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Effective approximations for concentration-polarization in Pd-membrane separators

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HIGHLIGHTS

- Approximate models for predicting the hydrogen flux of membrane separator are derived.
- The models combine ODE equations and algebraic relations to predict 2-D profiles.
- An analytical expression for Sherwood number is derived.
- The models are validated by comparison with experimental data and CFD simulations.
- The concentration polarization effect is relatively small in most cases.

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ABSTRACT

Approximate models are proposed to simulate the transmembrane hydrogen flux in an empty membrane separator. The hydrodynamic field is constructed under the assumption of constant density with a single unknown parameter – the normal wall velocity (v_w). The 2-D concentration profiles are derived using a known velocity distribution. The problem is closed by definition of v_w via the transmembrane flux, which admits Sievert's law. Such an approach allows to derive two approximate models that are governed by the set of ODE equations with respect to the average variables coupled with algebraic relations to describe the radial profiles. The first model accounts for analytical concentration profiles $c_i(z,r)$, the second one presents model reduction using the mass transfer coefficient (k_c) expressed as Sherwood (Sh) number. An analytical expression for local Sh is derived (Sh = 6 in a tube).

We identified a parameter Γ which represents the ratio of diffusive to permeating flux and suggest that for $\Gamma > 6$ the concentration polarization effect can be neglected. We address two axisymmetric geometries (i) a tube with transport at its wall, as is the case in a membrane of an integrated reactor; (ii) an annular cylinder with transport at an inner tube, as is the case in a separator. The proposed approximations are validated by comparison with experimental and CFD simulation data.

1. Introduction

Membrane reactors and separators are usually described by a 1-D model. With the incorporation of membranes of better permeance and the integration of heat supply to the reactor through its wall, radial gradients in membrane reactors may become important. The separation of hydrogen at the membrane wall will cause, in a wide reactor, its concentration to be different than that in the bulk, while that of the other species will be larger (concentration polarization). That will diminish the hydrogen gradient, and the effect may be compounded by increased permeance inhibition if one of the other species adsorbs well on the membrane.

Permeance measurements are usually conducted in empty (unpacked) shell and tube arrangement, with a hydrogen mixture in inerts (or in reactants or products). Measurements with pure hydrogen feed yield directly the permeance, the constant in Sievert's law [1]

$$J_{H2w} = K_{H2}\left(\sqrt{p^{ret}_{H2w}} - \sqrt{p^{per}_{H2w}}\right) \quad (1)$$

but such values usually differ than those made in a mixture. This suggests that hydrodynamic effects on diffusive transport are important and should be accounted for. The impact of concentration polarization on reducing the apparent constant of Sievert's law, compared with that measured in hydrogen, or its effect on deviation from the Sievert's law was measured experimentally in many systems [2–11]. Other sources for permeance inhibition, like

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Nomenclature

A_u	coefficient used to define the axial velocity profile (8)
B_i	constant used to define the radial concentration profile (37)
C	molar density
D_i	diffusion coefficient for i-th component in Fick's law
$f(r)$	function used to define the axial velocity profile (8)
$g(r)$	function used to define the radial concentration profile (38)
$G(r)$	function defined by Eq. (B.3)
J	molar flux
$F(r)$	function defined by Eq. (10)
k_c	mass transfer coefficient
K_{H2}	permeability coefficient in Sievert's law (1)
L	reactor length
M_i	molecular mass of i-th component
P	pressure
P	perimeter
r	radial coordinate
R	gas constants
S	reactor cross-section
Sh	Sherwood number
T	temperature
u	axial velocity component
v	radial velocity component
y_i	molar fraction of i-th component
z	axial coordinate

Greek letters

Γ	parameter defined by Eq. (66)
κ	parameter defined in Eq. (63)
μ	dynamic viscosity
ρ	density

Subscripts

i	component i
tot	total
w	permeable wall

Superscripts

an	annular
tb	tube
per	permeate
ret	retentate

competitive absorption, are known but are not addressed in the present paper.

Radial gradients may become significant in two common cases: (i) hydrogen transport into or from a stream of inert (sweep) gas, in the absence of catalyst and of reaction. This is the case in permeance measurements where hydrogen permeates from one stream to another, or in the design of a membrane hydrogen separator. This is also the case of transport to the permeate section in an integrated membrane reactor, where the separated hydrogen is swept in a stream of nitrogen or steam in order to increase the driving force for separation by the membrane. In these situations the velocity, $v(z,r)$, is usually laminar and radial diffusion (D_{er}) is molecular, which is small at high pressures. (ii) Radial gradients become important also in a packed catalytic membrane reactor, where the flow in the catalytic chamber is turbulent (assuming $u(r)$ to be flat) and the radial dispersion depends on flow rate and particle size (d_p), e.g. by commonly applied correlations [12]. In this case radial gradients are smaller due to turbulent dispersion and this case is not addressed here.

Prediction of radial diffusion effects in a channel follows the classical works by Taylor and Aris [13,14] where the approximate solution for the 2-D convection–diffusion problem was constructed for a laminar flow in a circular tube with an impermeable wall. The employed strategy there was based on a separate consideration of a "frozen" parabolic velocity profile corresponding to an incompressible (Poiseulle) flow and the concentration balance equations. This approach, known as the Taylor–Aris dispersion, was intensively developed in following studies accounting either for geometrical factors [15] or/and a catalytic wall reaction [16,17] and address the channels with impermeable walls. In such a case the hydrodynamic problem can be solved separately under the assumption of the incompressible flow.

To account for radial gradients in membrane reactors with permeable walls several studies have presented 2-D numerical simulations of mass and momentum balances for the permeance measurement application [2,9–11,18–21]. Such studies require special software like COMSOL or FLUENT, or original homemade codes and do not allow to derive a design criterion predicting when this effect can be ignored. Semi-empirical approximations in the form of effective mass transfer resistance or concentration polarization were addressed in Refs. [8,9,18,22–25]. The experimentally measured mass transfer coefficient (k_c) was expressed in the form of Sherwood number, as $\mathrm{Sh} = k_c R/cD = f(\mathrm{Re}, \mathrm{Sc})$ in Ref. [8].

The main objective of this contribution is to develop an approximation, based on a fluid dynamics model, to assess the effect of steady state concentration polarization in an empty membrane separator (case i above). The main effort is focused on predicting of the transversal velocity component due to the transmembrane flux (permeable wall conditions). The approximate 2-D solution of the hydrodynamic problem is constructed separately, under the assumption of an isothermal flow with a constant density, as functions of a single parameter – the normal velocity at the wall (v_w). The 2-D concentration profiles are derived using a known velocity distribution and a specific (Robin) type boundary conditions. The problem is closed by definition of v_w via the transmembrane flux which, in turn, depends on the wall concentrations.

Such an approach allows us to derive approximate models that are governed by the set of ODE equations with respect to the average variables coupled with algebraic relations to describe the radial profiles. We address two axisymmetric geometries (i) a tube with transport at its wall, (ii) an annular cylinder with transport at the outer channel. Both geometries can be considered either separately or as an integrated reactor with a retentate and a permeate channels.

Two approximate models are considered: the first one accounts for analytical 2-D concentration profiles $c_i(z,r)$, the second one presents its 1-D reduction using Sherwood (Sh) number (i.e. of k_c). We propose an analytical expression for local Sh and a parameter (Γ) which represents the ratio of diffusive to permeating flux and defines the concentration polarization effect. The proposed approximations are validated by comparison with experimental and CFD simulation data.

We show that indeed $\mathrm{Sh} \sim 6$ for a tube (when the diameter is the characteristic length), but since the driving force varies along the reactor, the average resistance depends on the fluid average velocity and apparently on Re. Moreover, analysis of experimental