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High Thermal Conductivity Structured Carriers for Catalytic Processes Intensification

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Process intensification is conceived as a way to optimize fixed and operating costs in an industrial plant. It is not only related to a reduction of the size of equipments, but also to the change of the production method, by enhancing both chemical that physical aspects of the process. In particular, when there has to deal with exothermic equilibrium reactions, such as the Water Gas Shift, the main problem is that the conversion is limited by the kinetics at the inlet of a catalyst bed, because temperature is low, and is thermodynamically limited at the outlet, because in the adiabatic reactor temperature raises, lowering the equilibrium value. A good solution would be the use of a high conductive carrier, able to redistribute the heat of reaction along the catalyst bed. The aim of this work was to study the heat transfer phenomenon on structured carriers such as open cell foams, by estimating also the thermal properties by a mathematical model elaborated for the heat transfer system.

1. Introduction

The strategy of the process intensification was conceived in the late 1970's as a philosophy of capital development, with the aim of achieving a cost savings; the idea was that if a reduction of the plant size does not compromise the output performance, a significant reduction in the costs of the plant would have occurred (Reay et al., 2008). Nowadays the process of intensification is related not only to the design of equipment of significantly reduced size but, more specifically, to the change of production methods which allow a better control of the kinetics of the reactors, improvements in activity and selectivity, improvements in energy efficiency, improvements in safety and environmental impact. More in general the process intensification strategy can be divided into two main areas, the process intensifying equipment and the process intensifying methods, the first one deals with the design of new reactors configurations for what concerns the mixing and the heat and mass transfer (Palma et al., 2014), the second deals with the integration of reactions, separations, heat exchanges or phase transitions and new process-control methods (Pouransari et al., 2014) (Barkaoui et al., 2013). In this context, the best example of a process that would benefit most from an intensification is, of course, the Water Gas Shift, which is the first stage of purification of the syngas in a hydrogen production plant. Actually, the Water Gas Shift is a two-stage process that exploits the excellent kinetics in the HTS and a favourable thermodynamic equilibrium at LTS stage; however, the use of two different catalytic systems, the need of two separate reactors or two separate zone of the reactor, and above the others the need for an intercooling, make it the ideal candidate to a massive intensification. The exothermicity of the WGS reflects negatively on the conversion rate of the CO, limiting the reaction rate at the inlet of the catalytic bed, where the temperature is low, and disfavouring the approach to the thermodynamic equilibrium at the outlet, where the temperature is high. It is therefore clear that the process intensification has to be targeted to a modification of the thermal profile along the catalytic bed. This could be done by enhancing the heat conduction along the catalytic bed, which would improve the overall reaction rate, by allowing a flat temperature profile and a better approach to the equilibrium composition with a single catalytic bed. In this context, the thermal conductivity of the catalytic materials plays a crucial role: the required catalyst should show not only high activity and selectivity but also high thermal stability and conductivity, low pressure drop

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and enhanced heat transfer (Palma et al., 2009). An interesting alternative to the traditional catalysts is represented by structured ones; in this case it is possible to exploit both the thermal conductivity of a metal structures such as open cell foams and the activity of a catalytic formulation in powder form, by coupling the two parts by means of a coating. On the basis of the literature review on heat transfer in foams monoliths, it was highlighted that two parameters effect on overall heat transfer coefficient: the void fraction (or porosity) and the pore density (PPI), in addition to the bulk thermal conductivity, of course. The effect of pore density on heat transfer coefficient seems to be conflicting in several papers, since in some cases it increases with pore density, in other cases it decreases. Some predicting expressions reported the dependence of Nusselt number from pore density (PPI), and underlined that it in a first range it quickly increased with PPI value, in the second range the increasing is less evident (Lu et al., 2006). The special trend, that define a "critical PPI value", is more evident for foam samples with higher diameters (> 0.010 m). A predictive expression of foam thermal conductivity was proposed by Bhattacharia et al (2002), in which the effective thermal conductivity of foam samples was evaluated.
In this work the heat transfer through open cell foams structured carriers is investigated, for the catalytic applications in industrial processes involved in the production of hydrogen and syngas. The thermal properties of the structured supports were estimated by means of a mathematical model by comparing analytical and experimental results.

2. Experimental

2.1 Structured carriers properties

For the purposes of this work, four different types of foams were purchased: in particular, three metallic foams (ferritic foam, FeCr Alloy foam and Aluminum foam), and an Alumina foam. The main geometric properties of these structured carriers are available in Table 1.

Table 1: Composition and geometric properties of the foams.

Sample name	Material code	Composition	Porosity (pores per inch, PPI)	Void fraction (%)
Vesuvius	AL92	100% Alumina	65	85
Belarus	Fe-FeO_x	Fe-FeO_x	20	92
Fraunhofer	FeCr Alloy	Stainless steel	30	93
ERG Duocel	AlFoam	Aluminum	40	88

While all foams were chosen in order to have almost the same void fraction, the PPI value of each sample change, in particular from a minimum value of 20 relative to the ferritic foam up to 65 PPI of the Alumina foam. This choice was made in order to study also if the tortuosity of the material can enhance significantly the heat transfer. On the other hand, the tortuosity of the system could also increase the pressure drop; for this last phenomenon, see Section 4.

2.2 Heat transfer tests

Table 2: Heat transfer tests: operating conditions.

Condition	Value
Tube internal diameter	23 mm
Oven temperature	200 – 600 °C
Volumetric flow rate	1.2-3.6 Ndm^3/min
Foam diameter	15 mm

In order to perform the heat transfer tests all the foams have been cut and shaped appropriately to obtain cylindrical monoliths. Several thermocouples were inserted at equidistant points of the foam to be able to measure both the temperature of the foam itself that the temperature of the gas. The monolith was then surrounded by a heat-expanding pad, to avoid by-pass phenomena, and placed inside a quartz tube.
The quartz tube has an internal diameter of 23 mm; this was placed in an electrical oven in order to assure an uniform temperature on the external surface of the reactor. A cold nitrogen stream was sent in the reactor, by varying the volumetric flow rate and the temperature of the furnace. The main test parameters were reported in Table 2. These tests were made by varying oven temperature and volumetric gas flow rate, in order to optimize and validate the mathematical model, which is explained in more details in Section 3. The temperature data of all tests were continuously recorded by the device Multicon CMC-141, purchased by Simex.

3. Modeling of the system

3.1 Development of the heat transfer model

The heat transfer mathematical model was developed starting by the system energy balance (Equation 1), inspired by what reported in the literature by Hayes et al. (1997):

$$IN - OUT + GEN = ACC \tag{1}$$

The whole model takes into accounts the following assumptions:
- No chemical reactions (GEN=0)
- Steady state conditions (ACC=0)
- Negligible radial thermal profile, both in gas that in solid phase
- No radiative phenomena.

With regard to the modeling of the gas flowing through the foam, it has been imagined that the two phases are a sort of *continuum*, so that the whole system can be seen as an annular cylinder of foam surrounding the gas phase. In Figure 1 a schematic representation of the model is displayed.

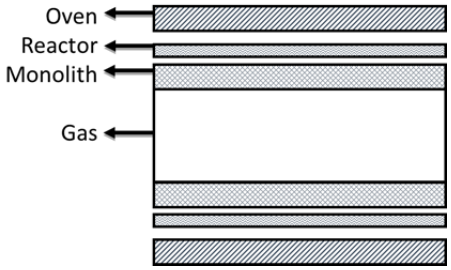

Figure 1: Schematic representation of the heat exchange model

So, starting from the assumptions available above, the gas phase and solid phase balances were performed. It has been used a differential element both in the gas phase that in the solid phase, with a length of Δz, by considering all the incoming and outgoing heat flows, as assumed. A detailed scheme of the two-phases balance is shown in Figure 2.

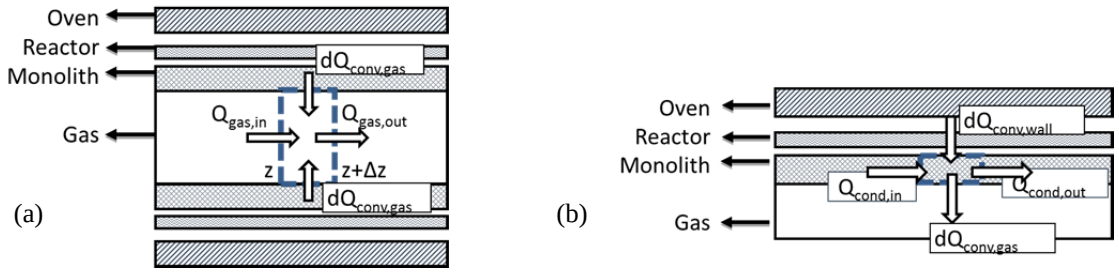

Figure 2: Gas (a) and solid (b) phase balance detailed scheme

By processing and rearranging the two balances, two differential equations can be obtained (Equation 2 and Equation 3):

$$\frac{dT_g}{dz} = \frac{h_g \cdot \pi \cdot D \cdot \varepsilon}{F \cdot c_p}\left(T - T_g\right) \tag{2}$$

$$\frac{d^2T}{dz^2} = 4\frac{\varepsilon}{1-\varepsilon}\frac{h_g}{kD}\left[\left(T - T_g\right) - \frac{h}{h_g - h}\left(T_{ov} - T\right)\right] \tag{3}$$

with the appropriate boundary conditions (Equation 4 and Equation 5):

$$T_g(z = 0) = T_g^0 \tag{4}$$

$$k \cdot \left[\frac{dT}{dz}\right]_{z=0} = k \cdot \left[\frac{dT}{dz}\right]_{z=L} = 0 \quad (5)$$

Symbols in the equations: T_g: gas temperature; z = axial coordinate; h_g: solid-gas heat transfer coefficient; D: foam diameter; ε: foam's void fraction; F: mass flow rate; c_p: nitrogen heat capacity; T: solid temperature; k: material thermal conductivity; h: global heat transfer coefficient; T_{ov}: oven temperature; L: foam monolith length.
This differential model was then discretized and processed in Microsoft Excel™, solving it by means of finding the optimum value of the two parameters h_g (gas phase heat exchange coefficient) and k (material thermal conductivity), through the least squares method.

4. Results and discussion

In Table 3 the results of the optimization of the heat transfer model are shown. The model was optimized only for the condition relative to a gas flow rate equal to 2.4 dm^3/min; the other data were processed to validate the mathematical model.

Table 3: Parametric optimization of the heat transfer model (volumetric flow rate: 2.4 Ndm^3/min).

Sample	T_{ov}, °C	k_{foam}, W/m/K	h_g, W/m^2/K	h, W/m^2/K	Q, W
Alumina	200	16.5	204.1	26.4	5.7
	400	12.7	250.0	31.0	12.1
	600	10.9	291.0	33.0	18.2
Aluminum	200	30.0	80.1	17.7	8.4
	400	60.1	90.3	27.9	15.9
	600	89.7	108.4	33.9	23.8
Ferritic	200	1.6	73.2	20.7	6.4
	400	1.5	96.8	30.0	18.1
	600	1.4	164.1	43.0	24.1
FeCrAlloy	200	1.5	81.2	28.9	6.8
	400	1.8	86.7	33.2	23.9
	600	2.0	91.4	36.0	37.2

Solid temperature profiles of tested samples are reported in Figure 3. In particular, here it is shown the condition in which the oven temperature is set up to 400 °C and the gas flow rate is 2.4 Ndm^3/min. All the other conditions, in the investigated range, showed qualitatively the same behavior.

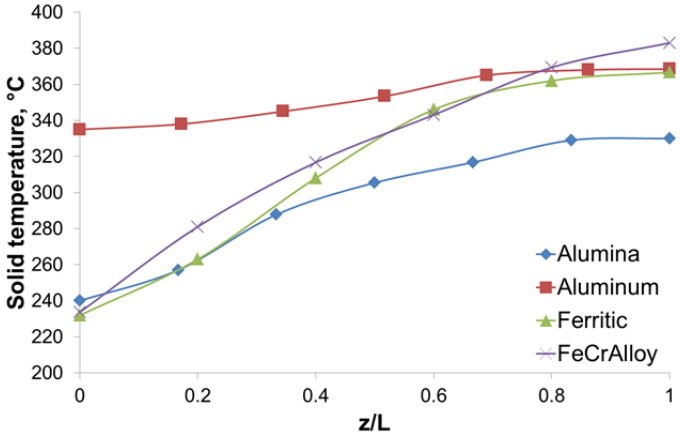

Figure 3: Solid temperature along the foam bed (T=400°C, Q_{tot}=2.4 Ndm^3/min)

The solid temperature profiles of the samples reflect in some way the thermal conductivity of themselves. As a matter of fact, Aluminum foam showed the most flat thermal profile, sign of a good redistribution of the heat along the monolithic bed. As evidence of this, the outlet temperature of this foam is even lower than other samples' one, such as the FeCr-Alloy and the ferritic foam, in which the difference between inlet and outlet

temperatures is very large. The alumina foam also showed a quite flat thermal profile, in fact the thermal conductivity calculated for this sample is much greater than ferritic and FeCr-Alloy foams and about a half of the Aluminum foam. Actually, there is another factor that has to be taken into account. In fact, it has to be remembered that the Alumina foam has the highest relative density, which of course contributed to enhance its thermal conductivity with respect to the other samples. The influence of the material's thermal conductivity can be observed also if looking at the gas temperature profiles, as shown in Figure 4.

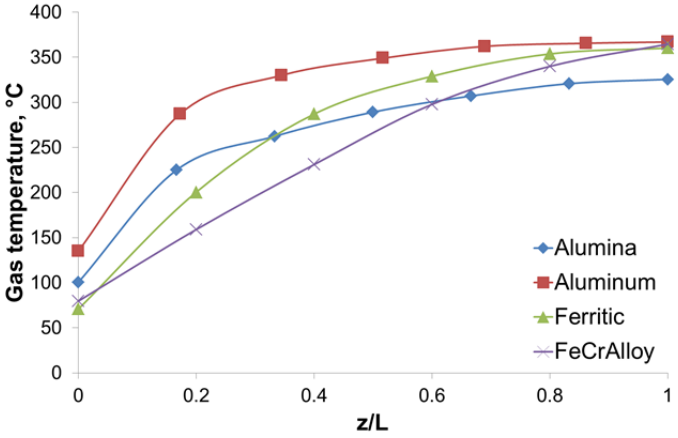

Figure 4: Gas temperature along the foam bed (T=400 °C, Q_{tot}=2.4 Ndm^3/min)

Also in this case the qualitative behaviour is similar in all the conditions. Here it can be noticed that the more conductive foams are those who guarantee an almost flat thermal profile of the gas, surely because they assure a more efficient heat flow along the structured carrier. In fact, looking for example at the Aluminum foam, the gas temperature raised straightaway yet in the inlet zone of the monolithic foam, because the solid temperature of the material is higher also next to the inlet of the foam. The same thing has been observed for the Alumina foam, but in this case the gas temperature was lower because also the solid temperature was lower. Another factor that can influence the gas heating is of course the pores per inch property, which can enhance the heat transfer by means of an enhancement of the turbulence of the system, and in parallel, higher PPI result in higher exchange area, which still enhance gas-solid heat exchange.
Another important characteristic for choosing an optimal catalyst's carrier is represented by the resistance offered to the gas flow. For this reason, on Alumina foam, which is without any sort of doubt the most compact foam between the tested samples, pressure drop tests at ambient temperature were conducted. These tests were carried out on a cylindrical foam (diameter 20 mm) inserted in a quartz reactor (inner diameter 25 mm). The main results are reported in Table 4.

Table 4: Pressure drop test, Alumina foam.

Air velocity, m/s	Pressure drop, bar/m
1.05	0.04
1.68	0.18
2.19	0.25
2.88	0.37
3.28	0.42
3.95	0.58
4.48	0.73
5	0.85

These data showed that pressure drops are not at all a problem in open cell foams, indeed at a gas velocity of 5 m/s (which corresponds to a total flow rate of about 5.6 m^3/h), a typical operating condition for a pilot plant, the ΔP didn't overcome 1 bar/m.

5. Conclusions

In this work four different types of open cell foams were purchased, in order to study the heat transfer in these structured support, evaluating their application in catalytic industrial processes as result of a process intensification. The thermal properties of the foams were estimated by using a mathematical model, discretizing it in Microsoft Excel™. Among the others, within the investigated temperature range, Aluminum foam was the most promising, showing an excellent heat exchange due to the high thermal conductivity value. This is also reflected on the thermal profile in the gas phase, by promoting a flattening of the profile, increasing the temperature in the inlet zone and decreasing next to the outlet. Pressure drops were also evaluated, not being a problem at all, as they were not relevant also with a value of the total flow rate typical of a pilot plant. These results configure Aluminum foam as a good candidate as a structured carrier for the intensification of processes such as Water Gas Shift, which is conventionally carried out in a medium-low temperature range, because of its exothermic nature, that bring thermodynamic and kinetic problems in the actual plant configuration.

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