Pore Model Prediction of CH_4 Separation from H_2S using PTMSP and γ -Alumina Membranes

H. Mukhtar, N. M. Noor, R. Nasir, D. F. Mohshim

Abstract— The main aim of this work is to develop a model of hydrogen sulfide (H_2S) separation from natural gas by using membrane separation technology. The model is developed by incorporating three diffusion mechanisms which are Knudsen, viscous and surface diffusion towards membrane selectivity and permeability. The findings from the simulation result shows that the permeability of the gas is dependent toward the pore size of the membrane, operating pressure, operating temperature as well as feed composition. The permeability of methane has the highest value for Poly (1-trimethylsilyl-1-propyne) PTMSP membrane at pore size of 0.1nm and decreasing toward a minimum peak at pore range 1 to 1.5 nm as pore size increased before it increase again for pore size is greater than 1.5 nm. On the other hand, the permeability of hydrogen sulfide is found to increase almost proportionally with the increase of membrane pore size. Generally, the increase of pressure will increase the permeability of gas since more driving force is provided to the system while increasing of temperature would decrease the permeability due to the surface diffusion drop off effect. A corroboration of the simulation result also showed a good agreement with the experimental data.

Keywords— Hydrogen Sulfide, Methane, Inorganic Membrane, Organic Membrane, Pore Model

I. INTRODUCTION

NATURAL gas is used primarily as a fuel and as a raw material in manufacturing. It is considered as an environmentally friendly clean fuel, offering important environmental benefits as compared to other fossils fuels. Natural gas found at the wellhead is not pure although contains primarily of methane. Natural gas that comes from the oil wells typically termed as 'associated gases. It is produced during crude oil production and is the gas associated with the crude oil. Natural gas from gas and condensate wells in which there is little or no crude oil is termed as 'non-associated gases. Regardless of the sources of natural gas, once separated from crude oil, it commonly exists in mixtures with other hydrocarbons and some impurities of acid gases such as H_2S, N_2, CO_2, H_2, Hg, H_2O and other substances.

Natural gas consists of 0-5 vol % of hydrogen sulfide and according to US pipeline specification; natural gas must not contain more than 2% CO_2 and 4ppm H_2S before being delivered to the customers [1]. Due to the rotten smell provided by its sulfur content, the gas commonly called 'sour gases. 'Sour gas' is undesirable because the sulfur compounds it contains can be extremely harmful, even poisonous to breathe[2-3]. The team of researchers reported that natural gas contained hydrogen sulfide has a low BTU value and has to be upgraded by removing the hydrogen sulfide. Therefore, before the distribution of natural gas is done, the separation of the impurities, specifically in this study refers to H_2S is very critical and must be the first priority in the gas processing. The process for removing hydrogen sulfide from sour gas is commonly referred as 'sweetening' the gas [4].

Currently, gas absorption using amine solvent is used to remove H_2S content [5]. However, few problems [1] regarding amine adsorption occurred due to the contaminants in the inlet gas which contains solid particles like iron sulfide and corrosion particles which form when H_2S comes in contact with the equipment metallurgy and also foaming causes a reduction in gas treating capacity, an increase in energy consumption, and excessive amine losses [6]. The other technology that has been used is cryogenic process which involves extremely low temperature condition. However, cryogenic plants are complex, require numerous moving parts and have high capital and operating costs. Therefore, another method of separation process has been greatly explored to avoid the reliance on the adsorption separation and cryogenic processes. Membrane has been a promising technology for this purpose compared to the other methods due to several reasons such as ease of installation, ease of operation, low space requirement make them the best alternative to be implemented at offshore [7-8].

According to [9], inorganic membranes currently suffer from several disadvantages, such as low selectivity and low permeability, which has thus far limited the performance of these membranes. Organic polymer on the other side, dominates materials for gas separation membranes. Many polymers exhibit sufficient gas selectivity and they can be easily processed into membranes. The two most widely studied polyacetylenes are poly(1-trimethylsilyl-1-propyne) (PTMSP) and poly(4-methyl-2-pentyne) (PMP). Gas permeabilities in these materials are orders of magnitude higher than those of conventional, low-free-volume glassy polymers, and are even substantially higher than those of poly(dimethylsiloxane), for many years the most permeable polymer known. The extremely high free volume provides a sorption capacity as much as 10 times that of a conventional glassy polymer. This combination of extraordinarily high permeabilities, together with the very high free volume, hints at a pore-flow contribution [10].

PTMSP polymeric membrane selectively permeates larger

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molecules of a gas mixture with moderate to high permeance and permselectivities over the smaller molecules. Thus, a gas stream enriched in the smaller components of the feed-gas mixture is produced as the high pressure effluent gas from the PTMSP membrane system, while a gas stream enriched in the larger components of the feed-gas mixture is produced as a low pressure effluent gas. It means very high rejection of hydrocarbon (methane) over hydrogen sulfide is exhibited by the membrane at low gas pressure based on molecular size of H_2S and methane 3.373 and 3.8 Å respectively. The Hydrogen sulfide enriched stream will be produced at the feed pressure [11].

The second membrane that is used in the simulation studies is inorganic membrane, γ-Alumina. γ-Alumina membranes are formed by colloidal deposition of Boehmite particle sols on macro-porous supports, followed by thermal processing which results in transformation of Boehmite (AlOOH) into γ-Al_2O_3 [12]. This inorganic membrane offers some advantages in term of operation at severe temperature and pressure. They are generally chemically stable and can withstand severe operating condition. However, inorganic membranes are likely to be 10 to 100 times more expensive than equivalent polymeric membranes which make them not preferable for the industry. This cost differential can only be tolerated in applications in which polymeric membranes completely fail to make the separation [13]. Table 1 shows the properties of both types of membranes.

TABLE I
PROPERTIES OF PTMSP AND γ-ALUMINA

Properties	(PTMSP)	γ-Alumina
Pore size range, (nm)	5-20	0.15-290
Membrane thickness (t_m), μm	50-70	0.10
Porosity, ε	0.3-0.7	0.603
Tortuosity, τ	1.5-2.5	1.658
Density (g/cm³)	2.2	3.41

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II. THEORY

Two models are used to describe the mechanism of permeation. He describes one of the model is the solution-diffusion model, in which permeates dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. The permeates are separated because of the differences in the solubilities of the materials in the membrane and the differences in the rates at which the materials diffuse through the membrane. The other model is the pore-flow model, in which permeates are transported by pressure-driven convective flow through tiny pores. Separation occurs because one of the permeate is excluded (filtered) from some of the pores in the membrane through which other permeates move. The difference between the solution-diffusion and pore flow mechanisms lies in the relative size and permanence of the pores [10].

For the pore models, the diffusion mechanisms are best described by viscous diffusion, Knudsen diffusion and surface diffusion. The viscous flow provides the permeability of gas molecule as a function of the membrane porosity, pore size, tortuosity and the viscosity of the gas but not pressure. [14] explained that viscous flow can be modeled in the pore membrane with pore size ranging from 1-7nm, as in this range the gas molecules will collide each against each other more frequently than their collision with the wall. According to [15], permeability of gas molecule through membrane pores can be described as follow:

$$P_i^{'} = \frac{q_p t_m}{A_m \Delta P} \tag{1}$$

Where q_p is given by

$$q_p = \frac{\varepsilon \pi R_m L_m r_p^2}{4\mu_i^t}(P_H - P_L) \tag{2}$$

Therefore permeability for viscous diffusion is given by;

$$p_{i,v}^{'} = \frac{\varepsilon r_p^2 \overline{P}}{8\tau \mu_i RT} \tag{3}$$

The permeability of gas predicted by using equation (3) is limited to the condition when the mean free path of travel of the gas molecule is smaller than the pore diameter (viscous mechanism) [16]. However, when the system temperature is held high and the pressure is held low, the mean free path of travel of the gas molecule became larger and the collision between gas molecules against wall predominates. Thus, Knudsen diffusion occurs [17] via the following relation;

$$P_{i,k}^{'} = \left(\frac{2r_p\varepsilon}{3\tau}\right)\left(\frac{8}{RT\pi M}\right)^{1/2} \tag{4}$$

When the temperature of the gas is such that adsorption on pore walls is important due to hindered pathway, experimental results show that the preceding laws for the gaseous flow are no longer valid. For relatively low surface concentrations, the surface flux, N_s for a single gas is described by the two-dimensional Fick's law [9].

$$P_{i,s}^{'} = \frac{2t_m\varepsilon^2}{r_p\tau}(1-\varepsilon)\frac{D_s\rho_m f}{zRT} \tag{5}$$

Where,

$$D_s = 1.6x10^{-2}e^{\left[\frac{-0.45(\Delta H_{ads})}{mRT}\right]} \tag{6}$$

The combination of those three diffusions will result in the total permeability as follow;

$$P_i^{'tot} = -\frac{\varepsilon}{\tau}\frac{1}{RT}\left(D_{kn} + \frac{B_0}{\mu_i}P + \frac{2t_m\varepsilon(1-\varepsilon)}{r_p}\frac{D_s\rho_m f}{z}\right) \quad (7)$$

Total flux of Gas in Mixture is calculated by using this correlation;

$$P_i^{'mix} = x_i\left(P_i^{'}\right) + x_j\left(P_j^{i}\right) \quad (8)$$

Which x_i, x_j, P'_i, P'_j is mole fraction and permeability of each gaseous respectively.

Separation factor can be used to describe the separation efficiency for a binary mixture, which is a measure of the enrichment of a gas component after it has passed the membrane. Reference [18-19] suggests the ideal separation factor for a binary system as follow;

$$\alpha^* = \frac{P_i^{'}}{P_j^{'}} \quad (9)$$

With $P_i^{'}$ is the permeability of species i and $P_j^{'}$ is the permeability of species j.

III. RESULT AND DISCUSSION

The permeability of single gases passing through the membrane has been calculated by using equation (7) while for binary mixture equation (8) has been used.

A. Permeability of Pure Gas: Effect of Membrane Pore Size on Gas Permeability
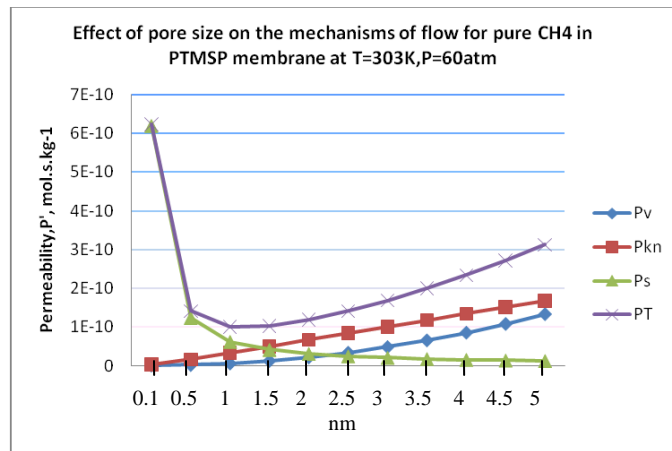

Fig. 1 Effect of pore size on the mechanisms of flow for pure CH$_4$ in PTMSP membrane at T=303K and P=60 atm.

Fig. 1 shows the effect of pore size on the mechanisms of flow for pure CH$_4$ in PTMSP membrane. While increasing the pore size from 0.1 to 5 nm, the operating pressure and temperature is kept constant at 60atm and 303K respectively. As can be observed from the figure, the surface diffusion is dominant at smaller pore size which is in the range of 0.1 to 0.2nm and it decrease as the pore size increase. At small size of pore, the pathway of travel for gas is hindered. Under this condition, the gas molecules have higher tendency to diffuse from the bulk gas film (feed) to the pore surface with the concentration gradient between bulk gas surface and the pore surface as the driving force. The difference of the absorbing rate for the two gaseous is the key for the separation to happen. At higher pore size, it can be observed that Knudsen diffusion started to increase and give a major effect on the total permeability of CH$_4$. This is due to the more mean freeways provided by higher pore size for the transport of gas molecules. The gas molecule can freely collide with wall of membrane pore and the amount of collision exceeding the amount of collision between CH$_4$ molecules.
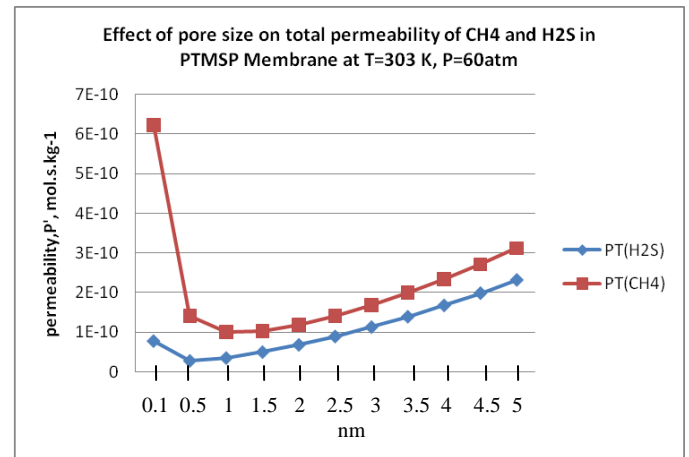

Fig. 2 Comparison for effect of pore size on the mechanisms of flow for H$_2$S and CH$_4$ in PTMSP membrane at T=303K and P=60 atm.

In general, increasing the size of membrane pore will increase the permeability of gas since hindered path is no longer a restriction for the movement of gas through out the membrane. However, it needs to be aware that when the permeability of gas increase excessively, the separation factor or selectivity of the gas will decrease as the permeability of CH$_4$ is getting nearer to the permeability of H$_2$S. This trend can be screened from Fig. 2. The ideal separation occurred when pore size is less than 0.5nm. After this value, the permeability of CH$_4$ and H$_2$S is following the same pattern can become closer.

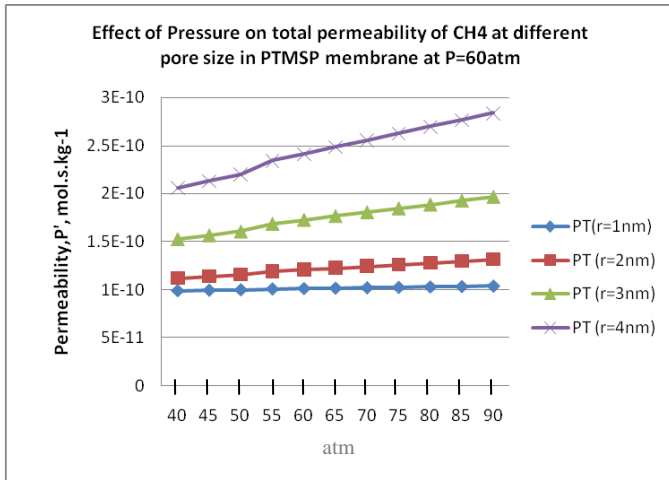*B. Permeability of Pure Gas: Effect of Pressure on Gas Permeability*

Fig. 3 Effect of operating pressure to the permeability of CH_4 for PTMSP membrane at T=303K

Fig. 3 shows the effect of operating pressure on the CH_4 permeability across PTMSP membrane. As the pressure is increased, the permeability of CH_4 is also increased. Here we can observe as the pore size increase, the dependence of pressure is become apparent and at smaller pore size (1nm), the permeability of CH_4 is almost independent of pressure. The increase of permeability of CH_4 is very obvious when the pore size is equals to 4nm. On other hand, the permeability of CH_4 at pore size equals to 1nm is nearly constant. Increasing the pressure woud increase in the driving force which makes the permeation of the gas molecules are more favorable. In region of larger pore size, Knudsen diffusion become dominant instead of surface diffusion.

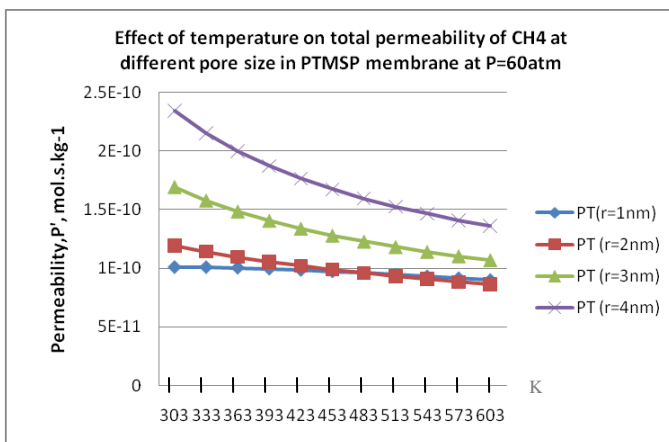### C. Permeability of Pure Gas: Effect of Temperature on Gas Permeability

Fig. 4 Effect of operating temperature to the permeability of CH_4 at P=60atm for PTMSP membrane

Fig. 4 shows the effect of temperature towards the permeability of CH_4 throughout PTMSP membrane at pressure equals to 60 atm. It can be observed that the total permeability of CH_4 is decreasing with increase of temperature. This is due to surface diffusion effect of the gas molecules when temperature varies which relates to adsorption of the gas molecules on the pore size. This influence of adsorption can be described by using thermodynamic relation between Gibbs free energy, enthalpy and entropy, $\Delta G = \Delta H - T\Delta S$. In adsorption process, ΔG is always negative, as well as ΔH and ΔS. When temperature rises, ΔG becomes less negative and adsorption process is not favored. Knudsen and viscous diffusion shows insignificant changes when temperature increases.

When the pore size is being varies from 1 to 4 nm, the results show that the permeability of membrane with larger pore size is higher. This follows the general trend, which describe that the higher availability of mean free pathways will result in higher permeability of gas molecules.

D. Permeability of Gas Mixture

In general, to study about permeability of gas components in a mixture, the average viscosity and interaction between gas components need to be taken into account. However, author has simplified the relation between pure gaseous and the mixture as per equation (8). The feed composition is consists of 80% CH_4 and 20% H_2S. The pure gaseous permeability and gas mixture of a binary system are compared under the same operating conditions at different pore size. It can be observed from fig. 5 that the gas mixture permeability lays between the pure gaseous permeability. The behavior of gas mixture follows the behavior of pure gaseous dependent on the percentage of gas in feed composition. The same trends are obtained when operating pressure and temperature is varies.
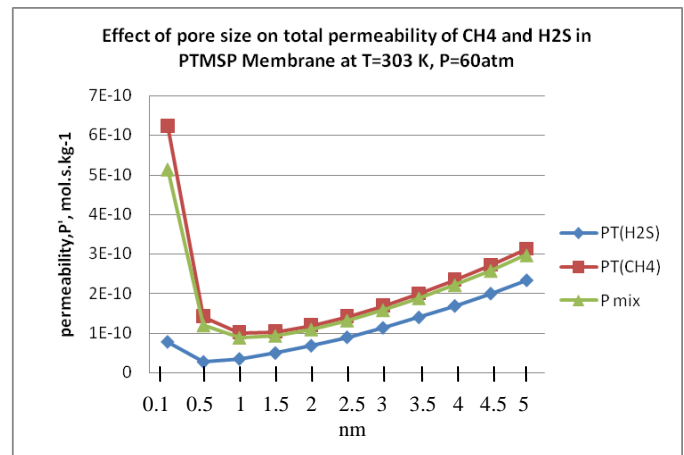

Fig. 5 Pure gas permeability versus mixture of gas permeability in PTMSP and P=60 atm. and T=303K.

E. Separation Factor

When evaluating the accomplishment of the separation process, the separation factor is very essential aspect to be taken into account. Higher separation factor would result in an effective separation between the species in the binary mixture. From Fig. 6, the separation factor for CH_4 with respect to H_2S

is decreasing as the pore size increased due to less hindered pathway. Therefore, when the mean free path is increase, there is no restriction for the movement of gas through out the membrane. As discussed earlier, this condition lead to less separation factor as the permeability of CH_4 is getting closer to the permeability of H_2S.
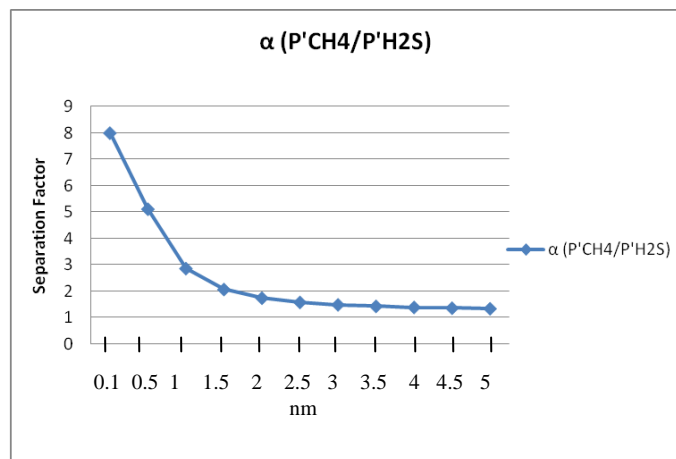

Fig. 6 Separation factor for permeability of gaseous with respect to each other

According to the industrial standard, the separation process between two gas species is possible if the separation factor is larger than 7 [20]. Therefore, in condition of P=60 atm, T=303K, the separation of H_2S from CH_4 is possible when pore size is smaller than 0.2nm. This is the optimum condition for separation process using PTMSP membrane.

A comparison between two membrane, PTMSP and γ-alumina has been illustrated in Fig. 7. Both membranes show a similar pattern, separation factor decreasing with the increase of pore size. It is apparent that the separation factor for PTMSP is higher compared to γ-alumina membrane. Other effect of pressure and temperature has been investigated as well. However, the pattern of separation factor with different pressure and temperature is not given paramount results and thus, it is concluded that the optimum operating condition is at P=60atm and T=303K.
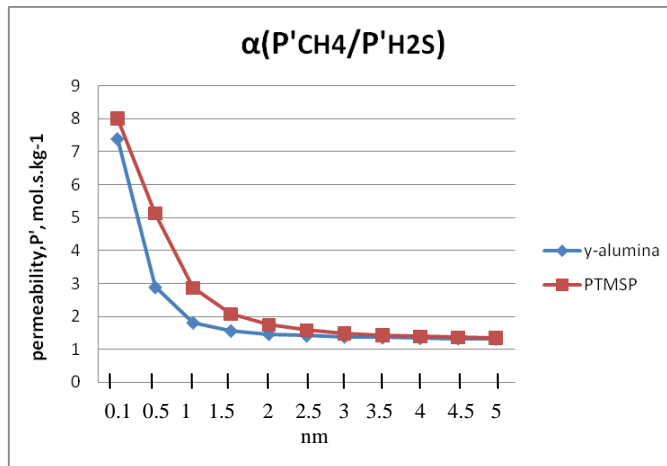

Fig. 7 Comparison of separation factor for permeability of gaseous with respect to each other by using different membrane

IV. CONCLUSION

As conclusion, the mathematical model that has been developed by combining three mechanisms of diffusion which are Knudsen, viscous and Surface is able to illustrate the separation of hydrogen sulfide from natural gas using membrane. The result shows that the gas permeability is dependent on operating pressure, temperature, pore size as well as feed composition. It increases with increasing of pressure and decrease with increasing of temperature. The variation of pore size gives significant effect for gas permeability as well. The permeability of gas mixture is lays between the pure gaseous dependent on feed composition. The validation result shows that the model developed is accurate and acceptable. From the result obtained, it can be conclude that the optimum condition for separation of gas using PTMSP and γ-alumina is at P=60atm, T=303K with pore size smaller than 0.2nm.

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