EFFECTS OF DELAYED EVAPORATION IN CELLULOSE ACETATE MEMBRANE PREPARATION TO SEPARATE CO_2/CH_4 AT LOW PRESSURE

By: **Adiwar**
Researcher at “LEMIGAS” R & D Centre for Oil and Gas Technology
Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA

First Registered on 10 October 2009; Received after Corection on 11 November 2009
Publication Approval on : 22 December 2009

ABSTRACT

The effect of delayed evaporation rate on CO_2/CH_4 *selectivity was investigated on cellulose acetate based membrane in composition of cellulose acetate and acetone (CA+ACE), cellulose acetate, acetone and formamide (CA+ACE+F) and cellulose acetate, acetone, formamide and polyethylene glycol 400 (CA+ACE+F+PEG). Delayed evaporation was carried out in acetone saturated air. The study shows that the presence of PEG in membrane composition gives a probability for the membrane to be used and kept in dry state. Evaporation time at standard evaporation rate for membrane composition CA+ACE+F andd CA+ACE+F+PEG to get better selectivity is not less than 60 seconds. SEM shows that macrovoids in membrane prepared by delayed evaporation rate compared to those prepared by standard evaporation are smaller in size but higher in numbers.Effects of 60 seconds of delayed evaporation rate on membrane selectivity and permeability is about the same with the effects of 15 seconds of standard evaporation. It brought abourt, in turn, a thought, that the effects of 8 seconds evaporation in spineret on hollow fibre selectivity and permeability can be increased by increasing evaporation rate.*

Keyword: evaporation, membrane, cellulose acetate, PEG

I. INTRODUCTION

CO_2 needs to be separated from natural gas because apart fron bringing down calorific value of the gas as fuel, CO_2 can cause corrosion on gas pipe line of the transportation pipeline system and cause plugging on processing pipes when the gas is liquefied[1].

Removal of CO_2 from natural gas can be carried out by various techniques such as separation by liquid absorption, cryogenic and membrane. Membrane technique is considered as a promising separation system because it consumes less energy and friendly environmentally[2].

Membrane technique commercially developped so far to separate CO_2 from natural gas is mainly directed for the separation of high pressurised gas using a solution-diffusion principle in membrane[3].

For separation of CO_2 in a low pressurised gas stock, because the driving force (pressure) is low, in order to increase separation performance, a chemical or a second polymer which is capable to reversibly reacts or dissolves CO_2 is added to the membrane so that in the membrane other mechanism apart from solution and diffusion also takes place [4].

In commercial application, membrane used is mostly in the form of hollow fiber because it produces much bigger separation area per volume compared to that of flat sheet membrane.

Optimal polymer solution composition and casting operational condition, for practical reason, is normally studied using flat sheet membrane. Transformation of flat sheet membrane into hollow fibre membrane by referencing to the optimal polymer solution composition and casting operational condition obtained in flat sheet quite often does not produce desired performance in hollow fibre membrane.

In flat sheet membrane preparation, apart from polymer composition and solvent and coagulant, some conditional factor of membrane preparation also influence the performance of the membrane produced. Conditional factor of the membrane preparation among others is evaporation condition[5].

The conditional factor that is quite difference in the hollow fibre membrane preparation compared to that of flat sheet membrane preparation is the availlability of evaporation time which is quite limited. Evaporation time in flat sheet membrane preparation can be as long as desired while evaporation time that can be allocated in hollow fibre membrane preparation in most cases is not more than 8 seconds depending on apparatus configuration.

In conjunction with the problem of the casting operational condition in membrane preparation, in this study observation is carried out on the effect of delaying evaporation rate in membrane preparation.

II. EXPERIMENTAL

A. *Membrane preparation*

Cellulose acetate with acetyl content of 39.8 % was obtained from Aldrich. Polyethylene glycol 400, acetone and formamide were obtained from Merck. Membrane was made by phase inversion process. Cellulose acetate, polyethylene glycol 400, acetone and formamide were first stirred until homogene. Flat sheet membrane was casted by a doctor knife, and evaporated for 60 seconds. Membrane was then dipped into a coagulation bath containing water with temperature of 10^0C for 1 hour. Membrane was then annealed by dipping it into water with temperature of 70^0C for 10 minutes. Membrane was finally kept in either water or desiccator.

Membranes were prepared with three different composition, they were composition of cellulose acetate and acetone (CA+ACE), cellulose acetate, acetone and formamide (CA+ACE+F), and cellulose acetate, acetone, formamide and polyethylene glycol 400 (CA+ACE+F+PEG). To variate evaporation rate, membranes were evaporated in two different condition viz. in ambient air and in air saturated with acetone. Condition of acetone saturated air was made by placing membrane in a box saturated with acetone.

B. *Gas*

Gases used in the study were individual CH_4 and CO_2. Both were obtained from PT. BOC with purity not less than 99%.

C. *Gas flux measurement*

Gas flux through membrane was measured using a permeation cell equipped with a flow meter. The scheme of the apparatus is shown in Figure 1.

A membrane to be tested was placed in permeation cell. Gas was introduced to permeation cell and permeated the membrane. Gas flux was measured using flow meter. Flowmeter consisted of a transparent tubing containing a drop of isopropanol and intervally marked. The time needed for isopropanol to pass the interval markers was recorded.

D. *Calculation of permeation rate and selec*tivity

Based on data of distance interval and time recorded for each of pressure variation, gas flux is calculated by equation:

$$Q = Ax\frac{dL}{dt} \qquad (1)$$

Flux at standard condition (STP) 1 atm and 273 K is then calculated by equation :

$$Q_{STP} = Q \ x \ \frac{273}{T + 273} \qquad (2)$$

and permeation rate is calculated by equation:

$$\frac{P}{l} = \frac{Q_{STP}}{Am(P_i - P_0)} \qquad (3)$$

Ideal selectivity (±) of the membrane is then calculated by equation :

$$\alpha_{ij} = \frac{P_i}{P_j} \qquad (4)$$

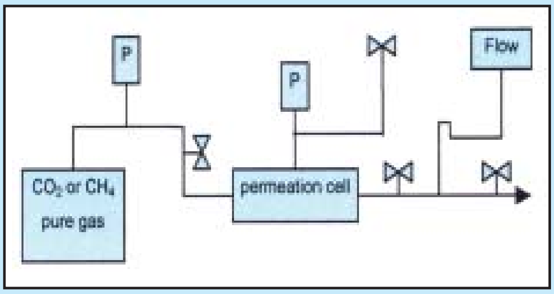

Figure 1
Scheme of gas flux measurement apparatus

Table 1
Composition and casting parameter of membranes prepared

Composition	Casting		Storage		Thickness (Micron)		Appearance
	Standard	Non-standard	Des	H_2O	Casting	Actual	
CA + ACE	v		v		200	84	clear
	v			V	200	91	clear
		Sat air		V	200	84	clear
CA + ACE +F	v		v		200	105	clear
	v			V	200	156	blurr
		Evap 15'		V	200	180	blurr
		Evap 30'		V	200	175	blurr
		Sat air		V	200	87	blurr
CA + ACE + F + PEG400	v		v		200	135	milky blurr
	v			V	200	165	milky blurr
		Evap 15'		V	200	133	milky
		evap 30'		V	200	133	milky
		Sat air		V	200	88	milky blurr

E. Membrane morphology observation

Membrane morphology is observed using a scanning electron microscopy (SEM).

III. RESULT AND DISCUSSION

A. *Membrane storage*

Membranes prepared together with their composition and casting parameter and storage are listed in Table 1. Selectivity of membranes kept in water (H) and those kept in desiccator (D) are shown in Figure 2. From the figure it can be seen that membranes kept in water have better selectivity than those kept in desiccator. This phenomenon indicates that those membrane kept in desiccator in dry condition might undergo stress causing part of the pore structures collapsed[6]. In field application, in CO_2 removal operation, however, membranes mostly deal with dry gasses. Means that a posttreatment should be given to the membranes.

B. *Membrane composition*

Selectivity of membranes for the three compositions are also shown in Figure 2. From the figure it can be seen that membranes

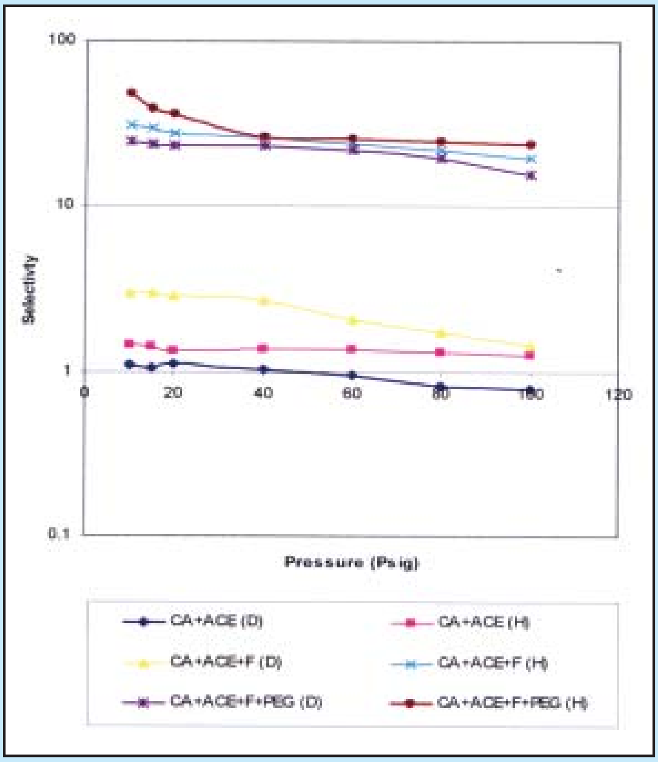

Figure 2
Selectivity of membrane CA+ACE, CA+ACE+F and CA+ACE+F+PEG kept in water (H) and desiccator (D)

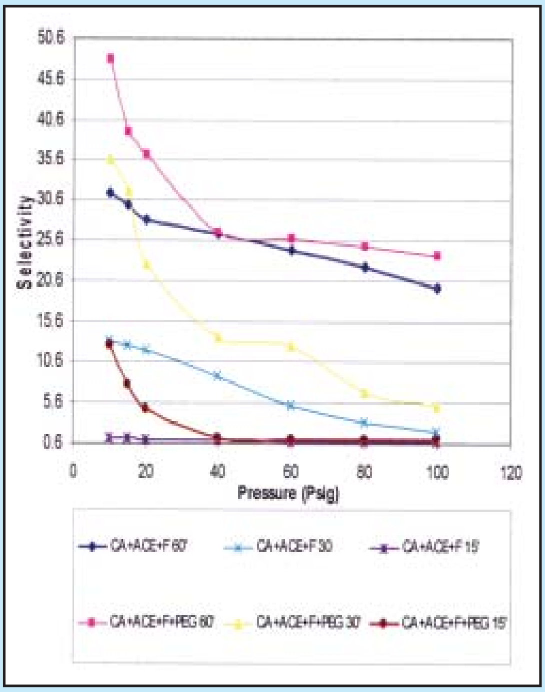

Figure 3
Selectivity of membrane with different evaporation time

CA+ACE both kept in water and desiccator does not have good selectivity. Membranes CA+ACE+F kept in desiccator also does not have good selectivity but the one that kept in water has good selectivity. Membrane CA+ACE+F seems to have higher selectivity than that of membrane CA+ACE. This is presumably because rate of acetone evaporation is relatively high[7] causing a possibility for top layer of the membrane to have defects. The presence of formamide might reduce the rate of acetone evaporation which in turn also reduce the possibility of defect formation.

Membranes CA+ACE+F+PEG both kept in water and desiccator have good selectivity eventhough the one kept in desiccator is relatively lower. Membranes CA+ACE+F+PEG have higher selectivity compared to membranes CA+ACE+F. Kuehne[8] reported that PEG can absorb CO_2 causing the selectivity of the membrane to increase.

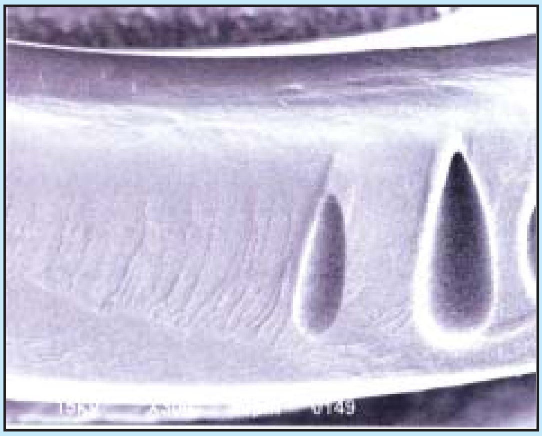

Figure 4
Cross section of membrane CA+ASE+F+PEG with evaporation time 60 seconds

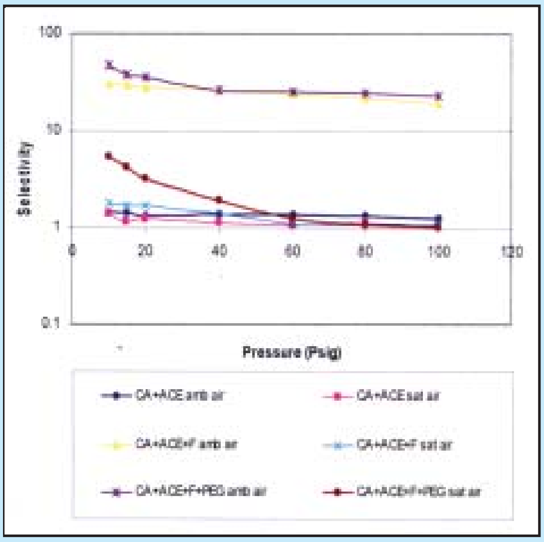

Figure 5
Comparison of membrane selectivity prepared by delayed evaporation and standard evaporation rate

C. *Effect of evaporation time*

Variation of evaporation time is observed on membrane CA+ACE+F and membrane CA+ACE+F+PEG, the result is shown in Figure 3. It can be seen that for both membrane composition, evaporation time of 60 seconds gives higher selectivity. For membrane CA+ACE+F selectivity ranges from 30 to 20 for pressure of 10 to 100 psi. For membrane CA+ACE+F selectivity ranges from 30 to 20 for pressure of 10 to 100 psi. For membrane CA+ACE+F+PEG selectivity ranges from 48 to 25 for pressure ranges from 10 to 100 psi. The shorter the evaporation time the lower is for shorter evaporation time for both membranes composition there is not enough time available to let some of the acetone at top layer casted polymer to evaporate before coagulation taking place so that the top layer is less dense and probably have some defects.

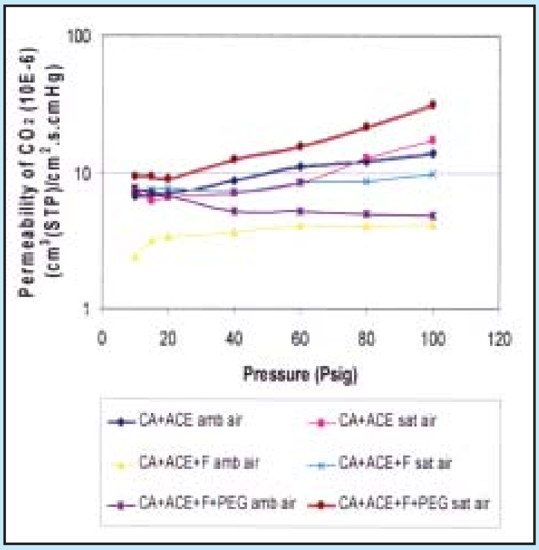

Figure 6
Comparison of membrane CO_2-permeability prepared by delayed evaporation and standard evaporation rate

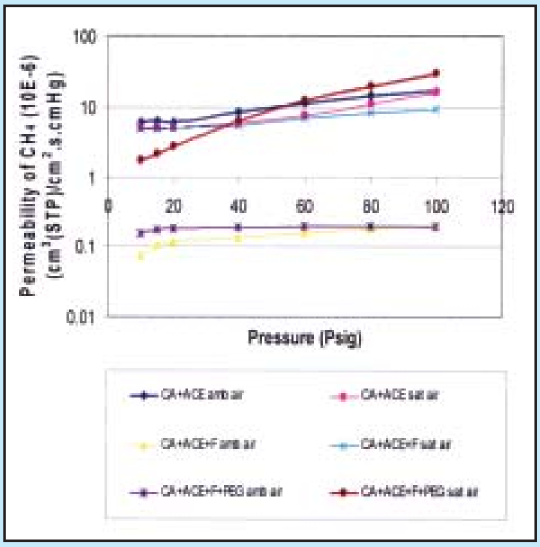

Figure 7
Comparison of membrane CH_4-permeability prepared by delayed evaporation and standard evaporation rate

A cross section of membrane CA+ACE+F+PEG with evaporation time of 60 seconds is shown in Figure 4. It can be seen that the membrane has dense layer at the top and relatively less dense support below it. The membrane also have some macrovoids.

D. *Efect of delaying evaporation*

Figure 5 shows comparison of selectivity of the membranes prepared by delayed evaporation rate to that of membranes prepared by standard evaporation rate. From Figure 5 it can be seen that except for membrane CA-ACE which have lower selectivity on both evaporation modes, membrane CA+ACE+F and membrane CA+ACE+ F+PEG prepared in delayed evaporation rate have lower selectivity compared to those membranes prepared in standard evapaporation rate.

Figure 6 shows comparison of permeability of CO_2 of the membranes prepared by delayed evaporation rate to that of membranes prepared by standard evaporation rate. From Figure 6 it can be seen that except for membrane CA-ACE which have relatively the same rate of CO_2 permeability on both

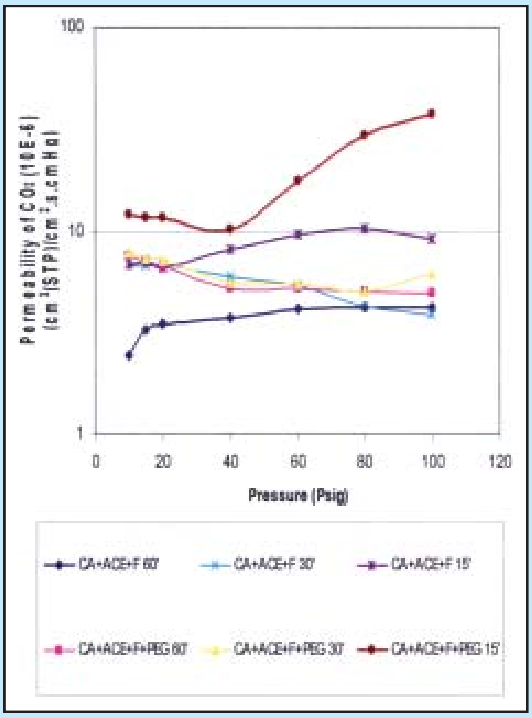

Figure 8
Membrane CO_2-permeability prepared by standard evaporation rate

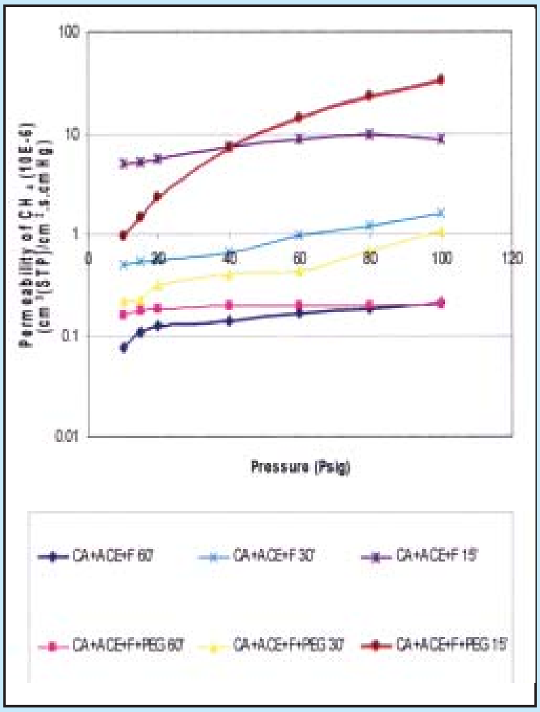

Figure 9
Membrane CH_4-permeability prepared by standard evaporation rate

evaporation modes, membrane CA+ACE+F and membrane CA+ACE+F+PEG prepared in delayed evaporation rate have higher CO_2 permeabilities compared to those membranes prepared in standard evapaporation rate.

Figure 7 shows comparison of permeability of CH_4 of the membranes prepared by delayed evaporation rate to that of membranes prepared by standard evaporation rate. From Figure 7 it can be seen that except for membrane CA-ACE which have relatively the same rate of CH_4 permeability on both evaporation modes, membrane CA+ACE+F and membrane CA+ACE+F+PEG prepared in delayed evaporation rate have higher CH_4 permeabilities compared to those membranes prepared in standard evapaporation rate.

Higher permeability of CO_2 and lower permeability of CH_4 will produce higher selectivity of a membrane in gas separation. But higher permeability for both CO_2 and CH_4 will not produce higher selectivity and can be an indication of lacking in separation, presumably due to membrane defects.

Comparing rate of CO_2 permeability of membrane CA+ACE+F and membrane CA+ACE+F+PEG prepared in delayed evaporation rate with those membranes prepared in standard evapaporation rate as shown in Figure 8, and comparing rate of CH_4 permeability of membrane CA+ACE+F and membrane CA+ACE+F+PEG prepared in delayed evaporation rate with those membranes prepared in standard evapaporation rate as shown in Figure 9, it can be seen that rate of CO_2 permeability and CH_4 permeability of membrane CA+ACE+F and membrane CA+ACE+F+PEG prepared in delayed evaporation rate is about the same with those membranes prepared in standard evapaporation rate with evaporation time of 15 seconds. It brought about, in turn, a

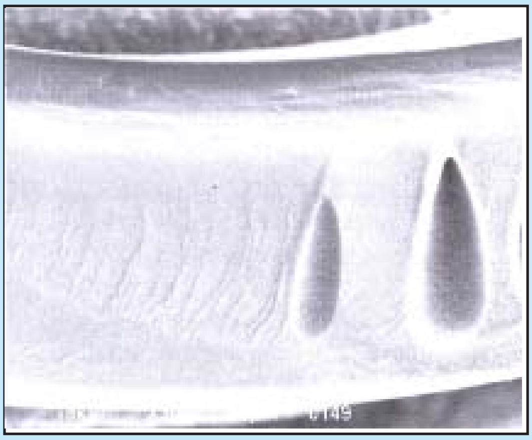

Figure 10
A morphology of a membrane prepared in standard evaporation rate with 60 seconds evaporation time

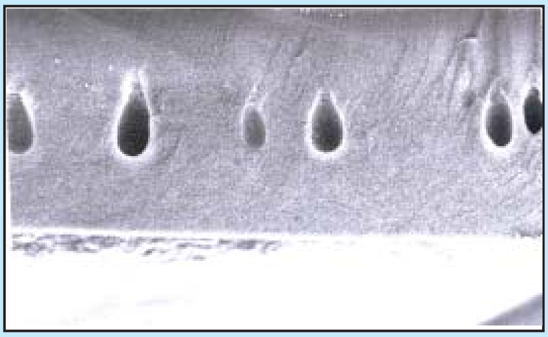

Figure 11
A morphology of a membrane prepared in delayed evaporation rate with 60 seconds evaporation time

thought that the effects of 8 seconds evaporation in spineret on hollow fibre selectivity and permeability can be increased by increasing evaporation rate.

Presumably both 60 seconds evaporation time with delayed evaporation and 15 seconds evaporation time with standard evaporation are not long enough to produce defect free membranes.

Below in Figure 10 is shown a morphology of a membrane prepared in standard evaporation rate with 60 seconds evaporation time and in Figure 11 is shown a morphology of a membrane prepared in delayed evaporation rate with 60 seconds evaporation time. It can be seen that there are macrovoids in both membranes. Macrovoids in membrane prepared by delayed evaporation rate nevertheless are smaller in size but higher in numbers.

IV. CONCLUSION

1. The presence of PEG in membrane composition give a probability for the membrane to be used and kept in dry state.
2. Evaporation time at standard evaporation rate for membrane composition CA+ACE+F andd CA+ACE+F+PEG to get better selectivity is not less than 60 seconds.
3. Macrovoids in membrane prepared by delayed evaporation rate compared to those prepared by standard evaporation are smaller in size but higher in numbers.
4. Effects of 60 seconds of delayed evaporation rate on membranes selectivity and permeability is about the same with the effects of 15 seconds of standard evaporation. It brought abourt, in turn, a thought that the effects of 8 seconds evaporation in spineret on hollow fibre selectivity and permeability can be increased by increasing evaporation rate.

V. LIST OF SYMBOLS

Q = Gas permeation flux of the steady state ($cm^3\ s^{-1}$)
A = Tubing cross section area (cm^2)
dL/dt = distance per time unit ($cm\ s^{-1}$)
$\frac{P}{l}$ = Permeation rate (cm^3 (STP).$cm^{-2}.s^{-1}.cm\ Hg^{-1}$)
Q_{STP} = Gas permeation flux at standard STP ($cm^3_{(STP)}.s^{-1}$)
Am = Membrane area (cm^2)
Pi = Upstream gas pressure (cmHg)
Po = Downstream gas pressure (cmHg)
i = CO_2
j = CH_4
α ij = Selectivity CO_2 /CH_4
$(P/l)_i$ = Permeation rate of CO_2 ($cm^3.cm^{-2}.s^{-1}.cmHg^{-1}$)
$(P/l)_j$ = Permeation rate of CH_4 ($cm^3.cm^{-2}.s^{-1}.cm\ Hg^{-1}$)
D = Difusivity
S = Solubility

REFFERENSES

1. Perry, Robert H., and Green, W., 1999. *Perry's Chemical Engineers' Handbook*. McGraw-Hill.
2. Jintong, Li., Nagai K., Nakagawa T., Wang, S., 1995. *Preparation of Polyethylen glikol and Celluloce Acetate (CA) Blend Membranes and Their Gas Permeabilities. Journal of Membrane Science* 58, *1455 – 1465.*
3 Baker, R W., 2000. *Membrane Technology and Application. Membrane Technology and Research,* Inc. McGraw-Hill. New York.
4. Chunhai, Yi., Zhi, Wang, Meng, Li, Jixiao Wang, and Shichang. Wang,. 2005. "*Facilitated Transport of CO_2 through Polyvinylamine/Polyethylene Glycol Blend Membranes*". *Desalination Journal,* 193, *90-96.*
5. Mulder, M., 2000. *Principles of Membrane Technology second* Edition. Kluwer Academic Publisher: Netherland
6. Minhas, B. S., Matsura, T. , Sourirayan, S., 1987, Ind. Eng. Chem. Res, 26, 2344-2348.
7. Kools, W. F. C., 1998. Membrane Formation By Phase Inversion In Multicomponent Polymer Systems. PhD Thesis, University of Twente.
8 Kuehne, D. L., and Friedlander S. K. , 1980, Ind. Eng. Chem. Prod. Res. Dev., 19, 609.