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Internal mass transfer enhancement in flow-through catalytic membranes

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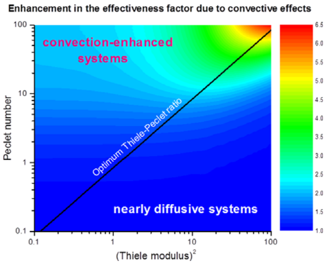
HIGHLIGHTS

- Design rules for maximum enhancement of internal mass transfer due to convection.
- Maximum enhancement when large Peclet number and Thiele modulus are comparable.
- Peclet–Thiele operating diagrams from analytical results.
- Effectiveness–conversion trade-off in radial flow membranes.
- Effects of uneven boundary conditions, flow direction and membrane curvature.

GRAPHICAL ABSTRACT



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ABSTRACT

Flow-through membrane reactors represent a strategy for process intensification, which benefits from the convective flow that is established due to a transmembrane pressure gradient. The interesting consequence from using these materials is the improved utilization of the catalyst dispersed in the membrane. We propose a theoretical analysis which quantifies the effectiveness factor (η) and the degree of conversion. More importantly, the regime of operation which maximizes the enhancement from convective effects is identified. It corresponds to conditions of not only high internal Peclet number (P), but also of comparable Thiele modulus (ϕ^2). We find that these two parameters are related by a simple analytically derived expression: $\phi^2 \simeq 1.26\ P$. When this relationship holds, an upper limit to the enhancement in the effectiveness factor that can be observed is proportional to $\sqrt{P}$. This result also provides an answer to the effectiveness–conversion trade-off in 'dead-end' operation, when both objectives are important. The analytical solutions enable the complete description of the system in Peclet–Thiele diagrams, where the different reaction-transport regimes are identified. Moreover, issues that become particularly relevant in membrane reactors are discussed: curvature, flow direction and the ratio between the concentration distributions at both surfaces. The simplified design rules obtained bridge the gap between materials synthesis (with permeability and thickness as tunable properties) and process design (enhancement of the internal transport and productivity).

1. Introduction

Non-permselective catalytic membrane reactors (where the contribution of viscous flow to the combined mass flux inside the membrane is not negligible) are a convenient realization of a long acknowledged need for improving the performance of reaction (Komiyama and Inoue, 1974; Rodrigues et al., 1982; Rodrigues

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and Quinta Ferreira, 1988) and separation (Rodrigues, 1997) processes, which would otherwise be controlled by slow diffusion towards the active sites. Other approaches in the same spirit include the introduction of (large) mesopores or macropores into the porous framework or the creation of pore size hierarchical distributions (Tao et al., 2011; Wang and Coppens, 2008, 2010). The membrane configuration is convenient because it represents the intersection between perfusive catalysis and structured materials, and can be integrated into several devices at the microscale (Xuan et al., 2012).

This class of membrane reactors can be found in a wide range of applications, when the membrane is itself catalytic (e.g. in catalysis or bioengineering) or inert (e.g. for controlled supply of reactant to membrane packed bed reactors (Papavassiliou et al., 1997)). In particular, they also appeared as 'open-wall' monoliths or as tubular reactors with porous catalytic walls. De Lathouder et al. (2004) used highly porous acicular mullite honeycombs as support for enzyme immobilization. They point out the advantages of the open microstructure compared with the conventional 'small pore' monoliths, namely: higher catalyst loading, reduced pressure drop, slower decrease in activity with time, and improved mass transfer in the cases where limitations existed. In the monoliths used, the pore diameter ranged from 5 μm to 16 μm. Bakker et al. (2005) studied the hydrodynamic properties of this 'open wall' monolith and promoted radial convection by using gas–liquid Taylor flow. Bakker et al. (2007) conducted a selective hydrogenation in the same type of monoliths. They reported an intrinsic permeability of 40×10^{-12} m^2 and interstitial voids with 45 μm, and used the pressure pulsing from Taylor flow to induce fluid velocities inside the wall of 10 mm/s. This effect was observed to reduce mass transfer limitation, increase activity and the maximum yield. Khassin et al. (2005a, 2005b, 2003) also made use of the 'permeable monolith' concept for the Fischer–Tropsch synthesis. Additional applications include microchannel enzyme reactors (Chen et al., 2010a), bioreactors (Chen et al., 2010b) or porous ceramic mesoreactors for multiphase gas/liquid/solid reactions (Aran et al., 2011; Centi et al., 2003; Jani et al., 2012). Other membrane reactors are also deeply related with these technologies and its modeling can be very similar (Nagy, 2010a, 2010b). In the cases where the performance of the membrane reactor is severely limited by diffusion, the advantages of perfusion have been well documented, for example in oxygen transport in hollow fiber bioreactors (Chen and Palmer, 2009; Coletti et al., 2006; Schonberg and Belfort, 1987). Flow-through catalytic membrane reactors have been also studied for multiphase reactions (Reif and Dittmeyer, 2003), destruction of VOCs and harmful chemicals (Motamedhashemi et al., 2011; Westermann and Melin, 2009). In some cases, the performance increased in comparison with conventional wall-coated monoliths. de Loos et al. (2012) took advantage of this concept to enhance the overall rate of gas–liquid–solid hydrogenation in a highly permeable carbon nanofiber catalytic layer. Increments by a factor of 3.5–4 were observed in comparison with the unsupported catalyst.

In the context of separation technologies, perfusion chromatography explored the same phenomena, e.g. for purification of proteins (Afeyan et al. (1990a, 1991, 1990b)). Recently, flow-through monolithic structures and columns operating in radial mode have also been explored for the purification of proteins (Lee et al., 1990; Podgornik et al., 2004), DNA and viruses (Trilisky et al., 2009; Trilisky and Lenhoff, 2009). A technology based on this concept is commercialized by BIA Separations and is based on their proprietary Convective Interaction Media® (CIM, 2006). This relates to the previously discussed work, since these configurations have been also used as immobilized enzyme reactors (Platonova et al., 2009; Podgornik and Podgornik, 2002; Vodopivec et al., 2003).

The idea conveyed by all these works is that diffusion limitations are reduced by permeation, and this is manifested in a significant increase in the catalyst effectiveness (Nir and Pismen, 1977; Rodrigues et al., 1982). However, a deep understanding of the reaction-transport processes occurring inside a pore-flow membrane is required, since: (i) the system does not benefit from blindly promoting internal convection, since the range of design and operating conditions which are actually optimum is very specific; (ii) there are trade-offs that must be accounted for when increasing the convective transport (namely, higher pressure drop and lower radial conversion); (iii) simple design rules are very useful in preliminary design and optimization, in the choice of operating conditions and in the screening of the applications that are the best candidates for the technology; (iv) analytical solutions reduce the computational effort in the simulation of these systems. In a recent review on flow-through catalytic membranes, Westermann and Melin (2009) recognize that "the choice of the appropriate pore dimensions [which will influence permeability, etc.] strongly depends on the intended application and the allowable pressure drop, preventing the establishment of general guidelines". Therefore, a theoretical analysis enabling a completely transparent relationship between performance measures (conversion, effectiveness factor, etc.) and governing parameters becomes extremely valuable. It may also link process and material synthesis considerations.

In this work, we consider convection–diffusion–reaction processes in a curved membrane. Using a perturbation technique, we derive approximations to the concentration profile and the effectiveness factor assuming that curvature is small (Section 3) – a restriction which will prove not to be of relevance in practice. We identify and characterize in detail the regime of operation leading to maximum performance (Section 4). This involved considering the increase in catalyst utilization, and also the attained conversion when the membrane is working as a radial flow reactor (in this case, both goals are combined in an overall objective function). Finally, the behavior of the system is mapped in Peclet–Thiele diagrams (Section 5), and the influence of the concentration distribution on the permeate side is discussed.

2. Mathematical model for a perfusive catalytic membrane

We consider a single channel made of a permeable material (membrane) with catalytic properties, in which a first-order isothermal reaction occurs (see Fig. 1). At least a fraction of the reactant stream that flows through the channel or in the extra-capillary space penetrates the membrane with superficial radial velocity $\hat{u}$, given by Darcy's law. The deviation of the membrane cross-section geometry from the annular shape can be translated by a shape factor σ (Lopes et al., 2012a; Mariani et al., 2003) ($\sigma = 1$ for a cylindrical or tubular membrane, $\sigma = 0$ for a flat sheet

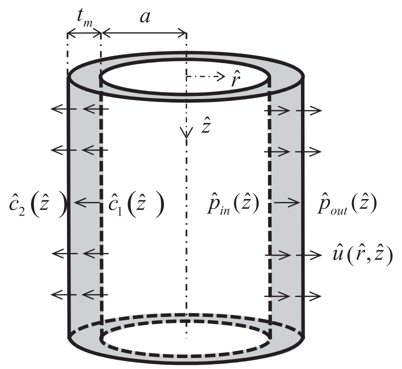

Fig. 1. Flow-through membrane with wall thickness t_m and radius of the circular open channel a. The intraparticular flow direction (outward) is represented for $\hat{p}_{in} > \hat{p}_{out}$ with (superficial) velocity profile $\hat{u}$. Surface concentrations are $\hat{c}_1$ and $\hat{c}_2$.