



An operability level coefficient (*OLC*) as a useful tool for correlating the performance of membrane reactors

S. Ted Oyama*, Hankwon Lim

Environmental Catalysis and Nanomaterials Laboratory, Department of Chemical Engineering (0211), Virginia Polytechnic Institute & State University, Blacksburg, VA 24061, United States

ARTICLE INFO

Article history:

Received 11 January 2009

Received in revised form 2 April 2009

Accepted 3 April 2009

Keywords:

Operability level coefficient

Damköhler number

Peclet number

Reforming

Hydrogen

Yield enhancement

Conversion enhancement

Correlation

Modeling

Simulation

ABSTRACT

An operability level coefficient (*OLC*), defined as the ratio of product permeation and product formation rates, and related to the inverse combination of the Damköhler number and the Peclet number ($1/DaPe$), is suggested as a useful tool for estimating performances of membrane reactors (MRs) operating as separators in equilibrium-limited reactions. The *OLCs* for product hydrogen formation in previously reported MRs for methane dry-reforming (MDR), methane steam-reforming (MSR), methanol steam-reforming (MeOHSR), and ethanol steam-reforming (EtOHSR) were correlated with conversion and yield enhancements. For values of *OLCs* ranging from 0.03 to 0.78, a clear universal trend for increasing conversions and hydrogen yields with increasing *OLC* was observed for these different types of reforming reactions. The *OLC* curve calculated from a numerical simulation without adjustable parameters was found to closely approximate experimental data obtained from the MRs, and was shown not to depend on the assumed kinetics. This study confirms that hydrogen selectivity (from the ratio of single-gas permeances) has a substantial influence on conversion and hydrogen yield enhancements in a MR, and demonstrates that a hydrogen selectivity of 100 is sufficient to achieve high performance in a MR.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Studies of packed-bed membrane reactors (MRs) combining catalytic reactions and separation have been carried out extensively for equilibrium-limited reactions, and improvements have been demonstrated in reactant conversions and product yields compared to packed-bed reactors (PBMRs). This has been particularly studied recently for reforming reactions that produce hydrogen such as methane dry-reforming (MDR) [1–3], methane steam-reforming (MSR) [4–8], methanol steam-reforming (MeOHSR) [9–11], and ethanol steam-reforming (EtOHSR) [12,13].

Kikuchi has proposed [14,15] that a membrane used in a MR should have three important properties: high permeability, high selectivity, and stability, and suggested that for hydrogen-producing reactors the hydrogen permeation rate through the membrane should be comparable to the hydrogen formation rate for better performance in the MR. Dixon has pointed out that, in general, the reaction rate, the permeation rate, and the reactant feed rate should be matched [16]. The effect of many parameters, such as temperature, pressure, space velocity, and sweep gas flow rate [17–19], as well as permeation rate and reaction rate [20] on the per-

formance of MRs have been considered. It has also been recognized in MR theory that two dimensionless groups, the Damköhler number (Da) and the Peclet number (Pe) are important for governing reactor behavior in isothermal [16,21] and non-isothermal [21–23,] operation, the latter in conjunction with the Stanton number. The inverse of the product of the two groups ($1/DaPe$) is a measure of the ratio of the permeation rate and the reaction rate (called the rate ratio δ by Mohan and Govind [21]), but despite its theoretical importance, it has not been used extensively to explain actual reactor behavior. Its use has been restricted to single reactions and it has not been employed across reactor systems.

This work presents a general parameter, the operability level coefficient (*OLC*), which can be used to correlate the performance of diverse membrane reactors. First, a general discussion of reactor theory is presented that describes the role of the Damköhler and Peclet numbers in MRs and explains their limitations. The *OLC* is shown to be related to the quantity ($1/DaPe$) which represents the ratio of the maximum permeation rate to the maximum reaction rate as generally obtained at feed conditions, but the *OLC* is evaluated at reaction conditions, so as will be shown, is easier to calculate. Second, the use of the *OLC* is shown to produce general correlations between conversion and yield enhancements for a variety of hydrogen-producing reactions [2–11,13]. Third, a MR model is used to reproduce the correlation curve, and to demonstrate that it is independent of the kinetic form of the rate

* Corresponding author. Tel.: +1 540 231 5309; fax: +1 540 231 5022.
E-mail address: oyama@vt.edu (S.T. Oyama).

Nomenclature

A_c	cross-sectional area of bed (m^2)
A_m	area of membrane (m^2)
d	reactor diameter (m)
$Da = (A_c L \rho_{\text{cat}} k P_{\text{tot}}) / F_{\text{tot}}$	Damköhler number (ratio of reaction rate to reactant feed rate) dimensionless
D_A	Fick's diffusion coefficient for reactant A ($\text{m}^2 \text{s}^{-1}$)
$1/DaPe = (Q_i A_m) / A_c L \rho_{\text{cat}} k$	inverse $DaPe$ product (ratio of permeation rate to reaction rate) dimensionless
F_A	molar flow rate of species A on retentate (shell) side (mol s^{-1})
F_A^O	inlet molar flow rate of species A on retentate (shell) side (mol s^{-1})
F_{Ar}	molar flow rate of argon on tube (permeate) side (mol s^{-1})
F_C^O	inlet molar flow rate of species C on retentate (shell) side (mol s^{-1})
F_i	molar flow rate of species i on retentate (shell) side (mol s^{-1})
F_i^{sweep}	molar flow rate of species i on permeate (sweep) side (mol s^{-1})
F_{tot}	total molar flow rate (retentate) side (mol s^{-1})
$F_{\text{tot}}^{\text{sweep}}$	total molar flow rate on tube (permeate) side (mol s^{-1})
k	reaction rate constant ($\text{mol g}^{-1} \text{s}^{-1} \text{atm}^{-1}$)
k_o	volumetric rate constant at inlet conditions ($\text{mol s}^{-1} \text{m}^{-3}$)
k_1	reaction rate constant of reaction 1 ($\text{mol s}^{-1} \text{g}^{-1} \text{atm}^{0.5}$)
k_2	reaction rate constant of reaction 2 ($\text{mol s}^{-1} \text{g}^{-1} \text{atm}^{-1}$)
k_3	reaction rate constant of reaction 3 ($\text{mol s}^{-1} \text{g}^{-1} \text{atm}^{0.5}$)
K_{CH_4}	adsorption equilibrium constant of CH_4 (atm^{-1})
K_{CO}	adsorption equilibrium constant of CO (atm^{-1})
K_{H_2}	adsorption equilibrium constant of H_2 (atm^{-1})
$K_{\text{H}_2\text{O}}$	adsorption equilibrium constant of H_2O (atm^{-1})
$K_{\text{H}_2}^P$	permeability constant of H_2 ($\text{mol m}^{-2} \text{g}^{-1} \text{s}^{-1} \text{atm}^{-1}$)
K_i^P	permeability constant of species i ($\text{mol m}^{-2} \text{g}^{-1} \text{s}^{-1} \text{atm}^{-1}$)
K_1	equilibrium constant of reaction 1 (atm^2)
K_2	equilibrium constant of reaction 2
L	catalyst bed length (m)
P_{tot}	total pressure on retentate (shell) side (atm)
$P_{\text{tot}}^{\text{sweep}}$	total pressure on permeate (sweep) side (atm)
$Pe = F_{\text{tot}} / (Q_i A_m P_{\text{tot}})$	Pelet number (ratio of reactant feed rate to permeation rate) dimensionless
Q_i	permeance of species i ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$)
r_i	reaction rate equation of reaction i ($\text{mol s}^{-1} \text{g}^{-1}$)
R_i^P	permeation rate equation of species i ($\text{mol s}^{-1} \text{g}^{-1}$)
R	gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R_o	outer radius of reactor (m)
R_1	inner radius of reactor (m)
t	thickness of membrane (m)
T	reactor temperature (K)
$Y_i = F_i / F_{\text{tot}}$	dimensionless molar flow rate of species i on retentate side
$Y_i^{\text{sweep}} = F_i^{\text{sweep}} / F_{\text{tot}}^{\text{sweep}}$	dimensionless molar flow rate of species i on permeate side
Z	dimensionless length of bed

Greek letters

α_i	hydrogen selectivity of species i
ρ_{cat}	catalyst density (g m^{-3})
ψ	catalyst loading

expression, explaining its ability to correlate results from widely different reactions.

2. Results and discussion

In the analysis of membrane reactors two groups of constants appear that have the form of Damköhler and Peclet numbers, and it is instructive to review how they originate. Although several mathematical descriptions are available in the literature, these are for specific cases [24–27]. A general derivation will be presented here, considering a very simple situation, to show that the solution will be different depending on the reaction kinetics, the geometry of the MR, and the functional form of the permeation equation. As will be argued, this puts limitations on the use of the Da and Pe numbers, and suggests the need of a more practical approach.

Considering a catalytic packed-bed membrane reactor where the catalyst bed is contiguous with the membrane and a sweep stream is used in the permeate side, the design equation for isothermal, steady-state conditions without radial gradients is:

$$\frac{dF_i}{dW} = r_i - R_i^P \quad (1)$$

where F_i is the molar flow of species i , W is the weight of catalyst, r_i is the specific rate of production of species i by reaction, and R_i^P is the specific rate of permeation of species i out of the catalyst bed. It will be assumed that the rate follows first-order kinetics, $r_i = -kP_i = -k(F_i/F_{\text{tot}})P_{\text{tot}}$, where k is the rate constant, P_i is the partial pressure, F_{tot} is the total molar flow rate, and P_{tot} is the total pressure, all on the retentate (bed) side. It will also be assumed that the rate of permeation is linear in partial pressure difference:

$$R_i^P = K_i^P A_m (P_i - P_i^{\text{sweep}}) \quad (2)$$

$$R_i^P = K_i^P A_m \left[\frac{F_i}{F_{\text{tot}}} P_{\text{tot}} - \frac{F_i^{\text{sweep}}}{F_{\text{tot}}^{\text{sweep}}} P_{\text{tot}}^{\text{sweep}} \right] \quad (3)$$

where K_i^P is the specific permeability constant, A_m is the membrane area, and P_i^{sweep} , F_i^{sweep} , $F_{\text{tot}}^{\text{sweep}}$ and $P_{\text{tot}}^{\text{sweep}}$ are the partial pressure, molar flow rate, total molar flow rate, and total pressure in the permeate (sweep) stream. The permeability constant is the permeance divided by the weight of the catalysts (Q_i/W). Using the fact that the differential catalyst weight, dW , is given by the product of the cross-sectional area of the bed, A_c , the bed length, L , the catalyst bed density, ρ_{cat} , and the differential dimensionless length of the bed, dZ , $dW = A_c L \rho_{\text{cat}} dZ$, and substituting this expression into the design Eq. (1) gives, after simple manipulation, the following expression which assumes the total pressure on the bed and sweep side are the same:

$$\frac{dF_i}{dZ} = A_c L \rho_{\text{cat}} k P_{\text{tot}} \left[-\frac{F_i}{F_{\text{tot}}} - \frac{K_i^P A_m}{k} \left(\frac{F_i}{F_{\text{tot}}} - \frac{F_i^{\text{sweep}}}{F_{\text{tot}}^{\text{sweep}}} \right) \right] \quad (4)$$

This expression can be expressed in dimensionless form by defining dimensionless molar flow rates based on the total inlet molar flow rate $Y_i = \frac{F_i}{F_{\text{tot}}}$ and $Y_i^{\text{sweep}} = \frac{F_i^{\text{sweep}}}{F_{\text{tot}}^{\text{sweep}}}$:

$$\frac{dY_i}{dZ} = Da \left[-Y_i - \frac{1}{DaPe} (Y_i - Y_i^{\text{sweep}}) \right] \quad (5)$$

Download English Version:

<https://daneshyari.com/en/article/152390>

Download Persian Version:

<https://daneshyari.com/article/152390>

[Daneshyari.com](https://daneshyari.com)