Gas Permeation Modeling through a Multilayer Hollow Fiber Composite Membrane

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Abstract

In this study, a time-dependent 2D axisymmetric model of a multilayer hollow fiber composite membrane for gas separation is proposed. In spite of the common multilayer membranes, which a dense layer coated on a porous support layer and subjected into the feed stream, here, the porous support is exposed to the feed gas. In this regard, the governing equations of species transport are developed for model domains and then solved by a finite element method (FEM). Gas permeation properties of pure H₂, O₂, N₂, CH₄, CO₂ and He are calculated and validated with experimental data with good conformity. Obtained results indicate that with increasing the temperature, the permeability and diffusion coefficient increased while the solubility decreased. Moreover, the permeability and solubility variations with temperature for a heavier gas, CO₂, were higher than those for the lighter ones, while the diffusion coefficient variation with temperature for the lighter gas, such as He, was more than the heavier ones. By increasing the CO₂ feed stream temperature from 25 to 75°C, its permeability and diffusion coefficient increased respectively from 245 to 307 Barrer and from 205 to 282×10⁻¹² m²/s, while the CO₂ solubility decreased from 0.85 to 0.76 cm³·cm⁻³·bar⁻¹. In the case of He and for the same temperature variation range, its permeability and diffusion coefficient increased respectively from 39 to 42 Barrer and from 2180 to 2834×10⁻¹² m²/s, while the solubility of He decreased from 0.013 to 0.011 cm³·cm⁻³·bar⁻¹.

1. Introduction

Industrial progress, an increase in machinery and development of electrical power plants have enhanced the fossil fuel consumption and the consequent emission of greenhouse gases such as CO₂ and CH₄ in the atmosphere which may have destructive impacts on the environment, global warming and reducing the efficiency of related processes [1-5]. Therefore, the need for elimination of greenhouse gases has gained considerable importance along with the development of gas refinery, processing, and transport as well as the introduction of new technologies in gas separation [6, 7]. In this regards, different technologies for gas separation such as adsorption, cryogenic distillation, absorption, and spray towers have been applied [8]. These methods suffer from several drawbacks such as flooding, foaming, and channeling [9, 10]. To overcome these circumstances, membrane technology can be used which has a better operating performance, as well as low operation and energy costs [11]. Many efforts have been made to create unique materials or structures with a better ability to improve the membrane performance [12-15]. Various membrane modules such as hollow fiber, tubular, plate and frame and spiral wound have been developed. Hollow fiber membrane (HFM) is one of the most applied membrane modules. High
surface area per unit volume is a reason for high efficiency of the hollow fiber configuration [16]. Qi and Cussler [17] are the first investigators who have used the porous polypropylene HFM for the absorption of CO2 by using the chemical absorbent. They studied the overall mass transfer coefficients and compared the HFM performance with the packed towers.

Because of the problems and constraints in membrane construction, modeling of membrane processes is important for evaluating and predicting membrane performance under different operating conditions. Ebadi Amooghin et al. [18] proposed a mathematical model for mass transfer of multi component-gas mixture through a synthetic polymeric membrane. They introduced a new mathematical method for calculation of permeability for three-component gas through a composite membrane. Moreover, they developed a new model for direct calculation of diffusion coefficient and showed that with increasing temperature, permeability is effective. This behavior is different for the various gases. With increasing the temperature, permeability increases for H2 and CH4, while it decreases for C2H6. Darabi et al. [19] presented a comprehensive 2D mathematical model to estimate the increase of CO2 absorption by filler incorporation in a HFM. The effect of filler loading on mass transfer increment across the membrane is justified by decreasing the tortuosity ratio of the membrane. Moreover, it was predicted that incorporating of 0.05 wt.% of silica nanoparticles can enhance the absorption rate about 16%, while adding the same amount of carbon nanotube (CNT) nanoparticles, the absorption rate increases up to 32%. The CNT nanoparticle had better performances due to its high absorption and hydrophobicity relative to silica nanoparticles. The addition of CNT nanoparticles with 0.03 wt.% resulted in the highest CO2 absorption in the HFM. Hosseini et al. [20] proposed a mathematical model for mixed gas absorption by using a polyacrylonitrile (PAN) hollow fiber membrane. They used the finite element method (FEM) for solving the problem. The effect of temperature and pressure on CO2/CH4 separation performance, respectively by using the immobilization- and Arrenhius-type equations, was examined. The obtained results showed that permeability increases with increasing temperature and decreasing pressure. Farjami et al. [21] proposed a model for CO2 elimination in polyvinylidene fluoride (PVDF) HFM in which distilled water is used as the liquid sorbent in non-wetting condition. The model was solved by the computational fluid dynamics (CFD) method. They investigated the changes in CO2 elimination performance by liquid sorbent velocity, fiber length, membrane porosity, and liquid sorbent temperature. All of these parameters, except for the liquid sorbent temperature, had an increasing effect on CO2 elimination performance. Tantkhajonggosol et al. [22] presented a 2D mathematical model for two HMFs and evaluated the physical absorption of CO2, H2S, and CH4 from high-pressure synthetic biogas. They assumed that Henry’s constants are dependent on pressure and temperature. Since H2S is a polar gas, its polarization was also considered to be effective in H2S diffusivity. The effect of temperature and pressure on CO2 and H2S absorption and also for CH4 loss is examined. The results indicated that the rate of adsorption increases with increasing the pressure and decreasing the temperature. In this case, the amount of CH4 loss is lower than 5-50%. Moreover, it was predicted that in high-temperature conditions, the permeability of PVDF membrane leads to better results such as more absorption rate of gases from biogas, while in partially wetting mode, the results of PVDF membrane had a good conformity with experimental data. Azari et al. [23] proposed a numerical model of mass transfer in a HFM in non-wetted and partially-wetted conditions for the separation of CO2 from CO2/N2 mixture. Mono-ethanol-amine (MEA), 2-amino-2-methyl-1-propanol (AMP) and NaOH were used as the sorbents. The effects of porosity, temperature, fiber radius, and solvent flow rate in the model performance were investigated. The results revealed that by increasing the gas flow rate, CO2 removal is reduced and its concentration in the outlet is enhanced. Also, by increasing the solvent flow rate and temperature, the concentration of CO2 at the outlet is decreased. Moreover, the membrane porosity enhancement and increase of the internal radius of the fiber lead to further elimination of CO2. Talaghat et al. [24] proposed a mathematical model for countercurrent gas-liquid flow in axial/radial directions and at fully-wet condition in polypropylene HFM contactor which applied in the removal of CO2 from the CO2/CH4 gas mixture. The model equations were solved by using the COMSOL Multiphysics software. The MEA and methyl diethanolamine (MDEA) were utilized as absorbents. The results showed that MEA leads to higher CO2 removal. Also, by increasing porosity-to-tortuosity ratio, fluid flow, the number of fibers, membrane length and solvent concentration, CO2 removal was increased, while it decreased by increasing the gas flow rate or decreasing the contact time. Moreover, polypropylene HFM with MEA as the absorbent has higher CO2 removal from PVDF and PTPE HMFs. In another work, a mathematical model to evaluate the separation of binary gas mixtures (CO2/CH4) in a HFM was presented by Dehkordi et al. [25]. The SRK and Joule-Thomson equations are used to predict non-ideal behavior and temperature variations in permeation of gas components. Also, the effect of temperature on the permeation was justified by the Arrhenius equation. The effect of physical variables such as fiber inner diameter, effective fiber length, module diameter, and the number of fibers on the model performance was also examined. The results indicated that the number of fibers and their effective length have a great effect on the gas separation. Also, by decreasing the effective length and number of fibers, the higher gas separation efficiency is achieved. Sharifzadeh et al. [26] developed a time-dependent mathematical model to study the separation of a gas mixture consist of CO2 and N2 through facilitated transport membranes (FTMs) which were composed of a porous polyvinyl alcohol (PVA) membrane filled with different amounts of diethanolamine (DEA). The model considered unequal diffusion coefficient for all carriers and complexes, and also a constant equilibrium parameter in the chemical reaction between carriers and permeant. Moreover, they presented a method for calculating concentration-dependent diffusion coefficients of all components passing through the FTMs. In addition, the effects of carrier concentration, reversible chemical reaction kinetics, and feed partial pressure on the model performance were investigated. The results indicated that CO2 permeability reduces with increase in the partial pressure. By increasing the concentration of carrier and the chemical reaction kinetics, CO2 permeability further increases.

In this work, a time-dependent 2D model is developed to calculate the permeability, selectivity, solubility and diffusion coefficient of various gases such as CO2, H2, He, N2, O2 and CH4 in a hollow fiber composite membrane. Unlike the common composite membrane models, in this model the porous support layer is subjected to the feed stream and the dense selective layer is placed on the opposite direction, the permeate side. The governing equations with relevant boundary conditions are developed for all zones of feed side, porous support, dense membrane, and permeate side and solved using the finite element method. In addition, the Frisch method is used to calculate the diffusion coefficient of gas components through the membrane. Additionally, the effect of temperature on gas permeation properties is investigated.

2. Model development
2.1. Theory

A time-dependent 2D axisymmetric model was developed for a hollow fiber composite membrane which is composed of poly (styrene-b-butadiene-b-styrene), triblock copolymer (SBS) with a rubbery character that is coated on a polyacrylonitrile (PAN) porous support [27]. A bundle of the membrane fibers is modulated in a dead end membrane holder. According to the experimental paper, in this study, in spite of the common multilayer membranes, SBS selective layer was coated on the external surface of the PAN support, and because of the porous PAN support is used only for mechanical stability, it has no important role in species transport, or in turn, in the mass transfer mechanism and the separation performance. As well as in a constant height for a fiber, its radius and consequently the membrane surface area is constant. Therefore, the amounts of species transport across the membrane or the mass flow rate increase that has no considerable effects on the permeability and selectivity.

Figure 1 shows a schematic of the model zones that considers a fiber consisting four sections: feed side, porous support, dense membrane, and permeate side. Feed gas comes into the feed side (at $z = 0$) at 25 °C and 1 bar and the permeate stream exits from the opposite side of the membrane model (at $r = r_e$).

The solution-diffusion mechanism has been utilized to describe mass transfer in this model [28]. Following assumptions are considered in the proposed model:

- The diffusion mechanism is based on Fick’s law.
- The gas flow arrangement in the model is radial and axial flow is neglected.
- The model is time-dependent.
- Ideal gas behavior is assumed.
- A pressure difference is a driving force in the model.
- There is no heat transport in the model.
- The laminar flow regime is considered for gas flow in the model.

2.2. Governing equations

The continuity equations in different sections of hollow fiber composite membrane are as follow [29, 30]:

\[
\frac{\partial C_i}{\partial t} + \frac{\partial (C_i u_i)}{\partial x} = D_{ii} \frac{\partial^2 C_i}{\partial x^2}
\]
\[
\frac{\partial C_{i,F}}{\partial t} + \nabla \cdot (-D_{i,F} \nabla C_{i,F}) = -u_{i,F} \cdot \nabla C_{i,F} \quad \text{(Feed side)}
\]

\[
\frac{\partial C_{i,S}}{\partial t} + \nabla \cdot (-D_{i,S} \nabla C_{i,S}) = -u_{i,S} \cdot \nabla C_{i,S} \quad \text{(Support layer)}
\]

\[
\frac{\partial C_{i,M}}{\partial t} + \nabla \cdot (-D_{i,M} \nabla C_{i,M}) = 0 \quad \text{(Membrane)}
\]

\[
\frac{\partial C_{i,P}}{\partial t} + \nabla \cdot (-D_{i,P} \nabla C_{i,P}) = -u_{i,P} \cdot \nabla C_{i,P} \quad \text{(Permeate)}
\]

where \( C \) is the concentration (mol/m\(^3\)), \( D \) is the diffusion coefficient (m\(^2\)/s), \( u \) denotes the velocity vector (m/s) and \( t \) is time (s).

To obtain the velocity distribution and concentration gradient in both feed and permeate sections, a momentum balance by employing the Navier-Stokes equation is investigated and simultaneously solved with the continuity equations. Additionally, coupling Navier-Stokes and continuity equations together is a conventional approach in this case of membrane modeling [31-33].

The velocity distribution of gas in the feed and permeate sections is calculated by the Navier-Stokes equation as following [34, 35]:

\[
\frac{\partial u_{i,P}}{\partial t} + \nabla \cdot (u_{i,P} \nabla P) = -\nabla \cdot \left( \nu \left( \nabla u_{i,P} + (\nabla u_{i,P})^T \right) \right) + \mathbf{F}
\]

where \( P, F, \eta \) and \( \rho \) are related to pressure (Pa), external forces (N/m\(^3\)), dynamic viscosity (kg/m.s) and density of the gas (kg/m\(^3\)); respectively. \( r_s \) is the Happle’s free surface which is obtained from Eq. (6) [36]:

\[
r_s(r) = \frac{1}{1-\alpha}
\]

\[
\alpha = 1 - \frac{m_s^2}{R^2}
\]

where \( n \) refers to the number of fibers and \( R \) is the module inner radius.

Because of the gas fluxes in the model are defined by the stiff-spring method, the boundary condition are defined as follow:

(i) Feed side

\[
\text{at } r = 0 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad 
\]
the diffusion coefficient and time lag, respectively. In this case, considering the ideal gas and by
applying the no slip and the slip condition, respectively. M is the ideal gas constant (no slip
and slip condition), respectively. The boundary conditions for solving the Navier–Stokes
equation in the feed and permeate sides are:

### (i) Feed side

\[ r = r_2 \]
\[ -n \cdot \nabla c = M \cdot (K \cdot C_j - C_{j+1}) \]
\[ N = -D_{ij} \nabla c_{ij} \]
\[ @ r = r_3 \]
\[ -n \cdot \nabla C_j = M \cdot (K \cdot C_j - C_{j+1}) \]
\[ N = -D_{ij} \nabla C_{ij} \]
\[ @ r = R \]
\[ -n \cdot (D_{ij} \nabla C_{ij}) = 0 \]
\[ @ z = 0; z = L \]
\[ n \cdot N = 0 ; \]
\[ N = -D_{ij} \nabla C_{ij} \]

### (ii) Permeate side

\[ r = r_3 \]
\[ -n \cdot \nabla C_j = M \cdot (K \cdot C_j - C_{j+1}) \]
\[ N = -D_{ij} \nabla C_{ij} \]
\[ @ r = R \]
\[ -n \cdot (D_{ij} \nabla C_{ij}) = 0 \]
\[ @ z = 0; z = L \]
\[ n \cdot N = 0 ; \]
\[ N = -D_{ij} \nabla C_{ij} \]

In addition, the boundary conditions for solving the Navier–Stokes equation in the feed and permeate sides are:

### (i) Feed side

\[ @ r = 0 \]
\[ \text{symmetry} \]
\[ @ r = r_1 \]
\[ u_{se} = 0 \text{ (no slip condition)} \]
\[ @ Z = 0 \]
\[ P = P_0 \text{ (initial pressure)} \]
\[ @ Z = L \]
\[ u_{se} = 0 \text{ (no slip condition)} \]

### (ii) Permeate side

\[ @ r = r_3 \]
\[ u_{se} = 0 \text{ (no-slip condition)} \]
\[ @ r = R \]
\[ P = 0 \text{ (vacuum)} \]
\[ @ Z = 0; Z = L \]
\[ u_{se} = 0 \text{ (no-slip condition)} \]

where \( C_{ij} \) and \( N \) refer to initial concentration (mol/m^3) and total gas flux (mol/m^3 s), respectively. In this case, considering the ideal gas and by dividing the inlet pressure by RT the initial concentrations are obtained \([37-40]\). The stiff-spring method is employed to overcome discontinuity in concentration profile due to discontinuity in the boundaries for gas flux calculation. Therefore the Dirichlet concentration boundary condition is substitute by the continuous flux condition is defined based on the partition coefficient (K) that resolves the flux discontinuity as follow \([6]\):  

\[ N = M \left| C_{ij+1} - K_i C_{ij} \right| \]  
\[ K_i = \frac{C_{ij+1}}{C_{ij}} \]  

where \( i \) and \( j \) are corresponded to each species and points, respectively. M is the Stiff-spring velocity (a non-physical parameter) and usually has a large amount (100,000 in this work). This parameter is employed in order to align the flux at both sides of two neighboring sections \([41, 42]\). \( K_i \) denotes the dimensionless partition coefficient which experimentally derived by Henry’s law \([43]\).

In order to prevent the creation of large numbers of nodes and elements due to the low thickness of the dense membrane, this section is scaled in the axial direction. Therefore, the correlating diffusion coefficient is utilized instead of the effective diffusion coefficient. The scaled \( z \)-coordinate can be defined as following \([17]\):

\[ \bar{z} = \frac{z}{\text{scale}} \]  

The correlating diffusion coefficient matrix in each section are obtained as follows \([41]\):

\[ D_{ij} = \begin{bmatrix} D_{ij} & 0 \\ 0 & D_{ij} \end{bmatrix} \]  

zones 1 and 4

\[ D_{ij} = \begin{bmatrix} D_{ij} & 0 \\ 0 & D_{ij} \end{bmatrix} \]  

zone 2

\[ D_{ij} = \begin{bmatrix} D_{ij} & 0 \\ 0 & D_{ij} \end{bmatrix} \]  

zone 3

The gas flux and solubility are obtained based on the Fick’s law and Henry’s law, respectively \([44, 45]\):

\[ J = -D_{AB} \frac{\partial C}{\partial r} \]  

\[ S = \frac{P_i}{D_i} \]  

where \( S, \frac{\partial C}{\partial r} \) and \( P \) are solubility (cm^3/cm^2.bar), concentration gradient (mol/m^3) and permeability (Barrer), respectively. The permeability can be defined as following \([46]\):

\[ P = \frac{J \times l}{\Delta P} \]  

where \( J, l \) and \( \Delta P \) refer to gas diffusive flux (mol/m^2.s), membrane thickness (m), and pressure gradient (Pa), respectively. Moreover, the ideal selectivity is calculated by the Eq. \((37)\) \([47, 48]\):

\[ \alpha_2 = \frac{P_1}{P_{N_2}} \]  

2.3. Time lag method

Time lag is an efficient method for evaluation of diffusivities even for the complex diffusional systems \([49-54]\). This method is applicable for ideal mass transfer and non-Fickian diffusion in systems. Also, it can be used for concentration, position, or time-dependent systems. Here, Frisch method is employed in order to drive the time lag, which is a main feature of diffusion mechanism \([55-58]\). The time lag value can be obtained by the intercept of the tangent line in the linear part of the pressure-time curve with the t-axis \([29, 59]\).

Frisch method is used in calculating both the concentration dependent and concentration independent diffusion coefficients \([49]\). Here, by using this method the diffusion coefficient and the value of time lag are obtained according to the algorithm in Figure 2 \([17, 60]\).

Based on the presented algorithm at Figure 3, in the first step physical properties and required operating conditions are defined. In the next step, Frisch method is investigated to calculate the diffusion coefficient and time lag values. Then, by using Eq. \((38)\) \([61, 62]\) and the derived time lag value from the p-t curve \([63]\), diffusion coefficients are obtained.
Fig. 2. Solution algorithm for calculating diffusion coefficient of a gas component.

\[ \bar{D}_{ij,m} = \frac{\int_0^1 c_{ij,m}(r) \, dr \, dr}{\theta_{ij,m} \rho_{ij,m}} \]  \hspace{1cm} (38)

where \( c_{ij,m} \) refers to the concentration distribution of penetrant gas. The solution loop is repeated as long as the desired diffusion coefficient is achieved. It is mentioned that the number of repetitions of this loop is different for each gas component. For instance, this loop was repeated up to 17 times for \( \text{N}_2 \). The time lag value can be obtained by Eq. (39) [17].

\[ \theta_{ij,m} = \frac{\int_0^1 c_{ij,m} \, dz \, dr}{J_{ij}^{0} \, dr} \]  \hspace{1cm} (39)

3. Model solution

The model equations all four domains with respect to the proper boundary conditions for various gases such as \( \text{H}_2, \text{O}_2, \text{N}_2, \text{CH}_4, \text{CO}_2 \), and \( \text{He} \) were solved by finite element method. In this regard, COMSOL Multiphysics version 5.2 was utilized with Intel Core i7 CPU M 460 @ 2.60 GHz and 8 GB RAM system. Finite error analysis was combined with error control and adaptive meshing using a solver which was matched for solving boundary value problems [64, 65]. Some parameters such as pressure, temperature and diffusion coefficients in the hollow fiber composite membrane were derived from the literature [27]. The other required parameters such as diffusion coefficients in feed and permeate sections were obtained from Wilke-Lee equation [66]. The generated mesh for each of the gas components was different. As shown in Figure 3, extra fine mesh is used for \( \text{H}_2, \text{N}_2, \text{O}_2 \), and \( \text{He} \), while it was implemented coarser mesh sizes for \( \text{CH}_4 \) and \( \text{CO}_2 \).
Fig. 3. The generated meshes in the model for (a) H₂, N₂, O₂ and He, (b) CO₂ and CH₄.

4. Results and discussion

4.1. The concentration gradient of gas in the membrane model

Figures 4 and 5 depict the gas concentration gradient in the model sections. Figure 4 shows a 2D concentration gradient with total flux vectors of N₂. In addition, a 3D concentration gradient of N₂ is also presented in Figure 5, just for a better visualization of mass transfer. The feed gas enters at z = 0 and due to their concentration gradient is transferred through the model sections in the radial direction. The gas concentration decreases from feed to permeate sections. The governing mechanism in feed and permeate sections is diffusion and convection, while in the dense membrane, diffusion is the dominant mass transfer mechanism because of the low contribution of velocity.

4.2. Effect of temperature on gas permeability and solubility

Figures 6 and 7 show the effect of temperature on the gas permeability and solubility at the temperature range of 25-75 °C. As can be observed, with increasing the temperature, the permeability of gases increases while the solubility decreases. At higher temperatures, enough energy to overcome the interaction forces between the polymer chains in the membrane matrix is provided and the polymer chains become more flexible [67]. In this case, more free volume fractions for gas transport through the membrane are created. Furthermore, with increasing temperature, the mobility of the gas molecules will increase. This condition makes the gas components can diffuse more easily through the membrane and subsequently the permeability is increased [68].

Increasing permeability and decreasing solubility with the temperature increase for heavier gas components, such as CO₂, is significantly higher than of lighter ones. The effect of temperature on the permeability and solubility is justified by Van’t Hoff–Arrhenius equations (Eqs. (40-42)) [69, 70].

\[
P = P_0 \exp \left(-\frac{E_p}{RT}\right) \tag{40}
\]

\[
S = S_0 \exp \left(-\frac{\Delta H_s}{RT}\right) \tag{41}
\]

\[
D = D_0 \exp \left(-\frac{E_d}{RT}\right) \tag{42}
\]

where \( E_p \) (kJ/mol) and \( \Delta H_s \) (kJ/mol) refer to the activation energy of permeation and the enthalpy of sorption, respectively. Also, \( E_d \) (kJ/mol) is the activation energy of diffusion. Due to the difference in \( E_p \) and \( \Delta H_s \) for various gas components, temperature has different effects on their permeability and solubility.
As can be seen in Figures 6 and 7, the same results are obtained in accordance with Van’t Hoff–Arrhenius equations [69, 70]. That is, with increasing temperature, the permeability and solubility are increased and decreased respectively.

4.3. Effect of temperature on diffusion coefficient and time lag value

Figure 8 illustrates the effect of temperature on diffusion coefficient of gases in the membrane at temperature range of 25-75 °C. The diffusion coefficient of all gases increases with increasing temperature. Due to the difference in activation energies of diffusion, the effect of temperature on the diffusion coefficient of lighter gases such as H₂ is higher than of heavier ones. As described above, the flexibility of polymer chains increases with increasing the temperature, and therefore the diffusion coefficient increases. This behavior can be justified by Van’t Hoff–Arrhenius equations (refer to Eq. (42)) [71, 72].

Due to the high solubility of gas components in rubbery membranes, direct predicting the diffusion time lag is complicated. In permeability measurements of a gas in rubbery polymers, the p-t curve shift to its steady state, and hence, it is almost hard-measurable the exact time of unsteady behavior in the beginning of experiment and the probable measured values can be along with a number of errors. To overcome the problem, the Frisch method is considered to calculate the diffusion coefficient and time lag values. The results of calculations through the method are presented in Table 1. As seen, by increasing the temperature, the time lag values decrease, in accordance well with the increase in diffusion coefficient and gas flux [28, 73, 74].

4.4. Model Validation

The model equations are solved for all four sections at a temperature range of 25-75 °C. In order to validate the model for verifying the accuracy of the obtained results, the model results are compared with the experimental data [27]. Table 2 shows the results of comparison for permeability, solubility, diffusion coefficient and selectivity of the model for H₂, O₂, N₂, CH₄, CO₂ and He. As can be seen, there is good conformity between the model results and experimental data with the maximum relative errors of 5.5, 4.5 and 9% respectively for the predictions of permeability, diffusion coefficient and solubility. The relative error is calculated by Eq. (43) [75]:

\[
\text{RE(\%)} = \left(\frac{\text{simulation value} - \text{experimental value}}{\text{experimental value}}\right) \times 100
\]  

(43)
Table 1
Time lag values obtained from the model at various temperatures.

<table>
<thead>
<tr>
<th>Penetrate</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.85</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.23</td>
</tr>
<tr>
<td>N₂</td>
<td>1.04</td>
</tr>
<tr>
<td>O₂</td>
<td>0.73</td>
</tr>
<tr>
<td>H₂</td>
<td>0.20</td>
</tr>
<tr>
<td>He</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 2
Comparison of the model results with experimental data at 1 bar and 25 °C.

<table>
<thead>
<tr>
<th>Gas Component</th>
<th>Presented study</th>
<th>Experimental Data</th>
<th>Ideal selectivity of permeability (%)</th>
<th>Relative error of permeability (%)</th>
<th>Relative error of diffusion coefficient (%)</th>
<th>Relative error of solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P (Barrer)</td>
<td>Dₓ₁₀⁻¹² (m²/s)</td>
<td>S (cm³/(cm².bar))</td>
<td>P (Barrer)</td>
<td>Dₓ₁₀⁻¹² (m²/s)</td>
<td>S (cm³/(cm².bar))</td>
</tr>
<tr>
<td>CO₂</td>
<td>245.7</td>
<td>214.3</td>
<td>0.856</td>
<td>248</td>
<td>205</td>
<td>0.907</td>
</tr>
<tr>
<td>H₂</td>
<td>66.4</td>
<td>1350.3</td>
<td>0.0367</td>
<td>66</td>
<td>1380</td>
<td>0.036</td>
</tr>
<tr>
<td>CH₄</td>
<td>43</td>
<td>134.5</td>
<td>0.239</td>
<td>44</td>
<td>139</td>
<td>0.24</td>
</tr>
<tr>
<td>He</td>
<td>37.67</td>
<td>2151.3</td>
<td>0.0131</td>
<td>39</td>
<td>2180</td>
<td>0.013</td>
</tr>
<tr>
<td>O₂</td>
<td>38</td>
<td>358.5</td>
<td>0.079</td>
<td>36</td>
<td>344</td>
<td>0.078</td>
</tr>
<tr>
<td>N₂</td>
<td>13.75</td>
<td>252.3</td>
<td>0.04</td>
<td>14</td>
<td>243</td>
<td>0.044</td>
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5. Conclusions

A 2D model for determination of pure gas permeation properties through a hollow fiber composite membrane was developed. A hollow fiber type membrane module with four zones of feed, support, dense membrane and permeate was considered to modeling the transport phenomena. Unlike the composite membrane models, in this model the porous support was subjected to the feed gas and the dense membrane layer was located in the permeate side. The gas permeation of various pure gas components such as H₂, O₂, N₂, CH₄, CO₂ and He are calculated. The permeation results from the model had good conformity with experimental outcomes. Moreover, the effect of temperature on the effective parameters on the model performance was investigated. The obtained results indicated that with increasing the temperature, the permeability and the diffusion coefficient of the pure gas components are increased while their solubility decreased.

Nomenclature

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<tr>
<td>0</td>
<td>Initial condition</td>
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<tr>
<td>1</td>
<td>Feed side</td>
</tr>
<tr>
<td>2</td>
<td>Support layer</td>
</tr>
<tr>
<td>3</td>
<td>Dense membrane</td>
</tr>
<tr>
<td>4</td>
<td>Permeate side</td>
</tr>
<tr>
<td>e</td>
<td>Effective</td>
</tr>
<tr>
<td>f</td>
<td>Feed</td>
</tr>
<tr>
<td>i</td>
<td>Species i</td>
</tr>
<tr>
<td>j</td>
<td>Zone j</td>
</tr>
<tr>
<td>m</td>
<td>Membrane</td>
</tr>
<tr>
<td>p</td>
<td>Permeate</td>
</tr>
<tr>
<td>s</td>
<td>Support layer</td>
</tr>
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</table>

Greek letters

<table>
<thead>
<tr>
<th>Greek letter</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>Viscosity (Pa.s)</td>
</tr>
<tr>
<td>P</td>
<td>Density (kg/m³)</td>
</tr>
<tr>
<td>D</td>
<td>Gradient</td>
</tr>
<tr>
<td>η</td>
<td>selectivity (-)</td>
</tr>
<tr>
<td>τ</td>
<td>Time lag (s)</td>
</tr>
</tbody>
</table>

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>D</td>
<td>Dimensional</td>
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<tr>
<td>Exp</td>
<td>Experimental</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
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<td>He</td>
<td>Helium</td>
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<tr>
<td>N₂</td>
<td>Nitrogen</td>
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<td>O₂</td>
<td>Oxygen</td>
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<tr>
<td>RE</td>
<td>Relative error</td>
</tr>
<tr>
<td>Sim</td>
<td>Simulation</td>
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References


