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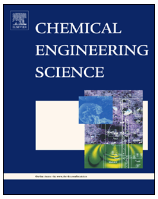

Multi-component mass transfer behavior in catalytic membrane reactors

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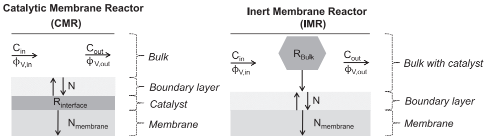
HIGHLIGHTS

- Comparison membrane reactors for different equilibrium reaction characteristics.
- Membrane reactors with catalyst confined on membrane surface or dispersed in bulk.
- Implications of multi-component mass transport on membrane reactor performance.
- Design directions for membrane reactors.
- Guidelines for optimal operation of membrane reactors.

GRAPHICAL ABSTRACT

Comparison between catalytic membrane reactor (CMR) and inert membrane reactor (IMR) for multi-component mass transfer behavior.



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ABSTRACT

Numerical simulations are presented to compare mass transfer at the bulk fluid-membrane interface of two types of membrane reactors, for arbitrary equilibrium reactions: the catalytic membrane reactor (CMR) in which the location of the reaction and separation coincide, and the inert membrane reactor (IMR) in which locations of reaction and separation distinct. The Maxwell–Stefan theory is adopted to describe this multi-component mass transport and to take friction between the species in the reaction mixture into account. Simulation results are presented that aid selection of the most appropriate reactor configuration for different reaction equilibrium characteristics. Effects of process conditions, membrane properties, and possibilities to optimize reactor design are discussed.

Three regimes can be distinguished, based on the value of reaction equilibrium constant (K_{eq}). At very low K_{eq}, the CMR outperforms the IMR, and in particular a high membrane area/reactor volume ratio (A/V), a high product permeance, and a large residence time are required. At moderate K_{eq}, the CMR potentially outperforms the IMR, and conversion benefits in particular from a high A/V ratio and sufficiently high mass transfer. For high K_{eq} the performance of the IMR is superior as compared to the CMR.

The simulation results indicate that, in particular for the CMR, a mass transport description that can properly address multi-component mass transport characteristics is vital. The results predicted based the Maxwell–Stefan theory will not be captured adequately by a model based on, for instance, the law of Fick.

1. Introduction

Process intensification combining two or more unit operations may reduce investment costs and increase energy efficiency. Examples include membrane reactors in which chemical reaction

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and membrane separation are united. A prospective major application of membrane reactors is the selective in-situ removal of one or more components from the reactor aiding a shift in the equilibrium of thermodynamically limited reactions to the product side. Typical examples of such reactions are dehydrogenation processes such as that of light alkanes to alkenes (Champagnie et al., 1992) or cyclohexane to benzene (Gryaznov, 1992; Itoh, 1987). In these two reactions, the selective removal of hydrogen from the reaction mixture using palladium membranes enhanced the reaction rate and conversion exceeded thermodynamic equilibrium. Additionally, the removed hydrogen could be coupled to a hydrogenation reaction at the permeate side of the membrane in a so-called coupling reaction as Gryaznov (1992) showed for the hydrogenation of pentadiene. Over the years, many more examples on the use of membrane reactors enhancing equilibrium limited reactions are reported, such as the water-gas-shift reaction (Criscuoli et al., 2000; Uemiya et al., 1991) and esterification reactions (Bagnell et al., 1993; Bernal et al., 2002; Keurentjes et al., 1994; Korkmaz et al., 2011). Different review articles are available that summarize the extensive work done in the field of membrane reactors (Armor, 1998; Coronas and Santamaria, 1999; Cybulski and Moulijn, 2006; Diban et al., 2013; Dong et al., 2011; Gallucci et al., 2013; Sanchez and Tsotsis, 2002; Zaman and Chakma, 1994).

Sanchez and Tsotsis (2002) distinguish six different membrane reactor configurations, each having its own characteristics. In this work we focus on two configurations that address the difference in multi-component mass transfer behavior the most

- Catalytic membrane reactor (CMR): In this reactor the membrane exhibits catalytic activity, causing the location of reaction and separation to coincide. The catalytic activity of the membrane can be inherent to the membrane material (e.g., zeolites (Bernal et al., 2002)) or can be achieved by coating the membrane with a catalytically active material (Peters et al., 2004). Technical complexity of CMRs will imply relatively high investment costs.
- Inert membrane reactor (IMR): In this reactor the membrane does not exhibit catalytic activity. The locations of reaction and molecular separation are distinct and reactants must be transported from the reaction zone (for instance the fluid bulk) to the membrane surface before they can be removed from the reactor. As compared to a CMR, the less complex design of an IMR will imply lower investment costs.

In literature these types of membrane reactors are often compared with more conventional fixed bed reactors (FBR). Typical early work is that of Sun and Khang (1988) who investigated if CMRs and IMRs could overcome equilibrium limitations for the dehydrogenation of cyclohexane (Sun and Khang, 1988). But also in more recent work, Bernal et al. (2002) evaluated the three earlier mentioned reactor configurations for the esterification of ethanol with acetic acid. They found the highest conversion for the CMR and the lowest for the FBR and attributed this to additional transport resistances in the FBR and the IMR, as compared to the CMR where the reaction occurs at the membrane (Bernal et al., 2002).

Much work is done on investigating the influence of process and material parameters on the conversion in membrane reactors. For example the effect of space time (Sun and Khang, 1988), reaction time/transport ratio, membrane selectivity (Lim et al., 2002), membrane area and feed ratio (Feng and Huang, 1996) is reported.

In addition to this, also membrane reactor design and the influence of the catalyst is subject of research. Yeung et al. (1994) concluded that a Dirac delta distribution of the catalyst placed at the feed side outperforms a uniform catalyst distribution. Basically this means that the reaction should take place as close to the membrane as possible, while the remainder of the membrane should operate as a separator (Saracco et al., 2006; Yeung et al., 1994). Work of Peters et al. (2004) described the mass transfer characteristics inside the catalyst layer of a CMR as the function of the catalyst thickness and compared that with an IMR. They found that CMRs outperform IMRs, but with an increasing catalyst thickness this advantages disappears due to diffusion limitations within the catalyst layer (Peters et al., 2004).

Although previous papers often compare the performance of CMRs and IMRs, mass transport towards the membrane is often neglected (e.g. gas phase) or described considering relatively straightforward theories such as Fick's law. Although the use of Fick's law is an elegant, very valuable and relatively easy to apply approach, it is a simplification of reality and the exact inaccuracy is difficult to estimate. Mass transport in CMRs is a complex multi-component process. The removal of one or more species through the membrane results in an overall drift flux, causing concentration polarization of reactants and products. The concentration of species that are retained by the membrane will increase at the catalytic membrane interface, and these species will diffuse back towards the liquid bulk. The concentration of species that permeate through the membrane will be lowered at the membrane interface, resulting in an increased diffusion towards the membrane.

In the present article, we use the Maxwell–Stefan theory to describe mass transfer in a membrane reactor. The Maxwell–Stefan approach inherently accounts for a drift flux and the friction between each component *i* and *j* present in the reaction mixture (Wesselingh and Krishna, 2000). We explicitly use this Maxwell–Stefan approach to describe mass transfer solely at the interface between fluid bulk and membrane to compare both reactor concepts (IMR and CMR), but we do not intent to provide an advanced mathematical description of an entire membrane reactor.

Simulation results are presented and the impact of different process and material properties the mass transfer is studied. While conclusion from existing literature are usually reaction specific and extrapolation to other reactions is not always straightforward, this work has a generic approach and can be translated towards any equilibrium reaction. As such, it describes mass transfer at the bulk fluid-membrane interface in an IMR and CMR for arbitrary equilibrium reactions, while taking into account the friction between the species in the reaction mixture.

2. Theory

2.1. Membrane reactor modeling

Two membrane reactor configurations are considered, as schematically depicted in Fig. 1.

Both reactors are operated in a continuous mode and their bulk is considered ideally stirred. For each component present, the corresponding mass balance over the bulk is given by:

$$0=(\phi_v x_i c_{tot})_{in}-(\phi_v x_i c_{tot})_{out}+\nu_i V R_{bulk}-AN_i \tag{1}$$

where ϕ_V is the volume flow [m^3/s], x_i is the molar fraction of species *i*, c_{tot} is the total concentration [mol/m^3], ν_i is the stoichiometric coefficient of component *i* [-], *V* is reactor volume [m^3], R_{bulk} is the rate of the reaction occurring in the bulk [$mol/m^3 \cdot s$], *A* is the membrane surface area [m^2] and N_i is the flux of component *i* through the boundary layer [$mol/m^2 \cdot s$].

Due to the overall molar production or consumption by chemical reaction and removal of components through the membrane, $\phi_{\text{V,out}}$ is not necessarily equal to $\phi_{\text{V,in}}$. There are *nc* mass balances, containing $2nc+3$ unknowns (x_1,.., x_{nc}, N_1,…, N_{nc}, *R*, c_{tot},