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Mathematical modelling and numerical simulation of CO₂/CH₄ separation in a polymeric membrane

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Abstract: CO₂ capture from natural gas was experimentally and theoretically studied using a dead-end polymeric permeation cell. A numerical model was proposed for the separation of CO₂/CH₄ using Polytetrafluoroethylene (PTFE) in a flat sheet membrane module and developed based upon the continuity, momentum and mass transfer equations. The slip velocity condition was considered to show the reflection of gas flow in contact with the membrane surface. The solution method was based on the well-known SIMPLE algorithm and implemented using MATLAB to determine the velocity and concentration profiles. Due to change in velocity direction in the membrane module, the hybrid differencing scheme was used to solve the diffusion-convection equation. The results of the model were compared with the experimental data obtained as part of this work and good agreement was observed. The distribution of CO₂ concentration inside the feed and permeate chambers was shown and the velocity profile at the membrane surface was also determined using reflection factor for polymeric membrane. The

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modelling result revealed that increasing the amount of CO₂ in gas feed resulted in an increase in the CO₂ in the permeate stream while the gas feed pressure increased. By changing the permeability, the model developed by use of the solution-diffusion concept could be used for all polymeric membranes with flat sheet modules.

Keywords: Mathematical modelling, Solution-Diffusion model, PTFE membrane, SIMPLE algorithm, CO₂/CH₄ separation, Cross flow membrane cell.

1. Introduction

Nowadays membrane technology is widely used in many areas, for instance the food, biotechnology and pharmaceutical industries. In the gas industry, the membrane units are also regarded as an excellent choice for a separation process due to its simplicity, ease of operation and its cost effectiveness. These properties have drawn the attention of both scientists and engineers to focus more on replacing the conventional separation methods with a membrane system [1]. Available data in the literature shows that significant work have been conducted to utilize the best material, such as metal, ceramic, polymers and liquid membranes to reach the desired separation efficiency [2, 3]. In the gas separation process, sweetening of natural gas accounts for the most important unit for elimination of undesirable components. For instance, CO₂ and H₂S in the presence of water forms acidic solutions and leads topipeline corrosion[4]. Chemical and physical absorption, solid adsorption and cryogenic methodsare chosen to eliminate CO₂ from raw natural gas, but these processes suffer from operational problems such as flooding, foaming, channelling and high capital and operating costs[5].In Malaysia, some of the offshore gas reservoirs are rich (about 70%) in CO₂ content[6], therefore the traditional absorption techniques using alkanolamine solution are not a good choice for gas treatment in offshore units due to the significant construction costs of platforms. For this, polymeric membranes are regarded as a high potential candidate for capturing ineffectual components due to economical and operational advantages. With respect to their advantages, such as low price, good chemical and physical stability, polymeric membranes become so valuable to use in offshore gas process in gas the weight of offshore platform structures significantly reduces and hence lower capital cost. Moreover, it is expected that remarkable cost saving of more than 15% could be achieved if a membrane process is selected [7] instead of other gas absorption units.

In membrane separation processes, the direction of gas flow towards the membrane sheet and also at the surface is important [3]. Generally, Navier-Stokes equations with the aim of accurate boundary conditions can determine the gas velocity profile at the surface of porous media. In the case of gas flow in the polymeric membrane, molecules of gas component show different movements considering the pore size and tortuosity. Hence, this causes the classification of different flow regimes, such as continuum, slip, transition and free molecular inside the membrane [8]. The solution-diffusion model can be used to pronounce transport theory of gas molecules through the polymeric membrane which is highly dependent on the gas diffusivity coefficient and solubility [9].

A Computational Fluid Dynamic (CFD) technique used in commercial software such as ANSYS, FLUENT and COMSOL is an appropriate method to specify the momentum, mass and heat transfer in a system. The implementation of CFD has improved the analysis of flow behaviour compared to experimental work which can be costly while complicated geometry is demanded. Yua et al.[10] performed CFD modelling of mass and heat transfer in Direct Contact Membrane Distillation (DCMD). Coroneo et al. [11] considered transport mechanisms of gas molecules through the membrane using the CFD technique. In their model, the permeability of the species through the membrane is regarded as the molecular diffusion. Moreover, the effect of pore size on fouling and backwash dynamics in dead-end microfiltration were considered and the model showed the fouling resistance factor of both particle and membrane in various permeate volumes[12]. Koukou et al. [13-15] developed a model to predict the effect of design parameters and operating variables on the performance of a membrane reactor while the slip condition at the membrane surface was not considered in the model development. Sohrabi et al. [16] developed a

mathematical model to predict the CO₂ concentration at the outlet of a hollow fibre membrane. In the case of model development, the flow of gas mixture was parallel to the fibre and the effect of the membrane surface on the velocity was ignored. Tan et al. [17] recently carried out a simulation to show the effect of gas permeation on the hydrodynamic characteristics of membrane-assisted micro fluidized beds, the membrane boundary condition was defined on the basis of membrane permeability and module pressure for a system without any reaction or transport for a multi components.

In this work, a two-dimensional model is suggested for the cross flow membrane cell. A binary gas mixture is fed to the dead-end and high pressure cell after sudden expansion, then passes through the membrane and finally desorbs from the low pressure side. The main objective of this work is to illustrate the slip boundary condition, its effects on the velocity profile and the concentration distribution in the permeation cell. For model validation, the result of modelling is compared with our own experimental data obtained using an in-house experimental rig (see Figure 1) and the procedure is explained in the following sections. The equations of motion and continuity for the system presented are numerically solved. The SIMPLE algorithm that is used in CFD software determines the fluid velocity and pressure in the case that gas velocity at the membrane surface is not zero and depended on the function of shear stress at the surface boundary layer [18]. Furthermore, mesh generation is carried out based on the control volume method. The velocity vector at each node on the membrane surface is obtained by momentum equations and then coupled to the concentration boundary as a convective term. The effect of physical parameters, such as pressure, velocity and concentration of gas components on the separation efficiency are considered to develop a robust model.

2. Model development

The model of CO₂ separation from gas mixture with different concentrations is developed for three chambers individually. Then, every chamber is individually discretized in order to solve the transport equations with specific boundary conditions. In the first chamber, the gas mixture enters after sudden expansion due to the change in pipe size (see Figure 1). It is predicted that the Navier-Stokes equations specify approximately the profile of gas velocity especially at the surface of the membrane and the reject stream. The reject coefficient, R , can be expressed by Equation(1)[19].

$$R = 1 - \frac{c_p}{c_r} \quad (1)$$

where c_p and c_r are the concentration of species i in the first chamber of the permeation cell. The reject stream is usually dependent on the membrane permeability Pe which is a function of solubility, S , and diffusivity, D , of the gas mixture. The feed stream contacts with the membrane surface area, A , one part of the gas flow forms a concentration boundary layer at the membrane surface but the other part is deflected towards the sides or follows the reject stream and finally exits from the outlet pipe. In the second chamber, the gas mixture diffuses through the membrane as per the solution-diffusion model and Fick's law. The equation of conservation leads to achieving the concentration of each component at the other side of the membrane. Moreover, the flow inside the membrane consists of diffusion terms to certify the transport phenomena. In the last chamber, permeation stream, P , with new concentration, C_p , leaves the other side of the membrane and then moves towards the outlet pipe after sudden contraction due to the change in pipe size.

2.1. Model assumptions

In this model, the following assumptions are made:

- a) Two gas streams (CO₂ and CH₄) are mixed with a static mixer to make the feed flow incompressible. The flow is also at steady state and isothermal conditions.
- b) The transport properties, such as viscosity and diffusivity are kept.
- c) Inside the permeation cell, the velocity profile is not fully developed in both the feed and permeate chambers.
- d) A slip condition exists at the surface of the membrane concerning the Beavers–Joseph boundary condition[20].
- e) Diffusion inside the membrane takes place in both the y and x directions.

2.2. Transport properties

In the first chamber, the mass transfer amongst gas molecules consists of diffusion between CO₂ and CH₄ molecules and convection in the bulk flow. The diffusivity coefficient for a binary system can be calculated both experimentally and theoretically. For a binary gas mixture at low temperature, diffusivity is a function of pressure and temperature as shown in Equation(2).

$$D_{AB} = \frac{1.858 \times 10^{-7} T^{3/2} (1/M_A + 1/M_B)^{1/2}}{(p/101325) \sigma_{AB}^2 \Omega(T_D^*)} \quad (2)$$

where M_A and M_B are the molecular weights, σ_{AB} is the collision diameter of components A and B and $\Omega(T_D^*)$ is the collision integral. D_{AB} , p and T represent the diffusivity coefficients, pressure and temperature of the binary system [21]. The diffusivity coefficient of the polymeric membrane is proportional to the tortuosity and porosity, and is expressed as follows:

$$D_m = \frac{D_{mixture} \cdot \varepsilon}{\tau} \quad (3)$$

The mass transfer through the polymeric membrane is described by the solution-diffusion model, in which gas molecules firstly dissolve at the surface, then diffuse inside the membrane and finally are released from the other side [22]. The movement of gas molecules through the PTFE membrane may take place using a miscellaneous mechanism. In this case, the pore size, H , and the bulk pressure, P_b , define three regimes inside the membrane which are expressed by i) Knudsen diffusion, ii) transition flow, and iii) adsorbed-phase diffusion. Thus, the total permeability of the PTFE membrane is defined by Equation(4):

$$P_t = P_k + P_t + P_a \quad (4)$$

where P_k , P_t and P_a are denominated to the Knudsen diffusion (pore diffusion), transition flow and adsorbed-phase diffusion (surface diffusion), respectively. This equation is certified in the case that bulk pressure is lower than the critical pressure [8].

When the gas mixture is desorbed from the permeate side of membrane, the mass transfer of gas molecules including diffusion and convection is similar to the first chamber while the gas flow approaches the outlet pipe.

2.3. Governing equations

A two-dimensional mathematical model is developed on the basis of continuity and momentum equations as follows:

2.3.1. Momentum and concentration equations in chamber 1

The equations for overall conservation of mass, momentum and concentration for CO₂ are as follows:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0 \quad (5)$$

$$\frac{\partial n_{CO_2x}}{\partial x} + \frac{\partial n_{CO_2y}}{\partial y} = 0 \quad (6)$$

$$u_x \frac{\partial C_{CO_2}}{\partial x} + u_y \frac{\partial C_{CO_2}}{\partial y} + D_{CO_2-CH_4} \left(\frac{\partial^2 C_{CO_2}}{\partial x^2} + \frac{\partial^2 C_{CO_2}}{\partial y^2} \right) = 0 \quad (7)$$

$$\rho \left(u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} \right) = -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} \right) + \rho g_x \quad (8)$$

$$\rho \left(u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} \right) = -\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} \right) + \rho g_y \quad (9)$$

where u_x , u_y , ρ , D and P denote velocity in the x and y directions, density, diffusivity and pressure, respectively. C_{CO_2} is the concentration of CO₂ in the first chamber.

2.3.2. Concentration equations in chamber 2

The convection mass transfer is neglected and only diffusion of gas molecules through the membrane is considered. Thus a steady-state continuity equation including diffusion term is defined as follows:

$$D_{PTFE} \left(\frac{\partial^2 C_{mCO_2}}{\partial x^2} + \frac{\partial^2 C_{mCO_2}}{\partial y^2} \right) = 0 \quad (10)$$

where D_{PTFE} is the diffusion coefficient of the gas mixture inside the membrane and the concentration of CO₂ through the membrane is shown by C_{mCO_2} .

2.3.3. Momentum and concentration equations in chamber 3

The equations for the overall conservation of mass, momentum and concentration for CO₂ are similar to the defined equations in the first chamber.

2.4. Boundary conditions

It is assumed that the velocity profile of gas flow after sudden expansion is not fully developed due to the small height of the cell. Thus, a parabolic flow forms near the membrane surface. The Navier-Stokes equations determine the velocity vector in different sections of the cell. The concentration of gas components is varied from the initial to the gas-solid interface where the concentration boundary condition is defined by diffusion and convection terms as follows:

$$C = C_i \text{ at } y = a^* \quad (11)$$

$$D \frac{\partial C_w}{\partial y} + u_{wy} R C_w = 0 \text{ at } y = b^* \quad (12)$$

$$u_x = 0, u_y = 0 \text{ at } 0 \ll x \ll l \text{ and } y = a^* \quad (13)$$

The velocity at the membrane surface is in two directions whereas the velocity at the solid surface is treated as zero (wall boundary condition). In this case, the y and x parts are determined by the theoretical equation presented by Saffman[23], which takes form as follows:

$$u_x = \frac{P e^{1/2}}{\alpha_{BJ}} \frac{\partial u_x}{\partial y} \text{ at } 0 < x < l \text{ and } y = b^* \quad (14)$$

$$u_y = \frac{P e^{1/2}}{\alpha_{BJ}} \frac{\partial u_y}{\partial y} \text{ at } 0 < x < l \text{ and } y = b^* \quad (15)$$

The velocity at the other side of the membrane is calculated with respect to the pressure drop between the two chambers, the concentration at the gas-solid interface in the permeate side is expressed as follows:

$$D \frac{\partial C_p}{\partial y} + (1-R) C_w u_{wy} = 0 \text{ at } y = c^* \quad (16)$$

$$u_{px} = u, u_{py} = u \text{ at } 0 < x < l \text{ and } y = c^* \quad (17)$$

In the third chamber, the velocity at the outlet pipe is determined using the upstream pressure which is lower than the downstream pressure to satisfy the process criteria.

$$u_{ox} = 0, u_{oy} = u \text{ at } 0 < x < l \text{ and } y = d^* \quad (18)$$

3. Numerical scheme

The constant parameters of mass and momentum equations as well as the operating conditions used in this process are shown in Table 1. In terms of model development, complexity of the system of partial differential equations and stiff boundary conditions are two major obstacles which impede choosing various numerical solutions. A combination between the continuity and the Navier-Stokes equations including convection, diffusion and pressure gradient terms, is carried out to find a method for prediction of the gas concentration in the permeate stream. In this study, the flow is incompressible and the equation of state is not required to determine the pressure [24, 25]. Moreover, the velocity is linked to the concentration boundary conditions at both membrane surfaces. The SIMPLE algorithm of Patankar et al. [26] is introduced as an effective method to find the accurate velocity and pressure in the defined domains. More detail of the computational procedure can be found in the literature [27, 28]. All equations were solved using MATLAB software (ver. R2012a). The computational code was written to solve the model's equations using the Finite Volume Method (FVM) and Finite Difference Method (FDM) with the Gauss-Seidel iteration technique. The main function code consists of three calculation parts: 1) velocity and concentration in the first chamber, 2) concentration through the membrane, 3) velocity and concentration in the third chamber. The code is run on a PC (Intel(R) Core(TM) i5-3470 CPU @ 3.20 GHz with 4.00 GB RAM) and a typical running time of about 30 minutes.

3.1. The geometry and computational mesh

The two dimensional mesh is similar to the real size of the permeation cell shown in Figure 1. According to the model theory given in section 2.1, the mass transfer equations, including convective and diffusive terms are developed for the first and third chambers. In the first chamber, the gas stream traces the direction from the entrance pipe to the membrane surface at which the slip theory causes deflection of the velocity vector. Therefore, a very refined grid is needed to show the effect of selected boundary conditions on the change in velocity and concentration profiles. There are 94 control volumes in the x -direction and 24 control volumes in the y -direction. Moreover, 5 control volumes near the membrane surface are resized to improve the result accuracy of velocity and concentration. The numbers for the control volume to solve the continuity equation inside and outside the membrane are the same as the defined grid for the momentum equations. The mesh generation inside the membrane to solve the mass transfer equation including a diffusive term, consists of 94 control volumes in the x -direction and 12 control volumes in the y -direction.

Figure 1. Dimension of permeation cell

3.2. Numerical procedure

As the SIMPLE algorithm is highly dependent on the numerical iteration to be converged, the pressure, velocity and concentration correction equations use the under-relaxation factor to accelerate the rate of convergence more. In this case, a new set of variables are required to use in the next loop of the Gauss-Seidel iteration method and is expressed as follows:[29]

$$W^{new} = \alpha_s W + (1 - \alpha_s) W^{old} \quad (19)$$

The direction of the velocity vectors changes on contact with the membrane surface. Thus, the diffusion-convection equations need the hybrid differencing scheme [30] which is the net combination of central and upwind differencing schemes [24].

4. Experimental

4.1. Materials

The PTFE membrane was provided by the Millipore Co. (Ireland) with a porosity of more than 60% and a pore size of $0.2 \mu\text{m}$. CH_4 and CO_2 gases were statically mixed so as to bring up a mixture containing the same specification as natural gas with varied CO_2 concentration. The gas supplier was the Linde Group (Malaysia), CO_2 was almost pure (99.98%) and CH_4 was 99.95%, with a corresponding density of 1.842 and $0.692 \text{ (kg/m}^3\text{)}$ at 20°C and 1 atm.

4.2. Equipment

The permeation unit was designed by the Chemical Engineering Group at Universiti Teknologi PETRONAS (UTP) and fabricated by Spectron Sdn. Bhd (Malaysia). More details about this experimental rig were published previously [31]. This unit consists of a pre-feed section in which the gas temperature is set to prevent freezing inside pipelines. Then the volumetric flow of the gas stream regarding the feed specification is also set with automatic control valves in the feed section. The separation section contains four storage tanks for feed, permeation and reject streams. Every storage tank is equipped with a pressure gauge in order to check downstream and upstream pressures. A vent stream is connected with an online analyser to measure the gas concentration during the separation process. Additionally, the inert gas N_2 is used for purging all the pipes in the piping network. As was mentioned, the permeation cell used in this experiment is

a dead-end type. The fourth storage tank stands before the hollow fibre module and is not used during the experiment. Furthermore, this pilot is equipped with a heater to set and keep the unit temperature constant. The separation unit can be run both manually and automatically in order to set the desired value for temperature and flow rates. Moreover, the experimental data are logged during the process and recorded on a computer for further consideration.

4.3. Method

The separation of CH₄ and CO₂ is carried out in the dead-end permeation cell. The schematic diagram of the experimental set-up is shown in Figure 2. More detail about this permeation apparatus is available in the previous work [31, 32]. A gas mixture containing different volume fractions of components is fed to the permeation cell at the atmospheric pressure and temperature of 30°C. The feed pressure was varied gradually up to 7 barg to set the desired feed flow rates and also alter the driving force for the separation pressure. In order to run the experiment in the steady state condition, the feed storage tank is filled with the desired CO₂ volume fraction while the on-line analyser detects the feed concentration before feeding into the permeation cell. The upstream pressure is kept sufficiently lower than the downstream to avoid any disturbance in the permeate flow rate. Initially, the pure CO₂ and CH₄ with a composition of approximately 99.99% are used for the calibration of the on-line analyser to ensure the accuracy of analysis in the experiment. The concentration of each component in the permeate stream is analysed during interval times in the steady-state condition and the digital flow meter measures the permeate flow rates. Similarly, the reject stream is transferred to the storage tank for the further analysis. In every concentration analysis of the concentration, the pipe connected to the on-line analyser is

purged with N₂ gas for 2 min before the next measurement. By using the log-data, the carbon dioxide absorption flux is estimated with the mass balance over the permeation cell [33].

$$J_{CO_2} = \frac{Q_{G,i}C_{G,i} - Q_{G,e}C_{G,e}}{A} \quad (20)$$

Figure 2. The schematic diagram of the experimental set-up

5. Results and discussion

As the inlet (feed stream) and outlet (reject stream) of the permeation cell are adjacent, the determination of velocity vector for every node is first carried out to specify the concentration later. This becomes very significant at the membrane surface at which the concentration is dependent on the gas velocity and this causes the formation of a low concentration gradient in the boundary layer[34]. The velocity is calculated by the SIMPLE algorithm using the iteration method with respect to the boundary condition at the gas-solid interface formed at the membrane surface. The experiment by Beavers et al.[35] verified the slip condition at the interface of the porous media and gas flows, then Saffman[23] suggested a new boundary condition including permeability and BJ factor (α_{BJ}). Beavers et al. [35] results revealed that the BJ factor depended on the structure of the porous material at the surface. Moreover, that can be dependent on the flow direction at the surface, the Reynolds number and the porous structure [20, 36]. The BJ factor is an empirical parameter and its quantity can be determined by the comparison between the modelling and experimental results in this study. The terms of fluid velocity at the membrane surface are used in the boundary conditions equation on both sides of the membrane as convective mass transfer. The acceptable range for α_{BJ} was estimated at approximately 0.78×10^{-7} in which the more accurate mole concentration of gas components was calculated in the first and third chambers. The effect of different values of α_{BJ} on the velocity profile in both the x and y

directions is seen in Figure 3 and Figure 4, respectively. The figure analysis shows various types of velocity regions formed at the membrane surface. In the centre, the reflection of the velocity vector, U_x , reaches the minimum that indicates that the effect of shear stress is negligible. In the part moving towards the cell wall, a very stable boundary layer is seen due to the reduction of velocity reflection within down layers. Figure 4 shows the velocity profile in the y direction, U_y , and demonstrates a monotonous distribution profile at the impact time. The accepted range of α_{BJ} shows a higher trend in satisfying the continuity equation solved using the SIMPLE algorithm and resulting in more accurate velocity and CO_2 concentration distribution profiles.

Figure 3. Effect of the Beavers–Joseph factor, α_{BJ} , on the velocity U_x at a total pressure of 7 barg and a temperature of 30°C

Figure 4. Effect of the Beavers–Joseph factor, α_{BJ} , on the velocity U_y at a total pressure of 7 barg and a temperature of 30°C

The initial operating condition is shown in Table 1. A binary gas mixture of CO_2 and CH_4 flows in a narrow pipe and then enters the first chamber where sudden expansion occurs due to the change in size of pipe diameter. In this case, the combination of energy, momentum and mass equations expresses the loss of the sudden expansion [37], the velocity profile can then be predicted. With respect to the inlet and outlet of the permeation cell, it is expected that the gas flow is divided into two streams. The primary stream contacts intensively with the membrane surface and adsorbs, then diffuses through the membrane and the second stream turns back and moves towards the outlet due to selected velocity boundary conditions.

Table 1. Operating conditions used in the separation unit

5.1. Velocity profile in the first chamber

Because of the symmetrical shape of the permeation cell, the velocity profile is considered for half of the total nodes in the x direction. The velocity profile, U_x , in the first chamber is shown in Figure 5. With respect to the node arrangements, the velocity U_x curve forms a maximum peak at node no. 20 that belongs to the outlet. The peak drops dramatically approximately at the same slope towards the inlet and the cell wall which indicates a distinct border between the inlet and outlet streams. Moreover, it is expected that the fluid velocity reaches zero near the cell wall as there is a slight slope towards the wall nodes. On contact with the membrane surface, the velocity of gas flow, U_x , reduces to a high degree due to the physical nature of the membrane and thus that prevents the fluid from passing completely through the surface. As a result, part of the gas flows tangentially and leaving the membrane surface to the upper layers. The influence of this phenomena can be highlighted throughout the inlet and outlet nodal rows.

Figure 5. Velocity profile in the x -direction, U_x , in chamber 1

Figure 6 shows the velocity at the y direction, U_y , with two distinct peaks. The first is seen in the inlet, the velocity is at the interface of the inlet where that is still under the influence of the change in pipe size. The second accrues at the outlet and that is attributed to the mean nodal rows where the velocity direction changes due to the conservation of momentum. At node no. 19, it is expected that similarly the velocity direction changes so that one part of the gas flow moves towards the membrane surface where the velocity U_y gradually reduces and the membrane shows

resistance against passing the gas flow with respect to the permeability and the Beavers-Joseph factor. The other part rises steeply due to the influence of high velocity suction at the outlet. In the same way, the slope of curves from node no. 3 to 17 reduces steadily. It can be interpreted that the velocity vector might slowly change the direction in the mean nodal rows and forms a border with the countercurrent velocity vector. An increase and decrease in the value of U_y velocity is seen in the corner of the permeation cell where a dead zone can be defined. It is predicted that the velocity profile in the first chamber tends to be fully developed in lower nodal layers where the velocity decreases considerably. In fact, the change in velocity direction makes three nodal regions with different properties in which the gas flow can be circulated or moved towards the membrane surface and outlet.

Figure 6. Velocity profile in the y-direction, U_y , in chamber 1

5.2. CO₂ concentration in the feed section

In general, the total mass transfer consists of diffusion and bulk flow transfer terms for all components [38]. Figure 7 shows the CO₂ concentration along the membrane length. The CO₂ concentration reduces successively due to the effect of diffusion and convection transfers in every node. In this case, the low CO₂ concentration is observed for the three rows of nodes near the cell wall where the fluid is circulated. The concentration in the other nodes besides the cell wall gradually begins to increase before the contact between the gas and membrane surfaces. The change in CO₂ concentration is attributed to the change of velocity direction while a gap point forms between two layers with different velocity directions and causes imbalance in the nodal pressures. On the other hand, the velocity vector accelerates towards the membrane surface

whereas the opposite velocity vector moves towards the upper layers and creates a borderline between two formed flows. The crossed curves which exist between nodes 3 and 14 shows the change in velocity vector as well. However, it is difficult to specify the accurate concentration in the first chamber. The effect of convective transfer is more significant than the diffusion for the layers near the inlet and outlet and also the role of diffusion is seen more than convection in the lower layers (near the membrane surface).

Figure 7. Profile of CO₂ concentration in the first chamber of the permeation cell

5.3. Velocity profile in the third chamber

As the gas flow passes through the body of the membrane by diffusion, it then enters the third chamber where the velocity vector firstly increases because of pressure drop between the two chambers, then gradually approaches the outlet where sudden contraction occurs. Figure 8 shows the velocity U_x profile within different nodal layers. It is seen that the velocity U_x vector from both sides of the cell move towards the centre line with a slight slope. Near the cell wall, a sharp slope is seen due to the boundary condition effect and the existence of the dead zone region in the corners. After 7 nodal layers from the membrane surface, the effect of sudden contraction is highlighted and the slope softly declined for all layers consecutively. Figure 9 shows the velocity U_y profile. In this case, all nodal layers are under sudden contraction and similarly velocity U_y reaches the minimum value near the cell wall. A cross section point is seen between nodes 8 and 10 that indicates the existence of two regions including circulating and outlet streams. According to Figure 8 and Figure 9, the gas velocity profile is not fully developed and the intensity of the velocity vector increases along the centre line and therefore the velocity in the x direction in the

upper layers is higher than the lower layers, especially towards the centre line. Moreover, the velocity in the y direction increases slowly towards the outlet and a semi-parabolic velocity profile can be predicted in the third chamber.

Figure 8. Velocity profile in the x -direction, U_x , in chamber 2

Figure 9. Velocity profile in the y -direction, U_y , in chamber 2

5.4. CO₂ concentration at the permeation section

The gas mixture with new concentrations of CO₂ and CH₄ enters the third chamber where the velocity profile is under the effect of the pressure drop and the sudden contraction. Figure 10 shows the CO₂ concentration profile while the change in CO₂ concentration is a function of both diffusion and convection mass transfers. It is seen that the CO₂ concentration is high in the lower layers especially for nodes near the permeate side. On the opposite side, the CO₂ concentration increases in the last four nodal layers near the outlet that can be interpreted by the influence of sudden contraction. Moreover, a low CO₂ concentration profile is seen near the cell wall which grows slightly while moving to the centre line. In the lower nodal rows towards the outlet, the gas flow passes through the outlet with a delay concerned with the velocity profile in that region and the change in diameter size of the third chamber and outlet pipe.

Figure 10. Profile of CO₂ concentration in the third chamber of the permeation cell

6. Model validation

The model presented for CO₂ removal from a binary gas mixture in the dead end membrane module is validated by comparing the modelling results with our experimental data carried out in the pilot plant under the same operating conditions. The parameters used in the modelling, such as diffusivity and viscosity coefficients, are taken from the literature [21, 39]. According to Figure 11, the results from the suggested model are in good agreement with the experimental data and also the derivation between the modelling and experimental results is estimated at 12.95% using the average absolute relative error (ARRE) calculation method.

Figure 11. Effect of feed CO₂ flow rate on CO₂ volume concentration in the permeate stream

7. Conclusions

The separation of CO₂ from CH₄ by PTFE membrane was investigated experimentally and numerically. The continuity and momentum equations with appropriate concentration and velocity boundary conditions for three sections of permeation cell were numerically solved. The SIMPLE algorithm determined the velocity profile inside the permeation cell by iterative sub-routine code developed in MATLAB. In terms of numerical solution, the mesh generation was carried out on the basis of the finite volume method and the hybrid differencing scheme was also used to highlight the change in the direction of the velocity vector. Moreover, the effects of sudden expansion and contraction on the gas velocity and concentration profiles were shown in the modelling results. In this study, the slip boundary condition was proposed to determine the velocity vector at the membrane surface. In this way, three distinctive regions were defined in the first chamber. Furthermore, the CO₂ concentration inside the chambers were estimated under the influence of both diffusive and convective mass transfers. The modelling results revealed that

the change in CO₂ concentration of the feed greatly affects the permeate concentration both by the diffusion and convection transfers. In terms of model validation, the results of the presented model were compared with the experimental data obtained using our in-house experimental rig and good agreement was finally observed. The model presented is highly recommended to be used for other polymeric membranes in which the penetration transport follows up the solution-diffusion model.

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Nomenclature

A	Membrane surface area (m ²)
a [*]	Width of permeation cell for the first chamber (m)
b [*]	Width of permeation cell for the first chamber (m)
C	Concentration (mol/m ³)
c	Concentration (mol/m ³)
c [*]	Width of permeation cell for the third chamber (m)
D	Diffusivity coefficient (m ² /s)
D _{PTFE}	PTFE Diffusivity coefficient (m ² /s)
d [*]	Width of permeation cell for the third chamber (m)
i	Node number in x axis
J	Molar flux (mol/m ² s)
j	Node number in y axis
G	Gravity (m/s ²)

H	Pore diameter (m)
l	Permeation length (m)
M	Molecular weight (g/mol)
n	Mass flux (kg/m ² s)
P	Permeability (barrer)
p	Pressure (bars)
Q	Flow rate (m ³ /s)
R	Reject coefficient
S	Solubility (kmol/m ³ bar)
T	Temperature (°C)
U	Velocity (m/s)
W	Iterative variable

Greek symbols

α_{BJ}	Beavers-Joseph factor
α_s	Under-relaxation factor
ρ	Density (kg/m ³)
Σ	Collision diameter (°A)
$\Omega(T^*)$	Collision integral

Subscripts

a	Adsorbed-phase
b	Bulk
e	Exit
f	Feed
g	Gas
i	Inlet
k	Knudsen
m	Membrane
p	Permeate

r	Reject
t	Total
w	Wall
x	x-direction
y	y-direction

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