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On the modeling of one-dimensional membrane reactors: Application to hydrogen production in fixed packed bed

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ABSTRACT

Hydrogen production by steam-methane reforming in membrane-assisted reactors has attracted substantial interest over the years. A variety of models for membrane-assisted reactors have been developed and suggested in the literature. In particular, examining the membrane models applied to the fixed packed bed reactor concept, there is no consensus or guidelines in the literature regarding the formulation of the heat balances (in terms of temperature). Thus, in the present study, different mathematical models for a fixed packed bed reactor with an integrated membrane have been compared in order to elucidate the effects of different model assumptions formulating the heat balance. The model formulations were examined by application to the steam-methane reforming process with hydrogen removal. The main findings of the present theoretical study are:

- With an increased temperature difference between the reaction and permeation zones, the enthalpy associated with the mass flux across the membrane has an increased effect on the temperature in the permeation zone.
- The temperature profile in the reaction zone is not influenced by the enthalpy difference across the membrane. Hence, in cases where it is not required with an accurate model prediction of the sweep gas temperature, the membrane reactor model can be simplified assuming isothermal condition in the permeation zone.

The present study presents a rigorous derivation and examination of cross-sectional averaged models for membrane-assisted fixed packed bed reactors. Considering the level of details in the model formulations analyzed in this study, there exists currently no appropriate experimental data for model validations.

1. Introduction

Steam-methane reforming of natural gas represents the principal commercial route to hydrogen production. To overcome the thermodynamical limitations the traditional process of steam-methane reforming may be modified through in-situ separation of one of the products to drive the reaction beyond its thermodynamic equilibrium. This can be achieved by combining the process of steam reforming with adsorption or membrane separation [1]. The combined technologies of CO_2-capture and hydrogen removal by membranes may even be unified in the same reactor configuration [2,3]. However, the present study is limited to focus on the membrane-assisted steam–methane reforming process.

A large number of scientific papers are published on the integration of membranes for hydrogen removal in steam-methane reformers. The mathematical modeling studies are particularly related to the development of mass flux models of hydrogen through the membrane and the development of membrane reactor models. In particular, evaluating the membrane reactor models in the literature there is no clear guidelines regarding the formulation of the heat balances. Thus, in the present study a plug-flow fixed-packed bed reactor with a Pd-Ag membrane is employed to investigate different assumption deriving the heat balances and their effects on the chemical process. The interesting assumptions related to the formulation of the heat balances are: (i) isothermal condition in the permeation zone, (ii) effect of the energy gained in the permeation zone due to the enthalpy transfer due to the mass flux across the membrane, and (iii) the relative impact on the temperature in the permeation zone induced by the overall

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Notation

Latin letters

A	area, cross-section, surface
A_p	cross-sectional area of permeation zone
A_r	cross-sectional area of reaction zone
B	permeability
$\mathbf{B}$	tensor or vector
C_p	heat capacity
d_p	diameter catalyst
e	internal energy
$\mathbf{e}$	unit vector
l	intersection of the control volume interface with the cross-sectional plane, line
$\bar{h}_c$	partial molar enthalpy of species c in a mixture ($= M_c \check{h}_c$)
$\mathbf{J}$	diffusive flux
$\mathbf{j}$	mass diffusion flux
$j_{m,\mathrm{H_2}}$	mass diffusion flux of H_2 through the membrane
$j_{m,\mathrm{H_2}}^{r\to p}$	flux of H_2 through the membrane from the reaction zone to the permeation zone
$\dot{m}$	mass flow rate
M_c	molecular weight of species c
$\mathbf{n}$	unit vector
N_{rx}	number of chemical reactions
N_{comp}	number of species
p	pressure
$\mathbf{r}$	radial vector
r_k	reaction rate of reaction k
$r_{i,i}$	internal tube internal radius
$r_{i,o}$	external tube inner radius
$r_{o,i}$	internal tube outer radius
$r_{o,o}$	external tube outer radius
Re	Reynolds number
R_j	source term of species j due to reactions
S	perimeter
$S_{i,i}$	perimeter, internal tube internal radius
$S_{i,o}$	perimeter, external tube inner radius
$S_{o,i}$	perimeter, internal tube outer radius
$S_{o,o}$	perimeter, external tube outer radius
s	length
T	temperature
$\mathbf{T}$	total stress tensor
t	time
U_i	overall heat transfer coefficient, internal tube
U_o	overall heat transfer coefficient, outer tube
$\mathbf{q}$	heat flux
$q_w^{r\to a}$	heat flux through a wall, defined in the direction from reactor zone to the ambient zone
$q_m^{r\to p}$	heat flux through a membrane, defined in the direction from reactor zone to the permeation zone
$\mathbf{v}$	velocity vector
y_j	mole fraction of species j
z	axial direction, coordinate

Greek letters

α	area fraction
δ	membrane thickness
ρ	density
ψ	generalized quantity
ϕ	source term
Ψ	generalized function
λ	thermal conductivity, transport coefficient
μ	dynamic viscosity
ω_j	mass fraction of species j

Subscript

A	area, surface
amb	ambient
c	species
i	species
i	inner
j	membrane permeable species
k	reaction
l	line
m	membrane
o	outer
perm	permeation zone
react	reaction zone
w	outer wall
w	wall
z	axial direction, coordinate

Superscript

n	exponent
out	outlet of the reactor
perm	permeation zone
react	reaction zone

Operators

$\langle\bullet\rangle_A$	area averaging operator
$\langle\bullet\rangle_w$	wall averaging operator

heat transfer flux versus the enthalpy transfer across the membrane because of the mass flux through the membrane.

Several mathematical operations are required to deduce the cross-sectional averaged temperature equation from the local instantaneous energy balance of total (internal and kinetic) energy. The main mathematical operations are:

(i)The mechanical (kinetic) energy balance can be deduced from the momentum balance by forming the scalar product between the velocity field and the balance of momentum.
(ii) The mechanical (kinetic) energy balance is subtracted from the total (kinetic and internal) energy balance to obtain the internal energy balance.
(iii) The enthalpy definition $h = e + p/\rho$ is used to deduce the enthalpy equation from the internal energy equation.
(iv) A relation between the enthalpy and temperature is given by the total differential of the enthalpy. This relation is used to deduce the temperature equation from the enthalpy equation.
(v) The manipulations of the different energy equations in (i)–(iv) can be performed based on the local instantaneous equations, or the averaged forms of these equations. The final form of the temperature equation depends on at which stage (i.e., (i)–(iv)) the averaging operator is introduced [4]. In particular, the order of these mathematical operations influences on the existence of a term in the temperature equation that considers enthalpy transfer due to the mass flux across the permeable wall (membrane).

The derivation of the temperature equation is examined and presented in detail.