

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

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Notation

af	multiplying activity factor [-]
CPSI	honeycomb monolith cell density [cells/in ²]
$(\text{CO}/\text{CO}_2)_F$	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, expressed 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]
ζ	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 H₂/CO/CO₂ mixtures and Cu/ZnO/Al₂O₃ 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].

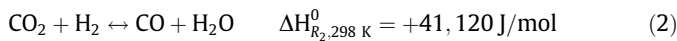
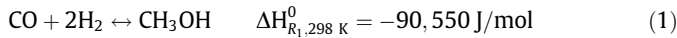
Such properties make conductive structured catalysts promising for the intensification of a number of existing catalytic processes, especially those involving highly exothermic/endothermic gas/solid or gas/solid/liquid reactions in which large temperature gradients must be avoided to control selectivity and/or catalyst deactivation [15,19,22–26]. In particular, thanks to their heat transfer properties being unaffected when scaling-down the reactor by shortening the tubes, such catalytic systems can be considered an interesting option for the operation of compact multitubular reactors, which is otherwise unfeasible with conventional packings [18].

In a previous simulation work, a comparison of the performances of full-scale externally-cooled methanol reactors loaded with a conventional random packing and with innovative highly conductive structured catalysts demonstrated the advantages of adopting washcoated copper honeycomb monoliths and open-cell foams in compact multitubular reactors for the methanol synthesis in terms of more limited hot-spot temperatures and recycle ratios with respect to conventional packings [8]. In that work, however, catalyst volumetric fractions were assumed to be as high as those typical of packed-bed reactors (i.e. roughly 60%). These loadings are hardly feasible when washcoating structured substrates, whose volumetric void fractions usually lie in between 70% and 90% [27,28].

This work is devoted to the optimization of a compact (2-meter long) structured reactor loaded with washcoated copper open-cell foams (OF) and honeycomb monoliths (HM) for the methanol synthesis at lower catalyst volumetric fractions than those typical of PBs. Specifically, we show and discuss the results of a parametric analysis addressing the effects of (i) catalyst intrinsic activity, (ii) coolant temperature and (iii) reactor tube diameter.

2. Methods

We used the commercial software gPROMS[®] [29] to develop three simulation codes for the PB, the HM and the OF multitubular reactor configurations. For all reactors, we adopted a 2-D steady-state heterogeneous pseudo-continuous description of the concentration and temperature gradients within one representative cylindrical tube along its axial and radial coordinates. We also included the mathematical description of the intraporous concentration profiles according to an isothermal–isobaric intraporous reaction–diffusion model. Graaf et al.’s kinetic model was adopted [30] (See Eqs. 1–3).



More details about the reactor models are provided in [8].

400 CPSI, 0.72 m³ void/m³ substrate washcoated copper honeycomb monolith and 40 PPI, 0.88 m³ void/m³ substrate washcoated copper open-cell foam were assumed as structured catalysts loaded in reactor tubes [8] (see Table 1 for typical values of the related heat transfer parameters).

2 meter-long tubes were considered as representative of the compact reactor configuration. A synthesis loop model was also considered to clearly quantify the effects of the reactor design on the overall synthesis loop performances. The synthesis loop included the reactor, an ideal condenser separating all water and methanol in the reactor effluent from the rest, variable recycle and purge ratios. The pressure in the recycle stream was virtually increased to the value set at reactor inlet to compensate for the pressure drop within the reactor. The inerts molar fraction at the

Table 1

Common values of heat transfer parameters in Cu-based structured reactors ($d_t = 42 \text{ mm}$).

	Axial effective thermal conductivity, λ_{ea} [W/m/K]	Radial effective thermal conductivity, λ_{er} [W/m/K]	Wall heat transfer coefficient, h_w [W/m ² /K]
HM	112 [31]	70 [31]	618 [20]
OF	16 [32]	16 [17]	817 [18]

reactor inlet, x_{inerts} , was fixed to saturate the last degree of freedom in the loop. Its value (i.e. 0.0882) was selected in line with industrial practice. Such a constraint, which is satisfied by adjusting the purge/recycle ratio, eventually forces the overall methanol productivity (and the overall syngas conversion) to keep constant across the synthesis loop. The reactor capacity was chosen so to be representative of the typical size of compact reformers/gasifiers [33]. Common input data for all simulations are summarized in Table 2.

With the aim of investigating the effect of the catalyst volumetric fraction ξ on the performances of structured reactors (SRs), we first simulated both HM and OF reactors by decreasing ξ , from the typical values of commercial PB reactor (i.e. 0.613 m³ catalyst/m³ tube) to 0.30. The corresponding washcoat thickness δ_w on HM was evaluated using the approach reported in [19], whereas for OF we adopted the following equation:

$$\begin{aligned} \frac{V_{\text{wash}}}{V_{\text{struts}}} &= \frac{\xi}{1 - \varepsilon} = \frac{(d_s + 2\delta_{\text{wash}})^2 - d_s^2}{d_s^2} \Rightarrow \delta_{\text{wash}} \\ &= \frac{d_s}{2} \cdot \sqrt{\left(1 + \frac{\xi}{1 - \varepsilon}\right) - 1} \end{aligned} \quad (4)$$

where d_s is the foam strut diameter, evaluated according to Lu et al.’s cubic cell model [34].

Then, keeping ξ at 0.30, we investigated the effect of the catalyst activity by applying a multiplying factor, af to all reaction rates. Similarly, we investigated the effect of the coolant temperature, T_{cool} in order to figure out if it can be used to compensate for the lower catalyst inventory in SRs. Eventually, we explored the possibility of operating SRs with larger reactor tubes diameter, d_t at fixed total reactor catalyst inventory in view of reducing reactor investment costs.

We performed all simulations assuming a safe upper limit for the hot-spot temperature in the catalytic bed of 553 K, which was set as a threshold value for preserving the process selectivity to desired products [5]. Accordingly, the simulated profiles shown in the following figures stop whenever this temperature value is reached.

Table 2

Input variables (reference case).

Variable	Input value	Units
T_g^0	473	K
T_{cool}	511	K
p^0	6.92×10^6	Pa
d_t	4.2×10^{-2}	m
L	2	m
F	18.82	mol/s
M_F	2.109	[-]
CO/CO ₂	7.7	[-]
x_{inerts}	0.0882	[-]
n_{tubes}	291	[-]

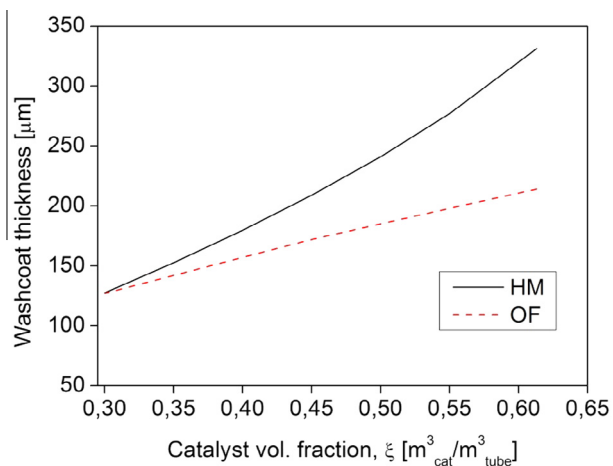


Fig. 1. Washcoat thickness as a function of catalyst vol. fraction ξ .

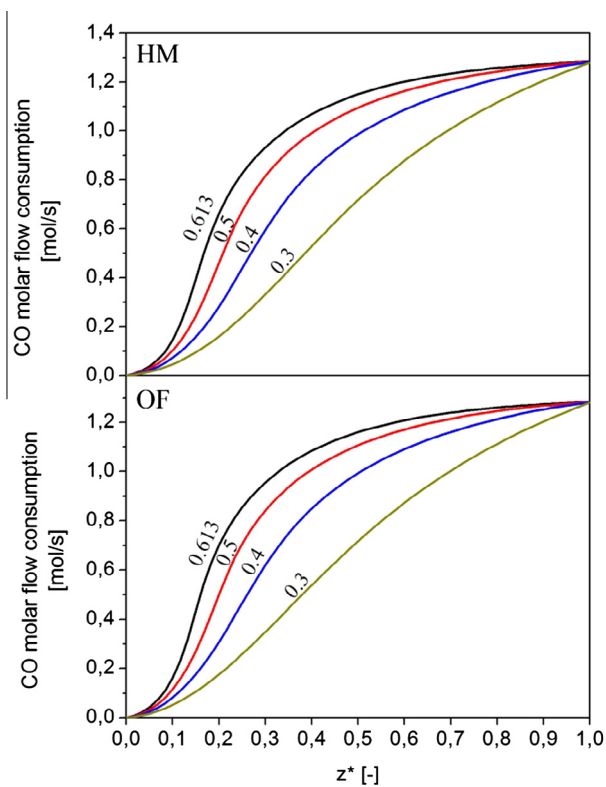


Fig. 2. CO molar flow consumption along the reactor as a function of the catalyst vol. fraction ξ ($d_t = 42$ mm, $T_{cool} = 511$ K, $af = 1$, HM at the top, OF at the bottom).

3. Results and discussion

3.1. Effect of catalyst load

In our previous work [8] we concluded that it is not possible to operate a compact (short tubes) PB reactor for the methanol synthesis due to its poor heat transfer properties associated with the low gas flow rates, which strongly penalize the dominating convective heat transfer mechanism. On the contrary, thanks to the dominant conductive heat transfer mechanism, which is flow-independent, temperature profiles in conductive SRs are substantially unaffected when reducing the reactor tubes length. However, catalyst volumetric fractions typical of PB methanol reactors (i.e.

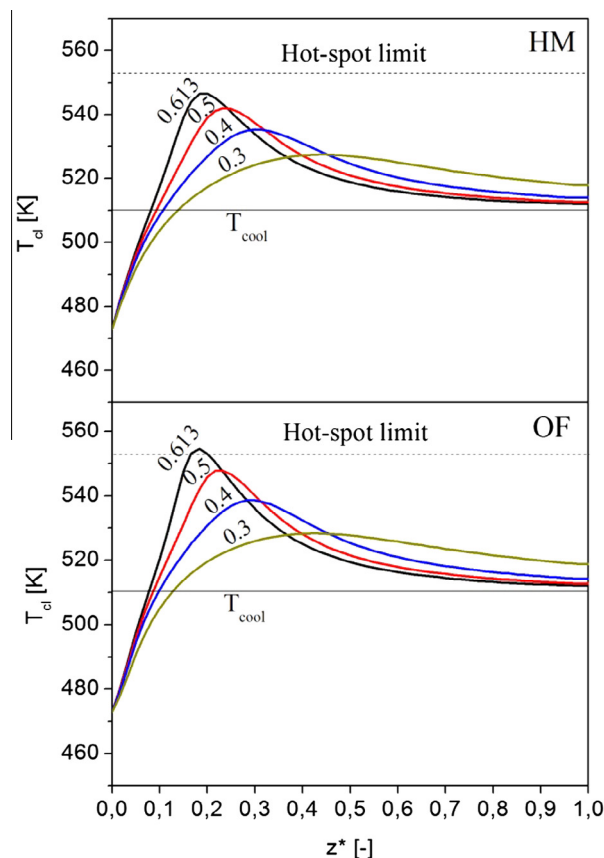


Fig. 3. Axial temperature profiles at centerline as a function of the catalyst vol. fraction ξ ($d_t = 42$ mm, $T_{cool} = 511$ K, $af = 1$, HM at the top, OF at the bottom).

$0.613 \text{ m}^3 \text{ catalyst/m}^3 \text{ tube}$) correspond to equivalent washcoat thicknesses of about $331 \text{ } \mu\text{m}$ in the case of HM [19] and $214 \text{ } \mu\text{m}$ in the case of OF [34] (Fig. 1), which are hardly feasible on such structured substrates with the current coating technology [27].

We therefore performed a parametric analysis of the catalyst volumetric fraction ξ to assess the possibility of operating compact SRs with lower catalyst loads than in PBs, resulting in more reasonable washcoat thicknesses down to $127 \text{ } \mu\text{m}$ in both HM and OF (Fig. 1). Similar values were experimentally obtained by Phan et al. [35] by coating a Cu/ZnO/Al₂O₃ methanol catalyst over steel monoliths prepared from corrugated and flat FeCrAlloy sheets.

Fig. 2 shows the axial profiles of the molar flow consumption of CO. Such profiles become less pronounced when decreasing ξ in both HM and OF reactors, and are very similar in both reactor configurations. Similar trends are found for CO₂, even if the numerical values are roughly one order of magnitude lower than those of CO: for this reason, we consider only CO in the present analysis.

The lower catalyst loads cause a significant drop of the activity within the reactor, which results in more limited axial temperature gradients, characterized by lower hot-spots shifting towards the reactor outlet (Fig. 3). Accordingly, lower CO conversions per pass are found, moving progressively away from equilibrium values (Fig. 4).

However, to keep the overall methanol productivity constant (as practically imposed by setting the total inerts molar fraction at reactor inlet), when decreasing ξ , the synthesis loop is forced to operate at higher recycle ratios, whose numerical values result essentially equivalent for the two structured reactor configurations (Fig. 5). This also explains why the molar flow consumption of CO at reactor outlet does not vary with ξ (Fig. 2).

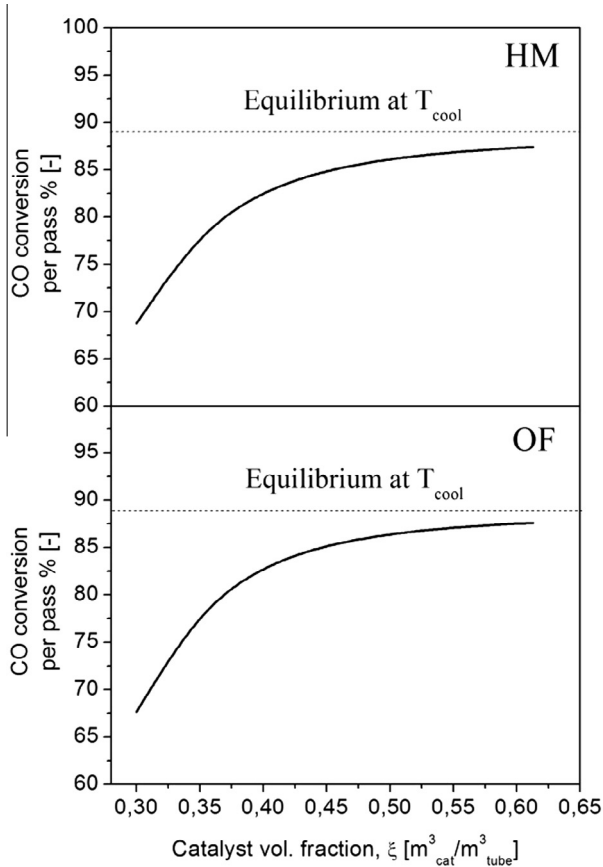


Fig. 4. CO conversion per pass as a function of the catalyst vol. fraction ξ in HM and OF reactors ($d_t = 42$ mm, $T_{cool} = 511$ K, $af = 1$). CO conversion at equilibrium was evaluated at reactor outlet and at $T = T_{cool}$.

It is worth noticing that the higher recycle ratios also contribute to increase the gas advection term of the reactor energy balance, which is responsible for further mitigating the axial temperature gradients within the catalytic bed.

By solving the momentum balance equation in both models, we were able to study the effect of the reactor configuration on pressure drop as well. Compact reactor configurations (i.e. with short tubes) operated with limited gas flow rates obviously imply a significant reduction in pressure drop with respect to that prevailing in full-scale industrial packed-bed reactors (which is typically in the order of 1 bar [8]). In particular, simulations pointed out that the pressure drop along the reactor tube was lower than 0.04 bar in OF for all the studied levels of ξ , whereas in HM, thanks to the

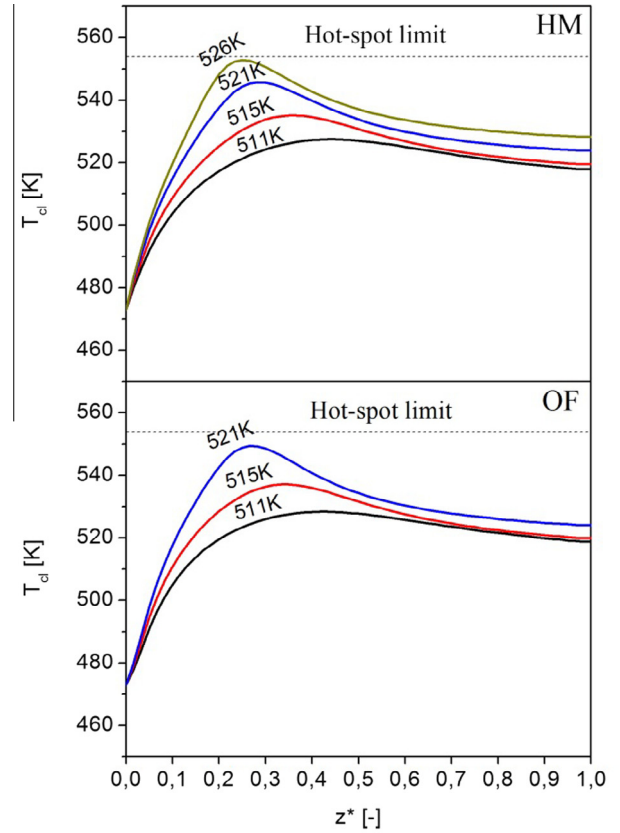


Fig. 6. Axial temperature profiles at centerline as a function of the coolant temperature, T_{cool} ($\xi = 0.30$, $d_t = 42$ mm, $af = 1$, HM at the top, OF at the bottom).

gas laminar flow in straight channels, the pressure drop was around 0.002 bar. This substantial reduction would surely represent a benefit for the process economics, as it would imply minimal re-compression costs of the recycle stream.

Interestingly, catalysts with enhanced intrinsic activity can be used to compensate for the decreased catalyst inventory in the reactor (see [Supplementary information - A](#)). Indeed, according to the model equations reported in [8], the introduction of a multiplying activity factor in all the reaction rates to study the effect of adopting more active methanol catalysts would have the same effect of changing the catalyst volumetric fraction, both parameters proportionally affecting the generation terms in the mass and energy balances of both HM and OF. Indeed, secondary effects on the intraporous mass transfer in both HM and OF and in the radial effective thermal conductivity of HM, which could be

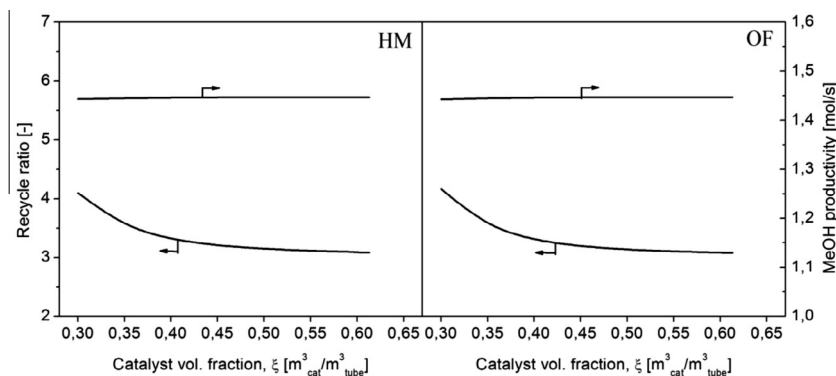


Fig. 5. Recycle ratio and MeOH productivity as a function of the catalyst vol. fraction ξ in HM (to the left) and OF (to the right) reactors ($d_t = 42$ mm, $T_{cool} = 511$ K, $af = 1$).

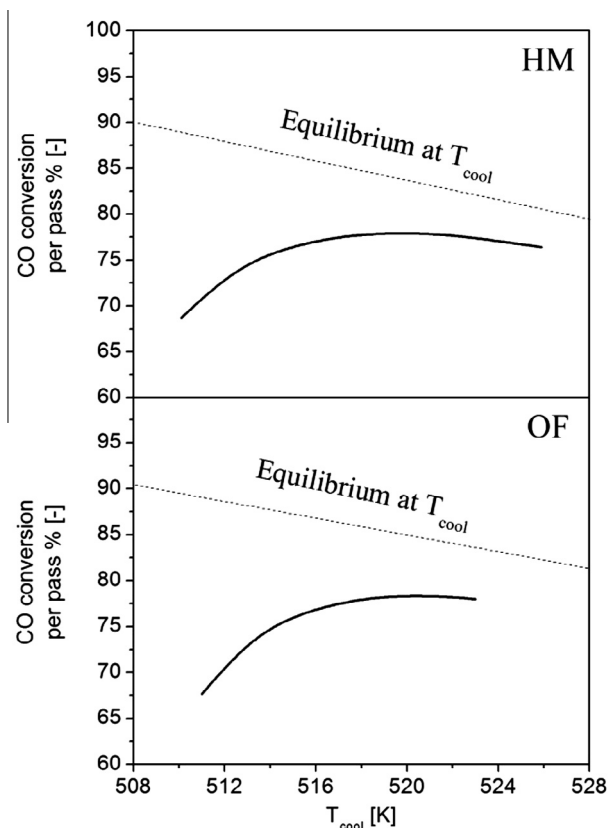


Fig. 7. CO conversion per pass as a function of coolant temperature, T_{cool} in HM and OF reactors ($\xi = 0.30$, $d_t = 42$ mm, $af = 1$). CO conversion at equilibrium was evaluated at reactor outlet and at $T = T_{cool}$.

expected in principle, were found to be negligible in the investigated conditions.

3.2. Effect of coolant temperature

We explored the tuning of the coolant temperature, T_{cool} , as another way to improve the performances of compact SRs when operated at low catalyst volumetric fractions. Fig. 6 shows that axial temperature profiles become sharper upon increasing T_{cool} . Both SRs exhibit indeed shorter pre-heating lengths, mainly due to the greater driving force available for the gas to heat up once entered in the reactor. Higher hot-spot temperatures are also found: indeed, when the catalyst temperature overcomes T_{cool} , the situation is reversed, being the driving force for cooling reduced and the heat of reaction removed less effectively from the catalyst.

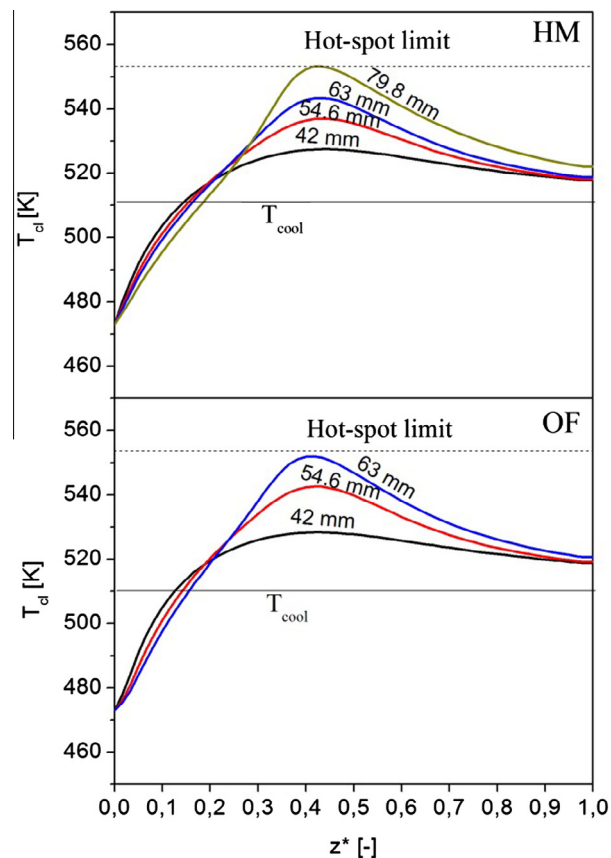


Fig. 9. Axial temperature profiles at centerline as a function of the tube diameter, d_t ($\xi = 0.30$, $T_{cool} = 511$ K, $af = 1$, HM at the top, OF at the bottom).

As a result, the CO conversion per pass goes through an optimum corresponding to a coolant temperature of about 520 K for both HM and OF (Fig. 7). This optimum is explained by the interplay between kinetics and thermodynamics: indeed, an increase in T_{cool} initially boosts the reaction rates, favoring the approach to equilibrium, whose upper limit, however, decreases with T_{cool} . Once the equilibrium is more closely approached, a further increase of T_{cool} causes the outlet gas mixture to leave the reactor at progressively higher temperatures, therefore penalizing the process thermodynamics, and this results in lower CO conversions per pass. Accordingly, the recycle ratio also passes through the same optimum upon increasing T_{cool} (Fig. 8).

It is worth mentioning that the safe hot-spot limit of 553 K is approached by the HM reactor at higher T_{cool} than that of OF

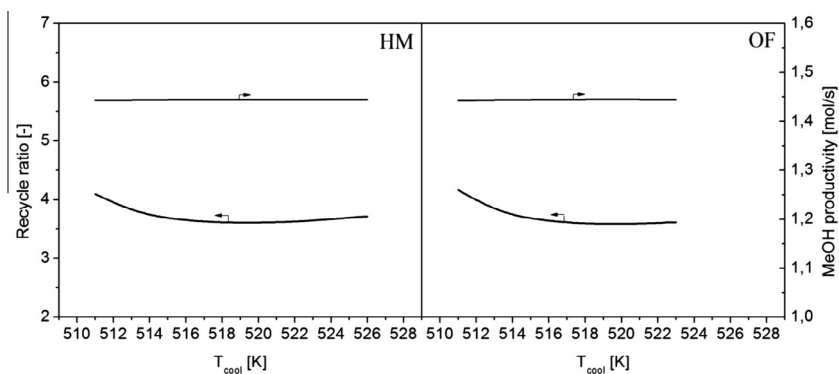


Fig. 8. Recycle ratios and MeOH productivity as a function of coolant temperature, T_{cool} in HM and OF reactors ($\xi = 0.30$, $d_t = 42$ mm, $af = 1$).

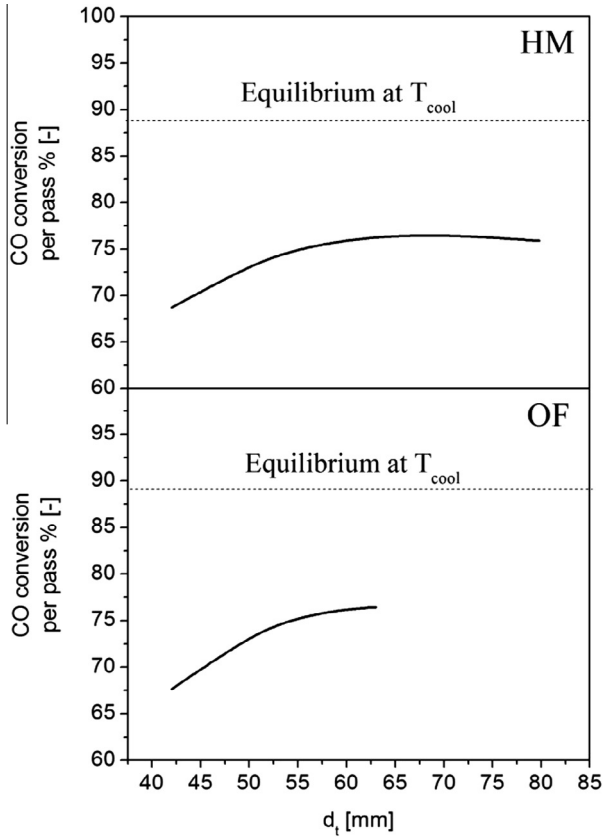


Fig. 10. CO conversion per pass as a function of the tube diameter, d_t in HM and OF reactors ($\xi = 0.30$, $T_{\text{cool}} = 511$ K, $af = 1$). CO conversion at equilibrium was evaluated at reactor outlet and at $T = T_{\text{cool}}$.

(526 K vs. 521 K) and this is again explained in terms of the more effective radial heat transfer of the HM reactor.

3.3. Effect of tube diameter

We investigated the possibility of adopting reactor tubes with a larger diameter. As both the number of tubes and the number of welding operations decrease with the square of the tube diameter at fixed catalyst inventory, tubes with bigger diameters would enable savings in the investment costs for the reactor. However, the removal of the reaction heat load becomes much more demanding in this case. Indeed, the catalyst load in each tube and hence the heat released by the reaction grow with the tube volume, which is proportional to the square of the tube diameter, whereas the heat exchange area increases only linearly with this

parameter. Accordingly, the surface-to-volume ratio (i.e. $4/d_t$ for a cylindrical tube) is proportionally decreased. For this reason, the tube diameter of externally-cooled multitubular reactors is generally maximized taking into account the need of effectively removing the reaction heat.

We investigated the effect of increasing the tube diameter in both HM and OF reactors, starting from a typical value adopted in commercial units (i.e. 42 mm) and increasing such a value as far as the hot-spot temperature keeps below the safe limit of 553 K. The number of tubes was correspondingly reduced at the same time in order to maintain the same overall catalyst load in the reactor.

Due to the higher thermal loads generated per unit heat transfer surface, more pronounced axial temperature gradients were found (Fig. 9). However, thanks to the effective radial heat transfer within the highly conductive substrates, the hot-spot temperatures keep limited and, as a consequence of a better approach to equilibrium at reactor outlet (Fig. 10), lower recycle ratios are required to keep the methanol productivity constant when increasing d_t in both HM and OF (Fig. 11). Coherently with the hot-spot limit, the analysis pointed out that tubes diameter up to 63 mm could be adopted in the case of OF reactor, which is a 50% larger diameter than those typical of commercial packed-bed units.

Interestingly, the hot-spot in the HM reactor is still 10 K below the limit (and below that of the OF reactor) in the case of the 63 mm tubes. Accordingly, as shown in Fig. 9, the tube diameter can be increased up to 79.8 mm before approaching the hot-spot limit. Nevertheless, at those values, the higher outlet temperatures markedly penalize the process thermodynamics, thus causing the CO conversion per pass and the recycle ratio to go through an optimum upon increasing d_t .

The higher flexibility of the HM reactor in managing higher thermal loads and the possibility to be operated at larger reactor tubes than in the case of OF can again be explained in terms of radial heat transfer rates. Indeed, according to the correlation for the estimation of the overall heat transfer coefficient, U [36] (Eq. (4)), which basically assumes the radial heat transfer across the reactor tubes as controlled by two *in series* resistances, one accounting for the heat transfer at the tube wall and the other one for the heat transfer across the catalytic bed, the second term of the sum represents a negligible resistance in the case of HM thanks to its very high radial effective thermal conductivity, λ_{er} [8], even when large tube diameters are employed:

$$\frac{1}{U} = \frac{1}{h_w} + \frac{d_t}{6.13 \cdot \lambda_{er}} \quad (5)$$

Accordingly, the adoption of HM reduces the impact of employing larger tubes and results in flatter radial temperature profiles than in OF, where instead the more limited λ_{er} does not compensate for the increased tube diameter, thus causing marked radial temperatures gradients (Fig. 12).

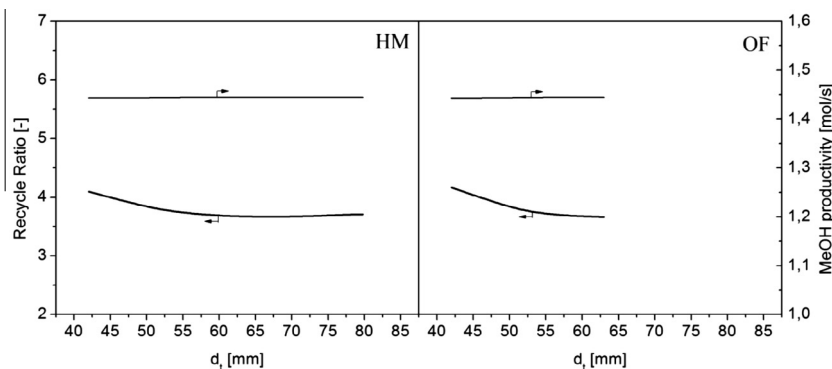


Fig. 11. Recycle ratios and MeOH productivity as a function of the tube diameter, d_t in HM and OF reactors ($\xi = 0.30$, $T_{\text{cool}} = 511$ K, $af = 1$).

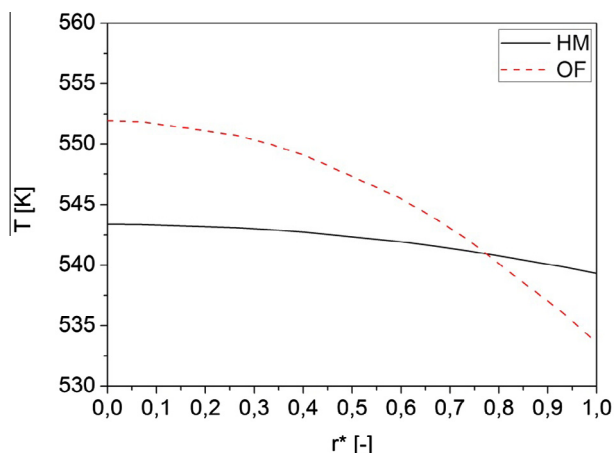


Fig. 12. Radial temperature profiles at the hot-spot ($d_t = 63$ mm, $\zeta = 0.30$, $T_{\text{cool}} = 511$ K, $af = 1$, solid: HM, dashed: OF).

Notably, while copper open-cell foams are currently manufactured and commercially supplied [37,38], copper honeycomb monoliths are not commercially available, but only a few prototypes were produced by Corning [39] and tested at the lab and pilot scale [24].

4. Conclusions

In this work we have addressed by simulation the optimization of a compact (2-meter long) multitubular fixed-bed reactor for the methanol synthesis loaded with highly conductive structured catalysts, namely washcoated copper honeycomb monoliths and open-cell foams.

It is well known that the high catalyst inventories per unit volume typical of commercial PB units are hardly feasible in the case of structured catalysts. In fact, our simulations confirm that compact SRs, operating with reduced catalyst volumetric fractions (i.e. down to $0.30 \text{ m}^3 \text{ catalyst/m}^3 \text{ tube}$), would grant limited CO_x conversions per pass, resulting in high recycle ratios. In this respect, however, we showed that the excellent radial heat transfer performances of the conductive structured reactors enable the adoption of catalytic materials with enhanced intrinsic activity, in line with the recent trends in manufacturing of methanol synthesis catalysts, and/or the optimization of the coolant temperature in order to compensate for the lower catalyst loads, eventually granting lower recycle ratios as well as limited hot-spot temperatures, which thus makes compact SRs configurations very appealing.

Similarly, we proved that the coolant temperature can be suitably incremented, up to an optimum, in order to recover the lower activity in the reactor and thus reduce the recycle ratio.

Interestingly, the advantages of operating such structured compact reactors are eventually emphasized by the adoption of larger reactor tubes diameter, in view of reducing the investment costs. Indeed, thanks to the efficient conductive radial heat transfer, hot-spot temperatures in compact SRs with larger (i.e. up to 63 mm) tubes can be kept limited, while the higher thermal loads grant more favorable temperature profiles in the reactor tubes which result in lower recycle ratios.

Compact SRs seem therefore promising in perspective for small-scale GTL (Gas-To-Liquid) processes, such as onshore remote location plants for converting stranded gas reservoirs into more valuable and easily transportable fuel, or for small-scale BTL (Biomass-To-Liquid) processes aimed at the valorization of biomass feedstocks available in limited amounts.

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Appendix A. Supplementary data

- Supplementary data associated with this article can be found, in the online version.

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