomb monolith (HM) or an open-cell foam (OF), with both high void fractions and high volumetric surface areas, thus (i) enabling low pressure drop; (ii) diminishing the risk of intraporous mass transfer limitations and (iii) granting efficient heat removal when adopting conductive (e.g. metallic) substrates [15]. In particular, structured catalysts made of highly conductive substrate materials, like e.g. aluminum or copper, exhibit remarkably high radial effective thermal conductivities when employed in multitubular reactors. This can be further enhanced by adopting substrates with low void fractions and appropriate substrate geometries [16–18]. The adoption of such catalytic systems causes indeed a dramatic change in the reactor heat transfer properties, which are found to differ from those typical of conventional random packings. Such differences are primarily related to the fact that heat exchange in conductive structured catalysts does not anymore rely on a convective mechanism, but on a conductive one within the continuous metallic matrix of the structured substrate, which is independent of the gas flow velocity inside the reactor tubes [17,19–21].