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Process intensification by exploiting Dean vortices in catalytic membrane microreactors

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HIGHLIGHTS

- A catalytic membrane microreactor is modelled analytically and numerically.
- A curved geometry is modelled to quantify the effect of passive mixing.
- An effective singularity treatment is devised for non-axisymmetric systems.
- Results depict a significant improvement in conversion and catalyst utilization.

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ABSTRACT

In this work, a mathematical model is developed for a heterogeneously catalyzed reaction in a porous membrane micro-reactor. Hydrogenation of an aqueous nitrite contaminant in water is analyzed as a model reaction. For a straight micro-reactor a numerical algorithm is developed to predict the behavior for non-linear kinetics. This is validated with a semi-analytical solution based on separation of variables under the assumptions of linear kinetics. Predictions of the non-linear model are compared with experimental observations reported in the literature. Analysis shows that the straight reactor is inefficient and catalyst utilization is poor when higher throughputs are required because the system is diffusion limited. A modified design is proposed which incorporates curving of the microchannel to induce passive mixing by generating "Dean Vortices". The velocity fields are obtained using a perturbation analysis. This is incorporated in solving the convection-diffusion-reaction system which governs the species transport. The non-linear system of equations is solved using an operator splitting technique. The numerical singularity at the center of the curved channel is dealt by transforming the governing equations in the vicinity of $r = 0$ using Cartesian coordinates. The curving of the reactor results in a significant improvement in conversion for higher flow rates, with enhanced catalyst utilization. The non-monotonic enhancement in Sherwood number is interpreted by analyzing the dynamics of the concentration depletion layer.

1. Introduction

Microreactors are well known to be a versatile and an efficient alternative to conventional reactors for small scale on-site production of chemicals (Elvira et al., 2013). This miniaturization of reactors is characterized by a high surface area to volume ratio, which is advantageous for mass transfer limited reactions. Membranes provide a "selective barrier" in microreactors, which enables us to control reactions (Fogler, 2013). The catalytically active sites inside the membrane provide a large surface area for the reaction to occur. Heterogeneously catalyzed membrane microreactors (CMMR) have been studied for more than a decade. Some of the earlier work on this was by Yeung et al. (2005). They miniaturized catalytic membrane reactors to micro-scale and attained supra-equilibrium conditions by incorporating zeolites. Inoue et al. (2007) and Pashkova et al. (2008) extended the idea of using catalyzed membrane microreactors for controlling direct synthesis of hydrogen peroxide. It was established that a higher yield and selectivity of desired product could be obtained by avoiding the explosive limit. Since then, a significant amount of modelling and experimental study has been carried out on various reactions which require controlled stoichiometry for higher yield (Pashkova et al., 2010; Selinsek et al., 2016, 2015). Recently, Jani et al. (2012) and Aran et al. (2012) have used CFD modelling and experiments for analyzing treatment of a nitrite contaminated aqueous stream using a heterogeneously catalyzed membrane microreactor. Using a CMMR allows us to reduce or eliminate

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undesired parallel side reaction giving rise to ammonia production in the effluent stream. Their process involves nitrite ion hydrogenation over a palladium catalyst. However, the process being diffusion limited gives a low yield at higher flowrates. The denitrification reaction (Chinthaginjala and Lefferts, 2010; Wehbe et al., 2010) is:

$$2NO_2^- + 3H_2 \overset{Pd}{\rightarrow} N_2 + 2OH^- + 2H_2O \tag{1}$$

In Section 2 of this work we propose a 2-dimensional steady state mathematical model for a CMMR based on experimental studies of Aran (2011). Kinetics established for denitrification reaction are non-linear. However under the assumption of first order or linear kinetics a semi-analytical solution is obtained in Section 3. A numerical algorithm based on finite differences is benchmarked with an analytical solution. This is extended to the full non-linear model, and its predictions are compared with the experimental data (Aran et al., 2011). The process is diffusion limited due to the low diffusion coefficient of nitrite in water and low internal diffusion inside the catalyst (Zhao et al., 2015). At higher Reynolds numbers the yield is low, catalyst exploitation is poor and hence achieving higher throughput poses a challenge.

Further we propose a modification in the reactor geometry which includes curving of the reactor for process intensification. This is analyzed theoretically. When a fluid flows through a curved channel because of the centrifugal forces the Poiseuille flow profile gets disrupted and Dean vortices are generated. These secondary vortices enhance transverse mixing and have been studied and employed in the past in ultrafiltration using coiled hollow fibers (Manno et al., 1998), heat transfer enhancement (Ligrani et al., 1996; Seban and McLaughlin, 1963), gas-liquid contactors in spiral and helical channels (Moulin et al., 1996; Jani et al., 2011) and extraction studies (Picardo and Pushpavanam, 2013). Nigam et al. (2001) and Balasubramanian et al. (2003) have performed theoretical study on bulk and surface reaction in curved microchannels. To the best knowledge of the authors, not much work has been done on inducing passive or active mixing in catalytic membrane microreactors to reduce external diffusion limitations in the process. The second part of this study focusses on the quantification of the enhancement obtained by curving a CMMR. It focusses on the interactions between hydrodynamics of the secondary flow coupled with the mass transport and reaction. Section 4 describes the flow-field and equations governing the species transport in the toroidal coordinate system. The operator splitting technique used in the numerical solution is discussed here. Since the flow is non-symmetric, the governing equation is satisfied at $r = 0$. The presence of $1/r$ terms poses a numerical singularity at the center of the channel. An effective singularity treatment methodology is devised which incorporates imposing a Cartesian coordinates in the toroidal grid in the vicinity of $r = 0$. The details of this method are provided in Appendix A. In Section 5, results of the reactor intensification are described using three characteristics: conversion, effective length of the reactor and utilization of catalyst inside the membrane. We observe a non-monotonic enhancement of Sherwood number for the curved geometry. This is found to be closely related to the development of concentration profile and mass transfer to the boundaries. The main conclusions of this study are discussed in Section 6.

2. Process description

A schematic of the membrane reactor is shown in Fig. 1(a). The reactor consists of a cylindrical core whose walls are made of a porous membrane. The aqueous solution (containing nitrite ions) flows in the axial direction in the reactor core. The hydrogen gas flows co-currently outside the membrane wall. The membrane wall is made of two porous layers. The inner layer is a γ-alumina catalyst embedded layer which is hydrophilic. This is wetted by the aqueous phase as shown in Fig. 1(b). The outer layer is an outer α-alumina (hydrophobic) support layer through which hydrogen gas enters the reactor.

The dissolved nitrite ions diffuse radially into the hydrophilic subdomain of the membrane, which has Pd embedded in it. Hydrogen gas diffuses freely through the outer support layer, and then through the liquid filled hydrophilic Pd-embedded layer. The hydrophobicity of the support layer ensures a stable gas-liquid interface as shown in Fig. 1(b). Consequently, the computational domain is separated into two sub-sections as shown in Fig. 2:

1. $0 < r < R$ (Region-I): This is the hollow central core through which the liquid flows axially and species transport takes place by diffusion in the radial direction. A radial concentration gradient is established by reaction in the hydrophilic part of the membrane. In the core region, no reaction takes place, the species transport here occurs by convection and diffusion.
2. $R < r < R + \delta$ (Region-II): Here H_2 is assumed to be saturated at the gas-liquid interface ($r = R + \delta$) and diffuses into the liquid phase in the membrane pores to react with the nitrite ions over the immobilized Pd catalyst. In this zone the transport of all the species is primarily by radial diffusion.

2.1. Reaction kinetics

Aran et al. (2012) and other experimental investigations (Chinthaginjala and Lefferts, 2010) have reported a kinetic rate expression of the form:

$$R_s = k_s C_l^n C_g^0 \tag{2}$$

where C_g and C_l are the concentrations of gas (H_2) and liquid reactants (NO_2^-) in the aqueous medium.

Chinthaginjala and Lefferts (2010) determined the exponent of nitrite ion concentration ‘n’ to be 0.7. The reaction rate was found to be independent of hydrogen concentration over a wide range of operating conditions. This suggests that the Pd catalyst surface is almost completely covered with hydrogen for the reaction conditions analyzed (Aran et al., 2011). Hence the H_2 dependency is neglected. The kinetic parameter rate constant used in this work is that reported by Jani et al. (2012).

The mathematical model is based on the following assumptions:

(1) In the core ($0 < r < R$) the axial diffusion is ignored because the ratio of time scales of diffusion to that of convection in the axial direction is very high ($\sim 10^4$).
(2) The pore size distribution is uniform and the system is axisymmetric.
(3) The gas-liquid interface is stable and lies at $r = R + \delta$, throughout the reactor length. Here a constant transmembrane pressure is maintained.
(4) The gas liquid interface is assumed to be saturated with hydrogen at the inlet pressure of H_2.

3. Analysis of the straight channel

3.1. Governing equations

Since the wall ($r = 1$) of the microchannel is permeable (non-rigid), a finite tangential velocity can exist at the wall. Beavers and Joseph (1967) have experimentally estimated the amount of slip on naturally permeable surfaces. Saffman (1971) have analytically estimated the slip being a function material properties using