

INFLUENCE OF VOLUMETRIC FLOW RATE AND TEMPERATURE ON MASS TRANSFER IN COMPOSITE CERAMIC MEMBRANES FOR MEMBRANE REACTORS

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ABSTRACT

A dimensionless analysis of isobaric diffusion process has been conducted on both membrane sides to see the influence of volumetric flow rate and temperature on mass transfer. This analysis is based on the reduced form of dusty gas model appropriate for the evaluation of isobaric diffusion process in membrane reactors. The component mass balances in the two gas compartments are calculated by ignoring axial dispersion in terms of Bodenstein's number. Influence of volumetric flow rate and temperature on mass transfer in membrane reactors is evaluated in this work. Results are presented in form of dimensionless quantities solved by subsequent transformations.

Keywords: Dusty gas model, Isobaric diffusion, axial dispersion, mass transfer, membrane reactor.

INTRODUCTION

Multilayer asymmetric membranes usually consist of permselective material as a thin film on one or a series of porous supports, which provide the required mechanical stability without dramatically reducing the total transmembrane flux (Biesheuvel *et al.*, 1999). Such membranes are the primary component of membrane reactors and every reactor model must describe transport kinetics through the membrane accounting for its complicated structure. Many researchers have contributed to the characterization of porous inorganic membranes for their use in membrane reactors by identifying and validating the mass transfer parameters of the membrane during the recent years (Meixner and Dyer, 1998; Beuscher and Gooding, 1999; Tuchlenski *et al.*, 1997; Tuchlenski *et al.*, 1998; Capek and Seidel-Morgenstern, 2001; Uchytíl *et al.*, 2000; Thomas *et al.*, 2001; Thomas, 2003). The axial spread along the membrane is characterized by a dispersion coefficient depending on the diffusivity and the fluid velocity. The influence of axial dispersion on mass transfer is normally neglected while modelling the membrane reactors. Though chemical reaction is not considered yet, the catalytic partial oxidation of hydrocarbons like butane to maleic acid anhydride is the background of the investigation. Thus present work focuses on the independent and separate analysis of isobaric binary diffusion through multilayer tubular ceramic membranes (porous aluminium oxide) to understand the effects volumetric flow rate and temperature on the diffusion process, which is necessary

for modeling and optimization of membrane reactors. The paper is organized by first giving an overview of the mathematical modeling of isobaric diffusion in tubular membrane reactors. Then the model used for mass transfer is transformed into dimensionless form. Subsequently, the results of simulation analysis conducted for the isobaric diffusion process are discussed.

Mass transfer model

The Dusty Gas Model (DGM) has been used to describe mass transfer through the porous membrane. The model is based on the idea of considering the solid phase as large molecules ("dust") in a multicomponent gas mixture in order to capture the complex combination of viscous flow, Knudsen diffusion and molecular diffusion in porous media (Mason and Malinauskas, 1983). Viscous flow is bulk, non-separating flow caused by total pressure gradients, while in the Knudsen regime the transport is controlled by molecule-wall interactions, so that the molecules travel independently from each other. In contrary, molecule-molecule interactions define the molecular (ordinary, continuum) diffusion.

In its general form, the dusty gas model for species *j* in a mixture of *N* components is expressed by the relationship

$$\sum_{k=1, k \neq j}^N \frac{\tilde{x}_k \dot{n}_j - \tilde{x}_j \dot{n}_k}{D_{jk}^e} + \frac{\dot{n}_j}{D_{k,j}} = -\frac{P}{RT} \nabla \tilde{x}_j - \frac{\tilde{x}_j}{RT} \left(1 + \frac{B_0}{\eta_j D_{k,j}} \bar{P} \right) \nabla P \quad (1)$$

where $j = 1$ to N .

The driving forces are included in the right-hand part of eq. (1) in terms of total pressure and molar fraction

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(partial pressure) gradients, while the resulting fluxes, \dot{n}_j , appear at the left-hand side of the equation.

The mass balance for gas flowing in the annulus has been formulated in one-dimensional way to

$$D_{ax,o} \frac{d^2 \tilde{x}_{j,o}}{dz^2} - \frac{d}{dz} \left(u_{g,o} \frac{n_{g,o}}{n_{g,o,in}} \tilde{x}_{j,o} \right) + \frac{2\pi r_{m,o}}{F_o n_{g,o,in}} \dot{n}_{j,m,o} = 0. \quad (2)$$

In the tube it holds

$$D_{ax,i} \frac{d^2 \tilde{x}_{j,i}}{dz^2} - \frac{d}{dz} \left(u_{g,i} \frac{n_{g,i}}{n_{g,i,in}} \tilde{x}_{j,i} \right) - \frac{2\pi r_{m,i}}{F_i n_{g,i,in}} \dot{n}_{j,m,i} = 0. \quad (3)$$

The boundary conditions at the inlet and outlet of annulus and tube are taken after Danckwerts, $z = 0$:

$$u_{g,o} (\tilde{x}_{j,o,in} - \tilde{x}_{j,o}) + D_{ax,o} \frac{d\tilde{x}_{j,o}}{dz} = 0, \quad (4)$$

$$u_{g,i} (\tilde{x}_{j,i,in} - \tilde{x}_{j,i}) + D_{ax,i} \frac{d\tilde{x}_{j,i}}{dz} = 0, \quad (5)$$

$z = L$:

$$\frac{d\tilde{x}_{j,o}}{dz} = 0, \quad \frac{d\tilde{x}_{j,i}}{dz} = 0. \quad (6a,b)$$

At the membrane-gas interphases it is:

$$\dot{n}_{j,m,o} = \beta_{g,o} n_{g,m,o} (\tilde{x}_{j,m,o} - \tilde{x}_{j,o}), \quad (7a)$$

$$\dot{n}_{j,m,i} = \beta_{g,i} n_{g,m,i} (\tilde{x}_{j,i} - \tilde{x}_{j,m,i}). \quad (7b)$$

The relationship between flow rates and fluxes can be written as

$$\dot{n}_{j,m,o} = \dot{N}_j / (2\pi r_{m,o} L), \quad (8a)$$

$$\dot{n}_{j,m,i} = \dot{N}_j / (2\pi r_{m,i} L). \quad (8b)$$

The coefficients for Knudsen and for molecular diffusion can be expressed in the form

$$D_{k,j} = \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi \tilde{M}_j}} \quad (9)$$

and

$$D_{jk}^e = F_0 D_{jk}, \quad (10)$$

respectively. Consequently the model has three parameters B_0 , K_0 and F_0 , for capturing the influence of

the structure of any specific porous body on viscous flow, bulk diffusion and molecular diffusion.

With the additional assumption of tortuous, mono-dispersed capillaries, which are neither interconnected, nor change their cross-sectional area with their length, the mentioned three parameters of the dusty gas model can be expressed as

$$B_0 = F_0 \frac{d_p^2}{32}, \quad (11)$$

$$K_0 = F_0 \frac{d_p}{4}, \quad (12)$$

$$F_0 = \frac{\varepsilon}{\tau}, \quad (13)$$

and are, thus, reduced to a set of only two morphological parameters, namely

$$d_p = \frac{8B_0}{K_0}, \quad (14)$$

the diameter of the assumed capillaries, and

$$\frac{\varepsilon}{\tau} = \frac{(K_0)^2}{2B_0}, \quad (15)$$

Binary diffusion coefficients, D_{jk} , have been calculated in the present work by means of the Chapman-Enskog equation Reid *et al.* (1987).

Non-dimensional form of the model equations

Axial dispersion represents the transport in axial direction superimposed on that due to convection (Gunn, 2004; Tsotsas and Schlünder, 1988). The inclusion of axial dispersion coefficient in the mass transfer model might cause concentration gradients at the entrance of measuring cell but it is generally assumed that it has no considerable influence on the overall diffusion process in composite membranes. Hence, the component mass balances in the two gas compartments are calculated by ignoring axial dispersion. At low gas velocities, i.e. in the laminar flow regime, the dispersion is mainly caused by diffusion. The component mass balance equations (eqs (2) and (3)) considering simultaneous convection and diffusion in the flow system have been transformed to dimensionless form for annulus and tube respectively, yielding

$$\frac{1}{Bo_{o,in}} \frac{d^2 \tilde{x}_{j,o}^*}{d\zeta^2} - \frac{d(u_{g,o}^* n_{g,o}^* \tilde{x}_{j,o}^*)}{d\zeta} + \frac{\dot{N}_{j,o}^*}{\tilde{x}_{j,in}^{av}} = 0, \quad (16)$$

$$\frac{1}{Bo_{i,in}} \frac{d^2 \tilde{x}_{j,i}^*}{d\zeta^2} - \frac{d(u_{g,i}^* n_{g,i}^* \tilde{x}_{j,i}^*)}{d\zeta} + \frac{\dot{N}_{j,i}^*}{\tilde{x}_{j,i}^{av}} = 0, \quad (17)$$

where

$$\zeta = \frac{z}{L}, \quad (18)$$

$$Bo_{o,in} = \frac{u_{g,o,in} L}{D_{ax,o}}, \quad Bo_{i,in} = \frac{u_{g,i,in} L}{D_{ax,i}}, \quad (19a,b)$$

$$\dot{N}_{j,o}^* = \frac{\dot{N}_j}{F_o n_{g,o,in} u_{g,o,in}}, \quad \dot{N}_{j,i}^* = \frac{\dot{N}_j}{F_i n_{g,i,in} u_{g,i,in}}, \quad (20a,b)$$

$$u_{g,o}^* = \frac{u_{g,o}}{u_{g,o,in}}, \quad u_{g,i}^* = \frac{u_{g,i}}{u_{g,i,in}}, \quad (21a,b)$$

$$n_{g,o}^* = \frac{n_{g,o}}{n_{g,o,in}}, \quad n_{g,i}^* = \frac{n_{g,i}}{n_{g,i,in}}, \quad (22a,b)$$

$$\tilde{x}_{j,o}^* = \frac{\tilde{x}_{j,o}}{x_{j,in}^{av}}, \quad \tilde{x}_{j,i}^* = \frac{\tilde{x}_{j,i}}{x_{j,in}^{av}}. \quad (23a,b)$$

The average inlet molar fraction of regarded component

$$\tilde{x}_{j,in}^{av} = \frac{u_{g,in} n_{g,in}^* F^* \tilde{x}_{j,o,in} + \tilde{x}_{j,i,in}}{u_{g,in} n_{g,in}^* F^* + 1}, \quad (24)$$

is calculated by considering

$$u_{g,in}^* = \frac{u_{g,o,in}}{u_{g,i,in}}, \quad n_{g,in}^* = \frac{n_{g,o,in}}{n_{g,i,in}}, \quad F^* = \frac{F_o}{F_i}. \quad (25a,b,c)$$

The required boundary conditions for mass transfer are also transformed to

$$\zeta = 0: \quad u_{g,o}^* = 1, \quad u_{g,i}^* = 1, \quad (26a,b)$$

$$\zeta = 1: \quad d\tilde{x}_{j,o}^*/d\zeta = 0, \quad d\tilde{x}_{j,i}^*/d\zeta = 0, \quad (27a,b)$$

$$\zeta = 0: \quad \tilde{x}_{j,o,in}^* - \tilde{x}_{j,o}^* + \frac{1}{Bo_{o,in}} \frac{d\tilde{x}_{j,o}^*}{d\zeta} = 0, \quad (28)$$

$$\tilde{x}_{j,i,in}^* - \tilde{x}_{j,i}^* + \frac{1}{Bo_{i,in}} \frac{d\tilde{x}_{j,i}^*}{d\zeta} = 0, \quad (29)$$

$$\tilde{x}_{j,o,in}^* = \frac{\tilde{x}_{j,o,in}}{\tilde{x}_{j,in}^{av}}, \quad \tilde{x}_{j,i,in}^* = \frac{\tilde{x}_{j,i,in}}{\tilde{x}_{j,in}^{av}}. \quad (30a,b)$$

The convective boundary conditions at the membrane have been transformed as

$$\frac{\dot{N}_{j,o}^*}{\tilde{x}_{j,in}^{av} n_{g,o,in}} = \frac{n_{g,m,o}}{n_{g,o,in}} NTU_{o,in} (\tilde{x}_{j,m,o}^* - x_{j,o}^*), \quad (31)$$

$$\frac{\dot{N}_{j,i}^*}{\tilde{x}_{j,in}^{av} n_{g,i,in}} = \frac{n_{g,m,i}}{n_{g,i,in}} NTU_{i,in} (x_{j,i}^* - \tilde{x}_{j,m,i}^*), \quad (32)$$

by considering

$$\tilde{x}_{j,m,o}^* = \frac{\tilde{x}_{j,m,o}}{\tilde{x}_{j,in}^{av}}, \quad \tilde{x}_{j,m,i}^* = \frac{\tilde{x}_{j,m,i}}{\tilde{x}_{j,in}^{av}}, \quad (33a,b)$$

$$NTU_{o,in} = \frac{\beta_{g,o} A_{m,o}}{\dot{V}_{g,o,in}}$$

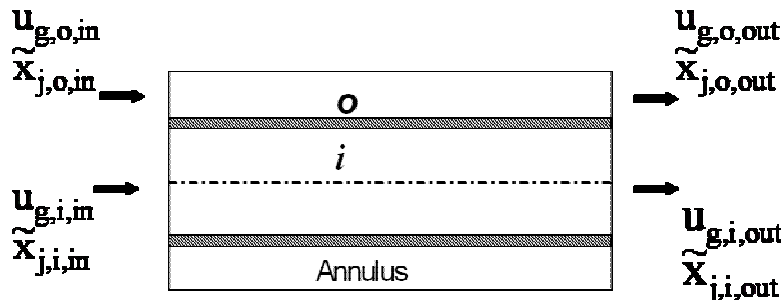


Fig.1. Experimental set-up for the isobaric diffusion experiment.

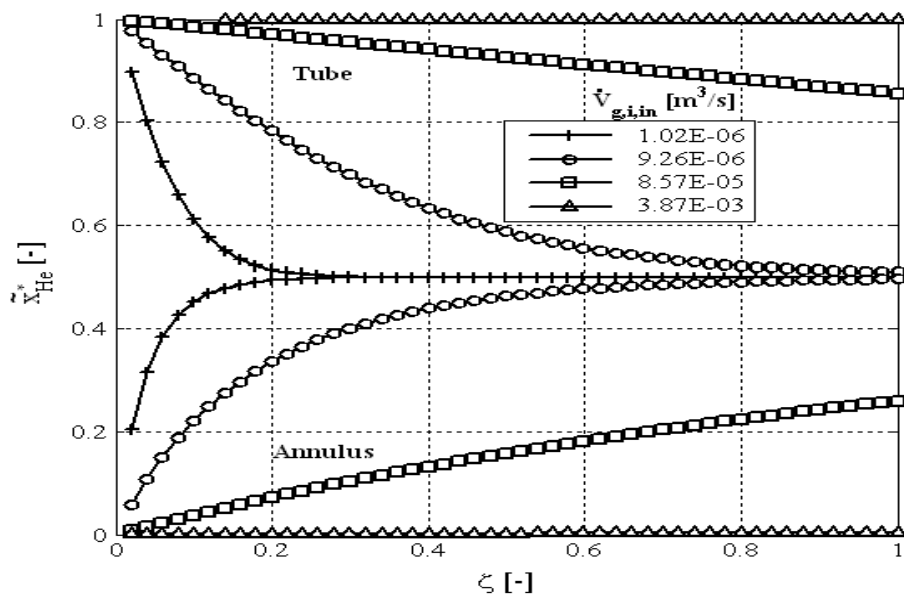


Fig. 2a. Mole fraction of helium (in annulus and tube) vs. dimensionless length; influence of volumetric flow rate on composition profiles of helium.

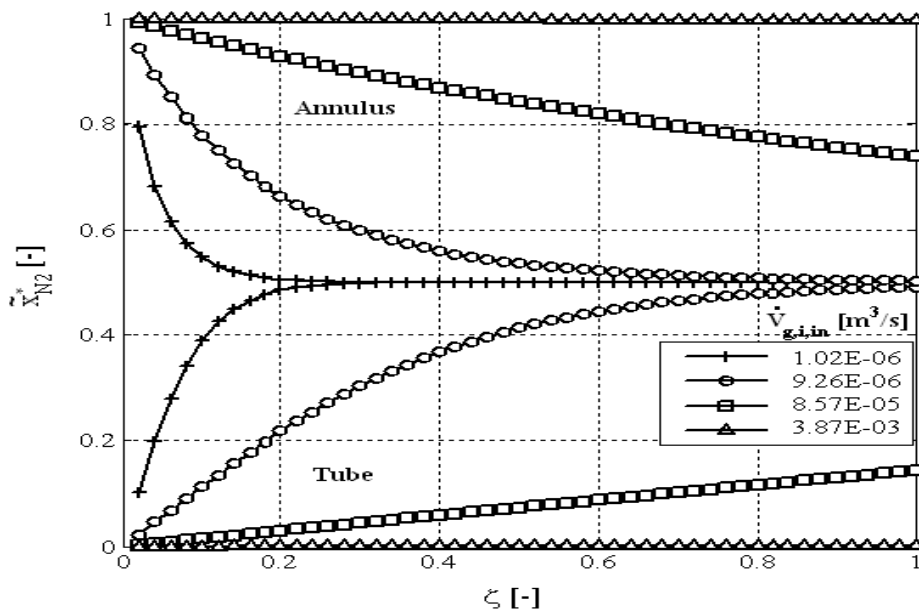


Fig. 2b. Mole fraction of nitrogen (in annulus and tube) vs. dimensionless length; influence of volumetric flow rate on composition profiles of nitrogen.

$$NTU_{i,in} = \frac{\beta_{g,i} A_{m,i}}{\dot{V}_{g,i,in}} \tag{34a,b}$$

Dimensionless gas volumetric flow rates are defined as

$$\dot{V}_{g,o}^* = \frac{\dot{V}_{g,o}}{\dot{V}_{g,o,in}}, \quad \dot{V}_{g,i}^* = \frac{\dot{V}_{g,i}}{\dot{V}_{g,i,in}} \tag{35a,b}$$

and are equal to $u_{g,o}^*$ and $u_{g,i}^*$ (eqs (21a,b)) for the isothermic case. All simulations have been conducted with ProMoT/Diva. The dusty gas model is applied for quantifying mass transfer in every membrane layer (M1). The structural parameters of investigated inorganic membrane (M1) have been successfully identified and validated "Hussain et al. (2006)". The values of structural parameters of the each membrane layer are given in Table

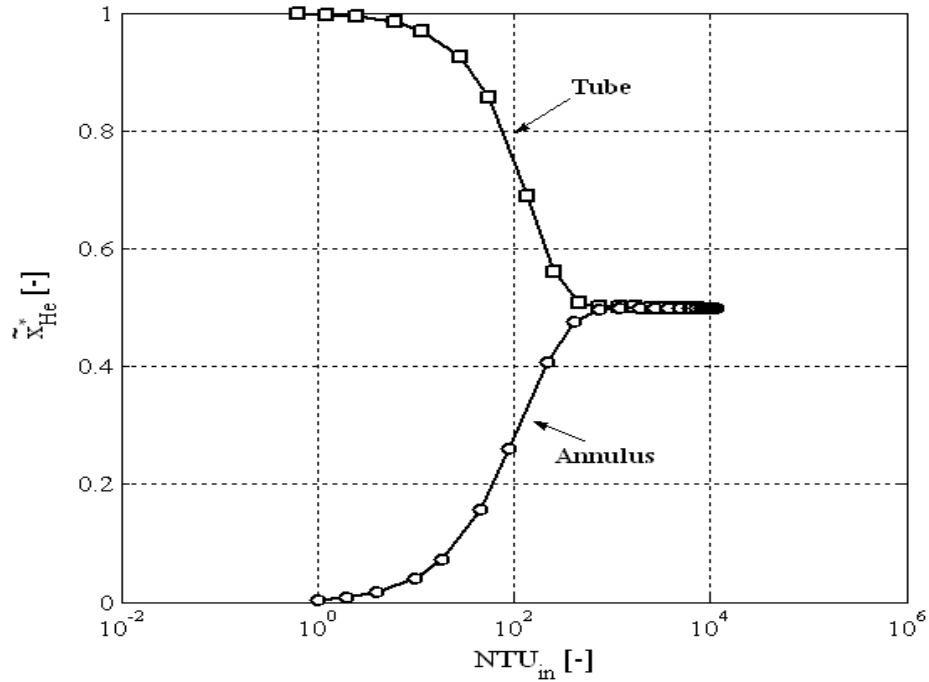


Fig. 3a. Mole fraction of helium (in annulus and tube) vs. the respective number of transfer units.

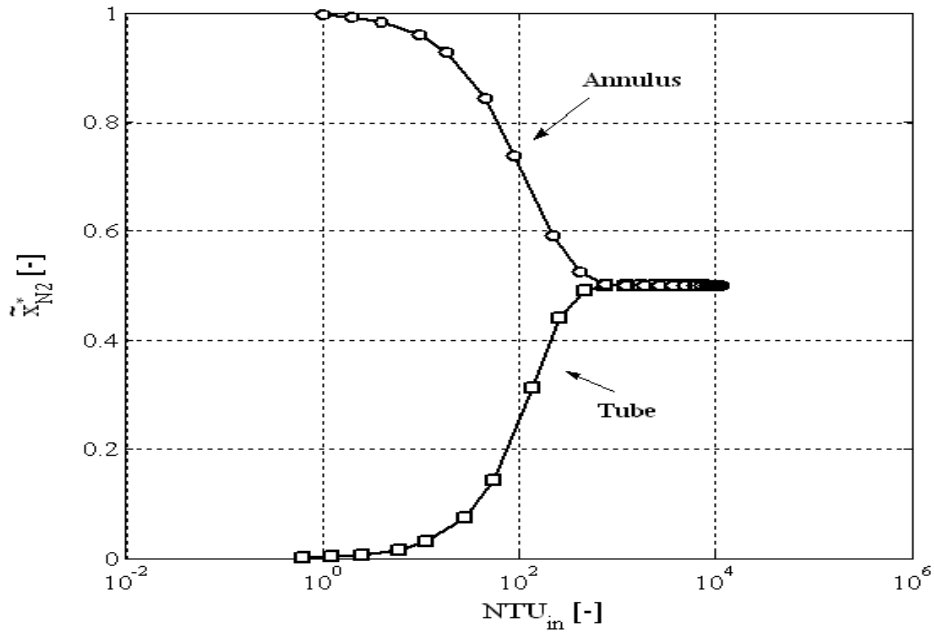


Fig. 3b. Mole fraction of nitrogen (in annulus and tube) vs. the respective number of transfer units.

1. A binary system of nitrogen (annulus) and helium (tube) has been considered for the simulations.

MATERIALS AND METHODS

Experimental method

Though focus is not on the experimental technique to investigate the diffusion process, however, figure 1 recapitulates the principle of isobaric diffusion

experiment used in order to validate the mass transport parameters of the membrane and study the influence of different parameters on isothermal, isobaric diffusion process in a tubular membrane reactor. Notice that the sketch realistically shows the reactor geometry, consisting of a shell-side (annulus, index “o”) and a tube-side (index “i”) space.

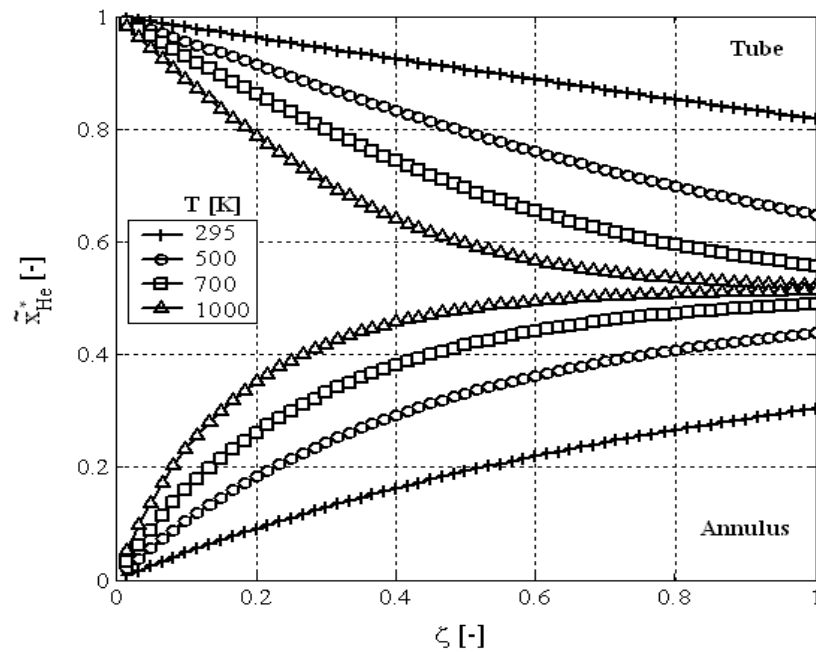


Fig. 4a. Mole fraction of helium (in annulus and tube) vs. dimensionless length; influence of temperature on composition profiles of helium.

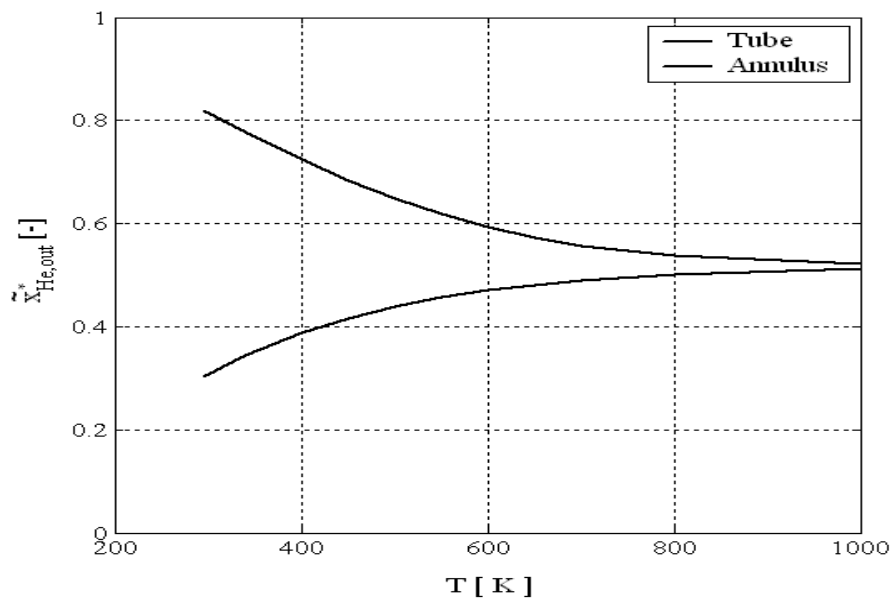


Fig. 4b. Mole fraction of helium at the outlet of annulus and tube vs. temperature.

RESULTS AND DISCUSSION

Influence of volumetric flow rate

In this case plug flow is assumed outside the boundary layer ($D_{ax} = 0$) and the influence of volumetric flow rate ($\dot{V}_{g,i,in} = \dot{V}_{g,o,in}$) on composition in terms of

dimensionless quantities and numbers is investigated. By keeping all other parameters constant at $D_{ax} = 0$, the inlet volumetric flow rate of tube (i) and annulus (o) is varied at the same rate from 1.02×10^{-6} to 3.87×10^{-3} m³/s. The boundary or operating conditions used for the simulations of Figs 2 and 3 are:

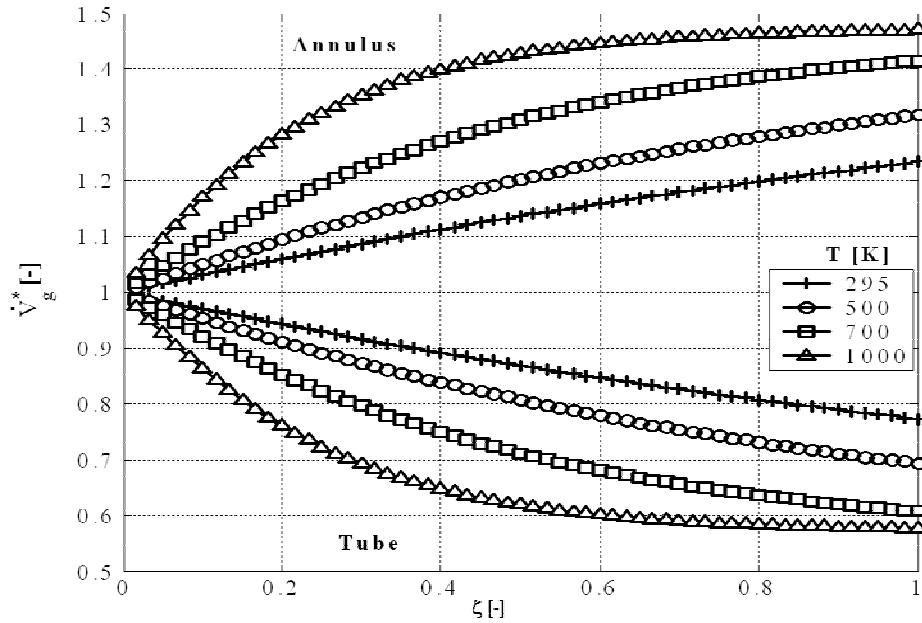


Fig. 5a. Dimensionless volumetric flow rate (in annulus and tube) vs. dimensionless length; influence of temperature on volumetric flow rates.

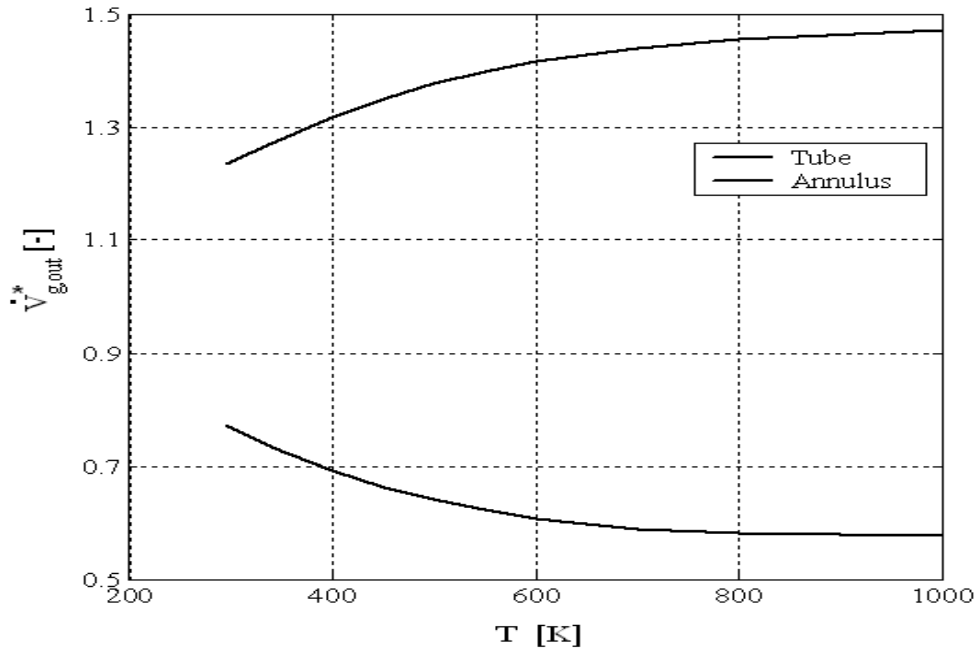


Fig. 5b. Dimensionless volumetric flow rate at the outlet of annulus and tube vs. temperature.

$$\tilde{x}_{He,i,in} = \tilde{x}_{N_2,o,in} = 1, \quad P_i = P_o = 1 \text{ bar},$$

$$T_m = T_{g,i,in} = T_{g,o,in} = 295.15 \text{ K}.$$

Figure 2 shows the dimensionless molar composition of helium and nitrogen plotted against the dimensionless length for varying gas volumetric flow rate in annulus and tube. It can be seen in figure 2a that by increasing the inlet flow rates helium composition tends to unity ($\tilde{x}_{He,i}^* \rightarrow 1$) in tube and tends to zero ($\tilde{x}_{He,o}^* \rightarrow 0$) in

Table 1. Producer information and identified mass transfer parameters of membranes (M1).

Layer	Composition	Nominal pore diameter (m)	Thickness (m)	K_0 (m)	B_0 (m ²)	d_p (m)	$\frac{\varepsilon}{\tau}$
Support	$\alpha\text{-Al}_2\text{O}_3$	3.0×10^{-6}	5.5×10^{-3}	8.16×10^{-8}	2.96×10^{-14}	2.90×10^{-6}	0.112
1 st layer	$\alpha\text{-Al}_2\text{O}_3$	1.0×10^{-6}	25×10^{-6}	7.99×10^{-8}	2.73×10^{-14}	2.73×10^{-6}	0.124
2 nd layer	$\alpha\text{-Al}_2\text{O}_3$	60×10^{-9}	25×10^{-6}	2.98×10^{-9}	2.85×10^{-17}	76.5×10^{-9}	0.156
3 rd layer	$\gamma\text{-Al}_2\text{O}_3$	10×10^{-9}	2×10^{-6}	2.03×10^{-9}	7.47×10^{-18}	29.4×10^{-9}	0.277

annulus and vice versa in Fig. 2b for the case of nitrogen. Similar effects are shown in Figs 3a and b, however in these figures, mole fraction of nitrogen and helium at the outlet is plotted against NTU. For instance Fig. 3a reveals that by increasing NTU (lower gas flow rate) gas composition reaches the equilibrium values. At low NTU (higher gas flow rate) helium composition tends to unity ($\tilde{x}_{\text{He},i}^* \rightarrow 1$) in tube and tends to zero ($\tilde{x}_{\text{He},o}^* \rightarrow 0$) in annulus and vice versa in figure 3b for the case of nitrogen. This can be attributed to the lower residence time of gases in the tube and annulus retarding the mass transfer of gases.

Influence of temperature

The influence of temperature on mass transfer at isothermal conditions is presented in this section. Simulations are conducted by varying temperature from 295.15 to 1000 K and the results for the steady state isothermal case are depicted in figures 4 and 5 for the following operating conditions:

$$\tilde{x}_{\text{He},i,\text{in}} = \tilde{x}_{\text{N}_2,o,\text{in}} = 1, \quad u_{g,i,\text{in}} = 0.096 \text{ m/s},$$

$$u_{g,o,\text{in}} = 0.058 \text{ m/s}, \quad P_i = P_o = 1 \text{ bar}.$$

The temperature has a positive effect on membrane's transport parameters and a negative effect on density, which in the combination lead to increasing fluxes for higher temperatures and the here considered membrane. Consequently, an increase of temperature will enhance the diffusion process resulting in steeper composition profiles (Fig. 4) and higher differences in volumetric flow rate in tube and annulus (Fig. 5).

CONCLUSION

A non-dimensional analysis of isobaric diffusion, based on simulations, has been done to see the influences of volumetric flow rate and temperature on the isobaric diffusion process in terms of mole fraction and gas flow rates. The analysis reveals that system attains equilibrium at lower gas flow rates and rise in temperature enhances

the diffusion process in composite membrane which will lead to reach the equilibrium faster.

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Nomenclature

B_0	m ²	Permeability constant in dusty gas model
B_0	-	Bodenstein number
d	m	Diameter
D_{ax}	m ² s ⁻¹	Axial dispersion coefficient
D	m ² s ⁻¹	Diffusion coefficient
F_0	-	Ratio of effective to molecular diffusion coefficient
F	m ²	Cross-sectional area
K_0	m	Knudsen coefficient in dusty gas model
L	m	Length
\tilde{M}	kg mol ⁻¹	Molar mass
n	mol m ⁻³	Molar density
\dot{n}	mol m ⁻² s ⁻¹	Molar flux
\dot{N}	mol s ⁻¹	Molar flow rate
NTU	-	Number of transfer units
P	Pa	Pressure
r	-	Radial coordinate
\tilde{R}	J mol ⁻¹ K ⁻¹	Universal gas constant
T	°C, K	Temperature
u	m s ⁻¹	Flow velocity
\dot{V}	m ³ s ⁻¹	Volumetric flow rate
\tilde{x}	-	Mole fraction
z	-	Axial coordinate

Greek symbols

β	m s^{-1}	Mass transfer coefficient
ε	-	Porosity
ζ	-	Dimensionless length
η	Pa s^{-1}	Viscosity
τ	-	Tortuosity

Indices

av	Average
D	Diffusivity
e	Effective
g	Gas
in	Inlet
i	Inner, tube side
j, k	Species in the mixture
K	Knudsen
m	Membrane
o	Outer, annulus side
out	Outlet
p	Pore
*	Dimensionless quantity

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