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A mathematical model for zeolite membrane module performance and its use for techno-economic evaluation of improved energy efficiency hybrid membrane-distillation processes for butane isomer separations

Nitish Mittal [a], Peng Bai [a], Adam Kelloway [a], J. Ilja Siepmann [a,b], Prodromos Daoutidis [a], Michael Tsapatsis [a,*]

[a] Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455, USA
[b] Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455, USA

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ABSTRACT

The aim of this work is to develop enabling tools that can assess the potential of zeolite membranes for industrial applications. The specific objectives are: (1) Develop a detailed mathematical model of a zeolite membrane separation process for accurate performance prediction under industrial conditions, and (2) Perform conceptual process design and techno-economic evaluation of the overall process for an application specific flowsheet. To this end, a detailed mathematical model, based on the real adsorption solution (RAS) theory and the Maxwell-Stefan formulation for transport was developed to describe permeation through a zeolite membrane. Effects like support resistances to transport, use of sweep gas and concentration polarization were included. The model is further applied to study butane isomer separation using a MFI-type zeolite membrane. A comparison of steady state flux and separation factor predicted by the model with the experimentally determined values suggests that the permeation in the real membranes is lower than that for the zeolite crystals. This lower permeance is attributed to the microstructural defects and suggests that there is a considerable scope of improvement in the performance of current state-of-the-art real MFI membranes. It is shown that up to a 10-fold increase in permeance through the membrane is practical, beyond which the external resistance starts to dominate. Furthermore, the detailed zeolite membrane model is integrated into a process level simulation, to evaluate the membrane performance in industrial settings, and a techno-economic analysis is also performed to this end. While single stage membrane process does not achieve the target purity and multi-stage membrane process requires prohibitively large area, a hybrid membrane/distillation process is found to be energy efficient and economically attractive.

1. Introduction

Zeolite membranes offer an attractive alternative to conventional energy intensive separation processes [1–5]. Their chemical and thermal stability, and well-defined pore structure with pore sizes ranging from 0.3 to 1.0 nm allow for high-selectivity separations at a wide range of operating conditions. Although zeolite membranes have shown remarkable progress at laboratory scale [6–14] and promising results have been obtained for various industrially relevant applications such as alcohol dehydration [12,15–18], butane isomer separation [11,19–23], xylene isomer separation [20–23] and natural gas purification [24–27], only hydrophilic membranes used in the dehydration of industrial solvents and fuels have been commercialized to date [5,13]. To explore the commercialization potential of zeolite membranes, rigorous models and process designs which can predict the currently achieved performance and set targets for membrane cost and performance improvements are essential.

In order to predict the separation performance of zeolite membranes, a fundamental understanding of transport phenomena underlying the membrane operation, and models that can quantitatively describe these phenomena, are necessary. Permeation through a zeolite membrane is a complex process that depends on both the adsorption and diffusion properties of the permeating species in the mixture [8,15,28–34]. When the size of the molecules permeating through the zeolite pores is comparable to the pore diameter, which is often the case for selective separation, molecules permeate at a regime commonly known as intracrystalline or configurational diffusion. The adsorption and diffusion properties at this microscopic level are obtained using

* Corresponding author.
E-mail address: tsapa001@umn.edu (M. Tsapatsis).

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experimental and simulation techniques, fitted to adsorption and diffusion models, and then finally used in continuum models to determine the flux through the zeolite membranes. While most modeling studies employ simple ideal theories based on single-component adsorption and diffusion properties [35–40], the intermolecular interactions can be far from ideal and may lead to the failure of these theories [41–47].

In addition to the adsorption and diffusion based transport through zeolite layer, factors such as mass transfer through the porous support, the use of a sweep gas and the concentration polarization phenomenon can also play a significant role [13]. The support is particularly important for membranes with thin zeolite films as the resistance of the support layer can dominate the transport through the membrane [16,37,48,49]. The use of sweep gas increases the driving force for permeation by carrying away permeating species. In most of the modeling studies aiming at interpretation of laboratory results, this effect is incorporated by assuming zero partial pressure of the permeating species on the permeate side [42,50,51]. However, even a low value of partial pressure can significantly affect the performance, especially for strongly adsorbing components where significant changes in loading occurs even at pressure below 1 mbar [52–54]. Moreover, there is also an adverse effect on permeation due to the counter flux of sweep gas [55,56]. The concentration polarization can occur because different species in a feed mixture permeate at different rates through the membrane, which may result in accumulation of the non-preferentially permeating species and depletion of the selectively permeating species in a thin layer (boundary layer) adjacent to the membrane surface. This phenomenon changes the concentration gradient through the membrane in an unfavorable manner and deteriorates the membrane separation performance [15,52,54,57]. Thus, mathematical models which can describe the support layer, permeation of sweep gas, and concentration polarization phenomenon should also be incorporated in the design of zeolite membrane systems.

These rather complicated models should be validated by comparison with experiments and included in the process models that describe permeation through membranes at a wide range of operating conditions as encountered by membranes in industrial use.

Here, a rigorous mathematical model is developed to describe the permeation through a randomly oriented 500 nm thick MFI zeolite layer. The Maxwell-Stefan formulation [58], which accounts for transport through an adsorption-diffusion mechanism is used to model permeation through the zeolite film. The mixture adsorption is modeled using the real (non-ideal) adsorption solution theory, while the non-idealities in the diffusion process are incorporated through a phenomenon known as intersection blocking [59]. The porous support is modeled considering contributions from Knudsen and molecular diffusion, and viscous flow. The pore size, porosity, and tortuosity of the support layer are considered to be 3 μm, 0.3 and 2.5, respectively. Support thicknesses of 1 mm and 3 mm are used. The sweep gas is regarded as an additional component and its permeation is modeled through both the zeolite layer and the support layer. The concentration polarization is accounted for by using a parameter known as concentration polarization index, which has been derived by solving the mass-transport equations in the boundary layer [60]. Furthermore, this detailed zeolite membrane model is incorporated into a conceptual level process model to analyze the performance of zeolite membranes in industrial settings. These models can be used to assess the commercialization potential of zeolite membranes in various industrially relevant applications. The separation of butane isomers (*n*-butane and 2-methylpropane or *i*-butane) using MFI-type zeolite is assessed here. The butane isomer separation is selected because the availability of both (i) molecular level transport properties and (ii) industrial scale distillation data allows for a rigorous mathematical description of membrane performance and its detailed comparison with the current industrial practice. Moreover, butanes offer a great opportunity for implementation of novel separation technologies since they are used as a fuel and as a feedstock to make plastics, and their global market is growing at an annual rate of ~2.5% and is expected to reach ~240 million tons by 2018 [61].

2. Theory

A schematic of the membrane structure in a typical laboratory setting is shown in Fig. 1a. The membrane structure consists of a zeolite layer on a porous support. The feed stream is passed across the retentate side facing the zeolite film, and the permeating species are collected by flowing a sweep gas across the permeate side. Compartments on both sides of the membrane i.e., the retentate side and the permeate side are assumed to be well-mixed.

2.1. Zeolite layer

Krishna and co-workers [50,58,62–65] have extended the Maxwell–Stefan approach, which provides a fundamental description of multi-component diffusion, to formulate the generalized Maxwell–Stefan model for permeation through a zeolite membrane:

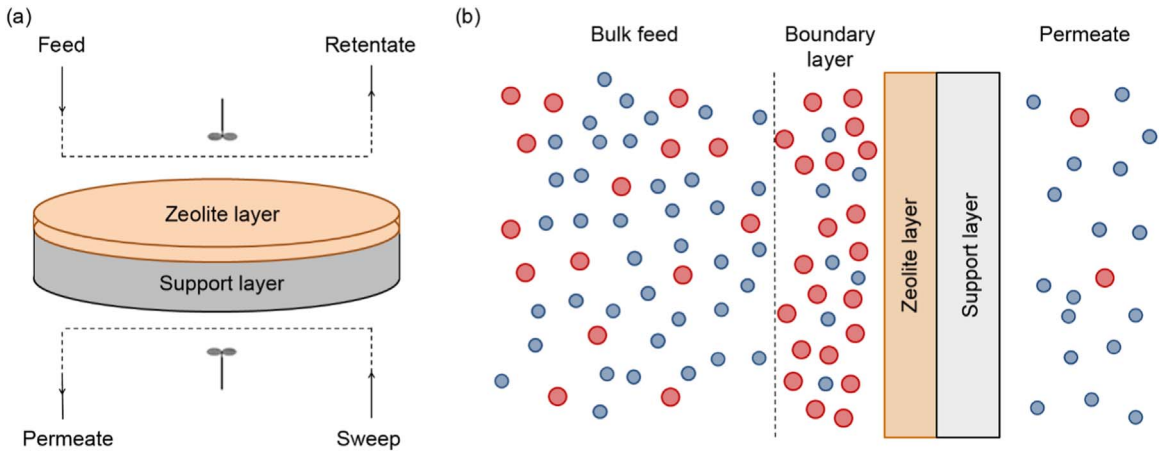

Fig. 1. (a) Schematic of a zeolite membrane in a typical laboratory setting. (b) Concentration polarization leading to depletion of preferentially permeating component (◦) and accumulation of less/slower permeating component (◦) at the membrane surface.