CHAPTER IV
RESULTS AND DISCUSSION

In the experiment, pure Ultem membrane and Mixed Matrix Membranes (MMMs) used in permeability and selectivity testing of gases are described as follow:

1. Pure Ultem Membrane (Ultem)
2. Activated Carbon/Ultem MMMs (AC)
3. Activated Carbon/Polyethylene glycol/ Ultem MMMs (PEG/AC)
4. Activated Carbon/1,2-Butanediol/Ultem MMMs (1,2AC)
5. Activated Carbon/1,3-Butanediol/Ultem MMMs (1,3AC)
6. Activated Carbon/1,4-Butanediol/Ultem MMMs (1,4AC)
7. Activated Carbon/2,3-Butanediol/Ultem MMMs (2,3AC)

All types of membranes were composed of 20 wt% Ultem polymer and 80 wt% N-methylpyrolidone (NMP). 20 wt% activated carbon and 30 wt% of each liquid additives (PEG, 1,2-, 1,3-, 1,4- ,and 2,3-butanediol) were added into MMMs based on Ultem polymer.

4.1 Effect of Liquid Loading into Activated Carbon

To find the optimum condition of liquid loading into activated carbon and prove that the solubility of polar gas (CO_2) in liquid additives or Glycol isomers increases, the experiment in the increasing of wt% liquid loading was conducted, which was varied from 10 to 40 wt%. The results are shown in Table 4.1.

Table 4.1 Effect of liquid loading into activated carbon

% liquid loading into activated carbon	Phase
10	dry
20	dry
30	dry
40	wet

In the experiment, each liquid additive was added into activated carbon in the range between 10 and 40 wt% and followed by heating at 150°C in an oven for 24 hr in order to evaporate excess NMP solvent and liquid additive that cannot stabilize in the pores of activated carbon. The activated carbon that can be used has to be in the dry-powder form after heat treating. In case of 40 wt% liquid additives added into activated carbon shown in Table 4.1, the treated activated carbon exhibited in wet-powder form. Owning to the liquid leakage from the pores of activated carbon, activated carbon cannot be dried and stay in dry-powder form.

The further study for selecting the most suitable condition in the range between 10 and 30 wt% liquid loading was the CO_2 permeance testing. MMMs were fabricated with each liquid additive adsorbed into activated carbon at 10, 20 and 30 wt% loading. The results are shown in Figure 4.1.
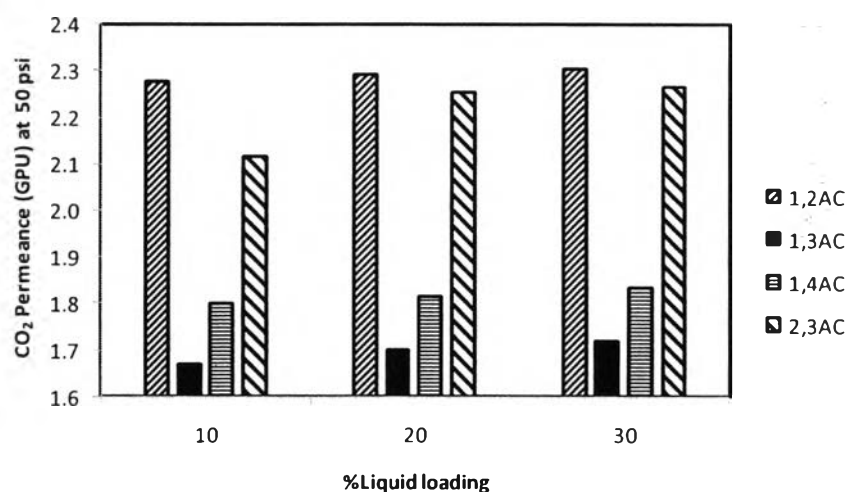

Figure 4.1 Effect of liquid loading on MMMs.

In Figure 4.1, CO_2 permeance as well as solubility of CO_2 in all types of liquid additives (1,2-, 1,3-, 1,4- and 2,3-butanediol) increase with increasing liquid loading from 10 to 30 wt%. As the highest CO_2 permeance, 30 wt% liquid loading was selected to be used in the fabrication of asymmetric and dense membranes in the next steps.

4.2 G as Permeances

4.2.1 Dense Membranes and Dense MMMs

Permeances of CO_2, CH_4, N_2 and H_2 determined from a flow rate of each gas at steady state through pure membrane and mixed matrix membranes at room temperature and pressure of 100 psi are shown in Figure 4.2.
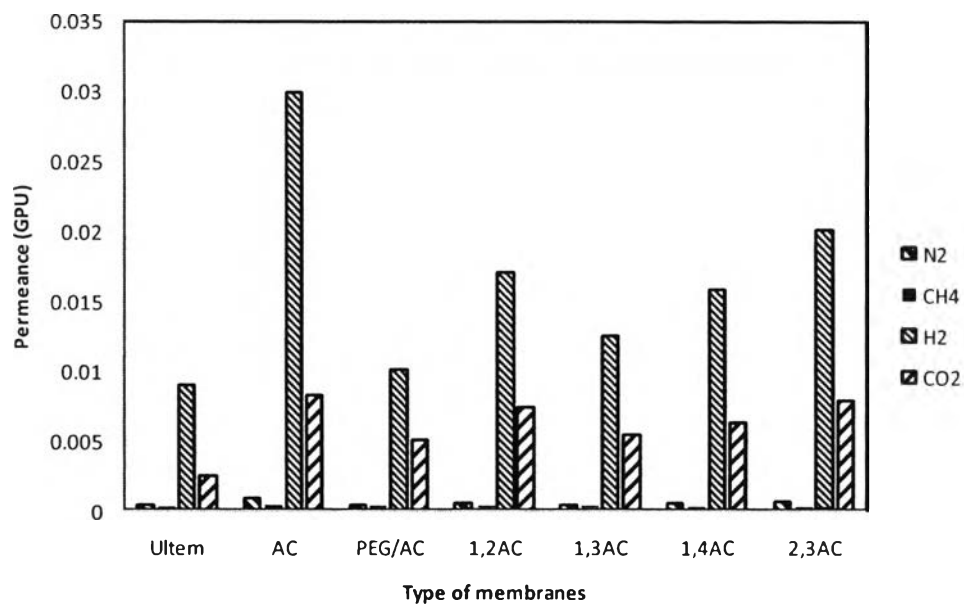

Figure 4.2 Permeances of the tested gases for pure dense membrane and dense MMMs at 100 psi.

Ultem membrane normally uses diffusivity term for characterization the performance of membrane, which refers to lower permeance as increasing the molecular size of gas; or the smaller size of gas molecule, the more permeation rate of gas. For pure Ultem membrane (Ultem), H_2 possesses the highest gas permeance followed by CO_2, N_2 and CH_4 in sequence for all membranes relating to the particle size of each gas shown in Figure 4.2. The permeation rates of gases depend on their molecular sizes or kinetic diameters represented in Table 4.2.

Table 4.2 Kinetic diameters of tested gases

Gas	Kinetic Diameter (A°)
N_2	3.64
CH_4	3.80
H_2	2.89
CO_2	3.30

AC (20wt% activated carbon/Ultem MMM) shows higher permeances for all gases when compare to pure Ultem membrane. This is due to the increase in volume fraction occupied by the filter that may produce both a contact between the carbon clusters and void spaces around the carbon agglomerate (Anson *et al.*, 2004). The permeance rates for AC still depend on molecular size of gases regardless of added activated carbon .

Gas permeances of solid-liquid MMMs, which are composed of Ultem, activated carbon and all types of liquid additives (PEG, 1,2-, 1,3-, 1,4- and 2,3-butanediols), are higher than that of pure Ultem membrane (Ultem) but lower than activated carbon/Ultem MMM (AC). The added glycol or liquid additive incorporated into activated carbon pores fills up the transient gap between polymer chains and hinders the diffusion path of gas molecules. As a consequence, most of the gases permeate slower.

The comparison between solid-liquid MMMs and pure ultem membrane shows that CO_2 permeance is significantly increased when compare to other tested gases. This is because hydroxyl groups present in each of PEG and butanediol isomers would be the major determiner of CO_2 solubility into membrane phase since the O-H bond is strongly polar, its polarity induces the formation of London force arisen from temporary dipole moment (Serivalsatit, 1999). Therefore CO_2 molecules, which are more polar than the other gases, can be more adsorbed into membrane phase and diffuses through the polymeric matrix for N_2, CH_4 and H_2 no effect of liquid additives or glycol isomers was observed.

From Figure 4.2, permeation rates of gases are somewhat different between MMM added PEG and those added butanediol isomers into pores of activated carbon. Mixed matrix membranes that consist of PEG (PEG/AC) illustrate that all gases pass through the membrane at slower rate than butanediol isomers MMMs

(1,2AC, 1,3AC, 1,4AC and 2,3AC). The explanation is that PEG has much bigger size than butanediol isomers with molecular weight of 400 and 90, respectively, which the path way for gas permeation was hindered and blocked resulting in slower permeation of CO_2 for PEG than butanediol MMMs.

In addition, the highest permeances of all gases were observed when activated carbon was added alone into membrane solution because of the increase in volume fraction. However, with liquid additives added into pores of activated carbon, permeances of all gases decreased because the transient gaps between polymer chains and diffusion path of gas molecules were filled up and hindered, respectively.

4.2.2 Asymmetric Membranes and Asymmetric MMMs

Permeances of CO_2, CH_4, N_2 and H_2 determined from flow rate of each gas at steady state at room temperature and pressure of 50 and 100 psi are shown in Figures 4.3 and 4.4, respectively.
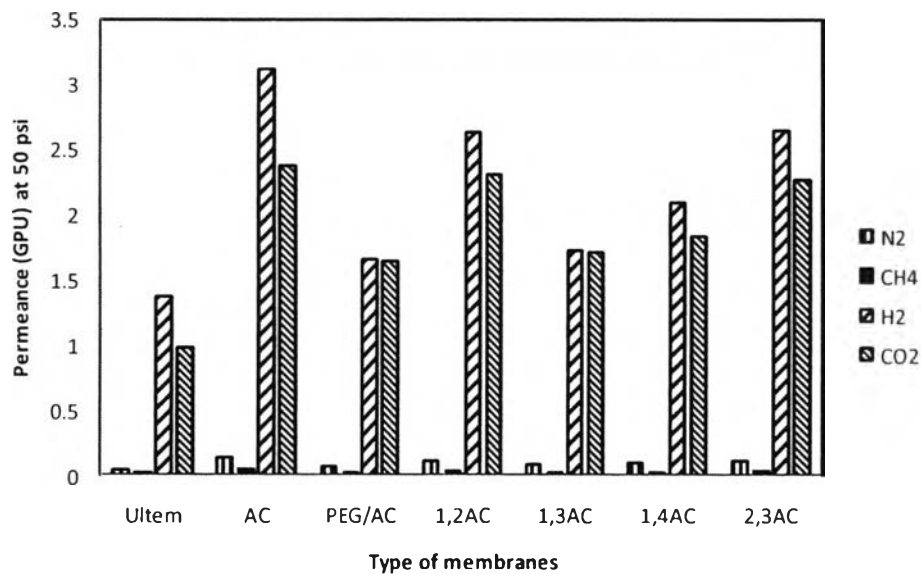

Figure 4.3 Permeances of the tested gases for the pure asymmetric membrane and asymmetric MMMs at 50 psi.
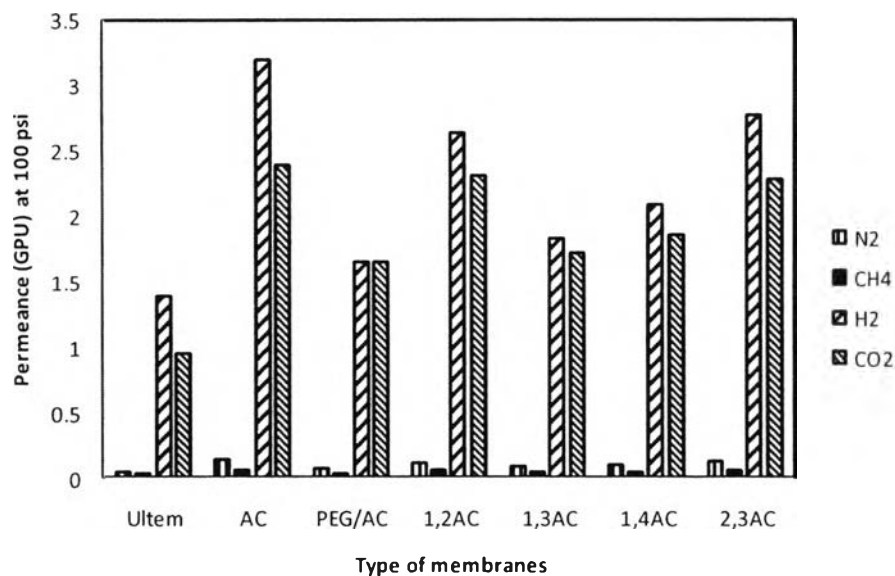
Figure 4.4 Permeances of the tested gases for the pure asymmetric membrane and asymmetric MMMs at 100 psi.

Permeances of all tested gases for asymmetric membranes and MMMs are much higher when compare to those of dense membranes and MMMs, which could be an evidence for verifying the characteristic of membrane types. It is due to the structure of asymmetric membrane that consists of a dense skin layer and a porous support layer, which lead to the higher permeances for all gases in porous layer. The results from asymmetric membranes could be more accurate than dense membranes owing to the shorter time to get result; flow rate of each gas at steady state. Asymmetric membranes were tested at both 50 and 100 psi due to the more flow rate of gases that passed through the membranes and would be used to study the effect of pressure. Whereas dense membranes had very low gas flow rates as well as permeance of gases even at high pressure (100 psi). However, permeances of all gases for dense membranes and asymmetric membranes have the same tendency, and the explanation of asymmetric membrane permeance could be described as the same in dense membranes.

4.3 G as Selectivities

4.3.1 Dense Membranes and Dense MMMs

Aromatic Polyimides are a class of high-performance polymers and have high selectivities for H_2/N_2, O_2/N_2 and CO_2/CH_4 when compare to other polymers, for instance, silicone rubber.

Selectivities of CO_2, CH_4, N_2 and H_2 calculated from average permeance of each gas at steady state through membrane and mixed matrix membranes at room temperature and pressure of 100 psi are shown in Figure 4.5.
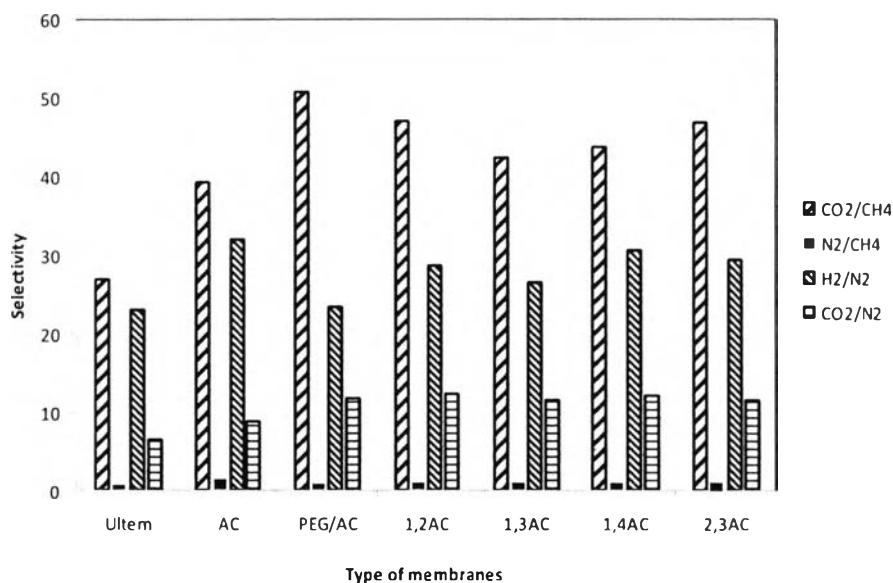

Figure 4.5 Selectivities of the tested gases for the pure dense membrane and dense MMMs at 100 psi.

It is revealed that the solid mixed matrix membrane that incorporates with activated carbon and Ultem (AC) can enhance the permeance and selectivity of CO_2/CH_4 when compared to neat Ultem membrane. The results could be explained by considering the existence of a surface flux through the micro-mesoporous carbon media, with a mechanism of preferential surface diffusion of CO_2 (more adsorbable gas) over the other experimental gases (N_2, CH_4 and H_2).

All of Solid-liquid MMMs (PEG/AC, 1,2AC, 1,3AC, 1,4AC and 2,3AC MMMs) demonstrate the higher CO_2/N_2 and CO_2/CH_4 selectivities resulted from the higher diffusion rates of CO_2 into liquid additives or glycol.

PEG/AC MMM provides higher CO_2/CH_4 selectivity than all butanediols MMMs. In spite of the lower permeance of CO_2 in PEG/AC MMM than in bu-

tanediols MMMs, the bigger size of molecule and strong polar property of PEG play important roles in obtaining the higher solubility of CO_2 in PEG/AC MMM.

The effect of glycol isomers has been studied by changing butanediol isomers added into MMMs. As can be seen in Figure 4.5, 1,2AC and 2,3AC MMMs provide the relatively higher CO_2/CH_4 selectivity than 1,3AC and 1,4AC MMMs. The possible explanation is that 1,2- and 2,3-butanediols have the hydroxyl groups attached to the adjacent carbon atoms. It is postulated that the position of the hydroxyl groups attached to each carbon atom on carbon backbones plays an important role in permeability and selectivity of polar gas molecules. Molecular structures of PEG and butanediol isomers are shown in Figure 4.6.
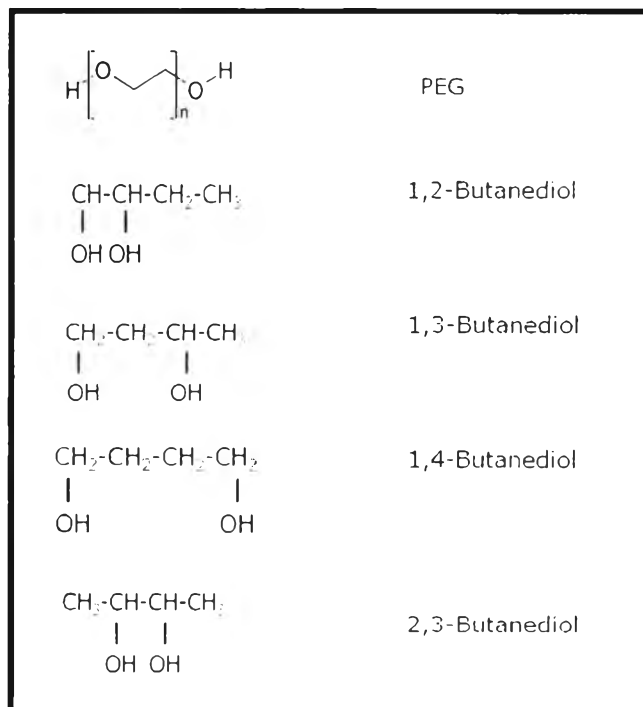

Figure 4.6 Molecular structure diagram of glycol isomers.

The polarizability of butanediol isomers has been investigated and reported by S. Taniewska-Osi'nska et al., (1997). In Figure 4.7 shows the polarizability relation among diol isomers: 1,2-ethandiol (1,2ED), 1,2-propanediol (1,2PD), 1,2-Buatanediol(1,2BD), 1,3-Buatanediol(1,3BD), 1,4-Buatanediol(1,BD) and 2,3-Buatanediol(2,3BD).
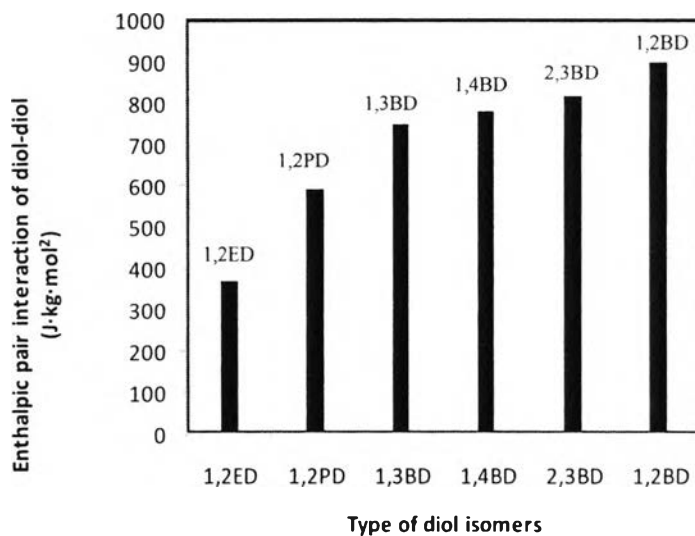
Figure 4.7 Diol-diol interaction energy of glycol isomers.

The increment of CH_2 groups from 1,2-ethandiol (1,2ED) to 1,2-propanediol (1,2PD) and 1,2-Buatanediol(1,2BD) results in the increase of hydrophobicity of diol groups, and therefore influences the interactions between diol molecules, as well as between diol molecules and electrolyte ions.

For isomeric butanediols, the distance of OH hydrophilic groups also influences these interactions, and probably changes the molecular conformations in water. It is worth noting that the interaction energy between diol groups decreases in the following order: 1,2BD-2,3BD-1,4BD-1,3BD (Taniewska-Osi'nska et al.; 1997).

The results of CO_2 permeances and CO_2/CH_4 selectivities in Figures 4.8 and 4.9, respectively are consistent with the polarizability indicated in Figure 4.7. As the highest CO_2 permeance of 1,2-buatnediol results from highest didol-diol interaction between hydroxyl groups. On the other hand, 1,3-butanediol shows the lowest permeance of CO_2 on the condition that 1,3-butanediol has the lowest didol-diol interaction.
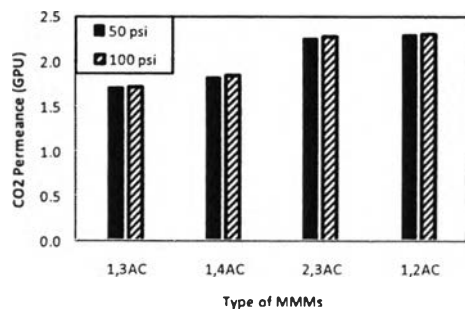
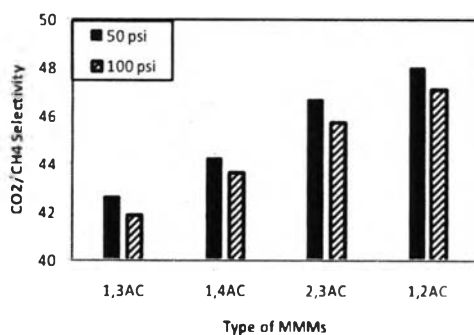**Figure 4.8** CO_2 permeances of diol isomer MMMs at 30 % loading.

Figure 4.9 CO_2/CH_4 selectivities of diol isomer MMMs at 30 % loading.

4.3.2 Asymmetric Membranes and Asymmetric MMMs

Selectivities of CO_2, CH_4, N_2 and H_2 calculated from average permeance of each gas at steady state through membrane and mixed matrix membranes at room temperature and pressure of 50 and 100 psi are shown in Figures 4.10 and 4.11, respectively.
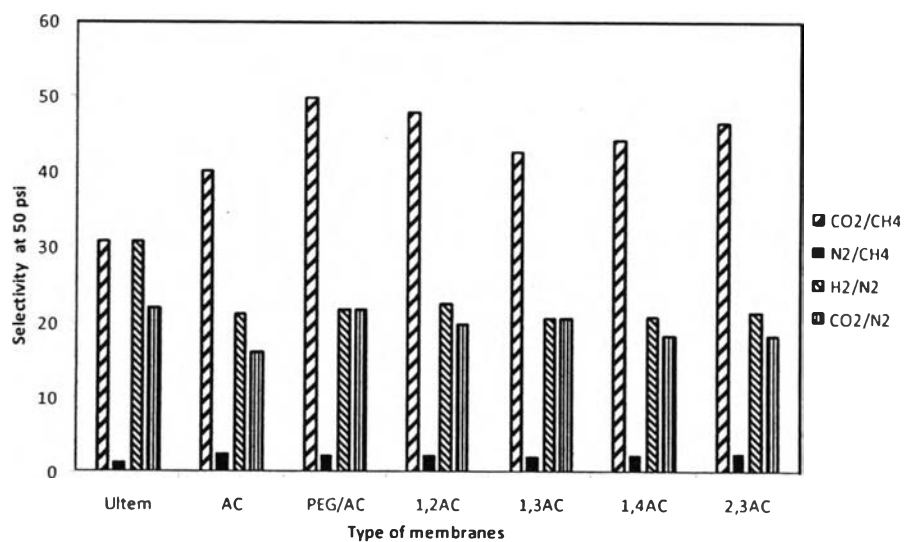
Figure 4.10 Selectivities of the tested gases for the pure asymmetric membrane and asymmetric MMMs at 50 psi.
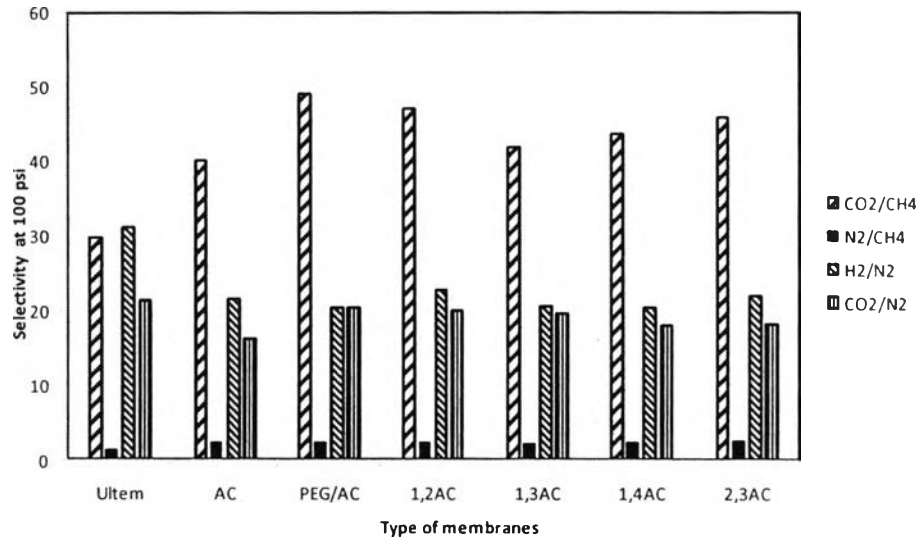

Figure 4.11 Selectivities of the tested gases for the pure asymmetric membrane and asymmetric MMMs at 100 psi.

Selectivities of all gases for asymmetric membranes are in the same manner as dense membranes at 100 psi except that the more precise and clear results are shown in Figure 4.11.

4.4 Effect of Pressure

Membrane-based separation technology normally operates under a high pressure to achieve both high permeance and selectivity. The comparison between 50 and 100 psi was compared for the effect of pressure on the MMMs studied.

Since CO_2 permeance and CO_2/CH_4 selectivity were considered as comparative parameters, the effective factor (A) was introduced by relating the two parameters mentioned. Theoretically, the higher the effective factor value, the higher the membrane performance. Such values of those parameters at different pressure are presented in Table 4.3.

Table 4.3 CO_2 permeance, CO_2/CH_4 selectivity, and effective factor of butanediol isomers MMMs at different pressures

MMMs	CO_2 Permeance (P)		CO_2/CH_4 Selectivity (α)		Effective Factor (A = P x α)	
	50 psi	100 psi	50 psi	100 psi	50 psi	100 psi
1,2AC	2.305	2.309	47.98	47.14	110.60	108.86
1,3AC	1.718	1.727	42.62	41.88	73.21	72.31
1,4AC	1.833	1.852	44.19	43.67	81.00	80.86
2,3AC	2.264	2.280	46.68	45.79	105.69	104.41

As indicated above, CO_2 permeance, CO_2/CH_4 selectivity and effective factor at between 50 and 100 psi are insignificant for all membranes. CO_2 permeance slightly increases at 100 psi. It was due to the higher driving force or pressure across the membrane surface. Although CO_2 permeance is higher at an elevated pressure, CO_2/CH_4 selectivity exhibits lower for all MMMs. At a high pressure, the selectivities of all gases slightly decrease as a consequence of shorter contact time between molecule of gas and membrane phase. At a given pressure, 1,2AC and 2,3AC MMMs possessed higher effective factor as well as higher performance of membrane than 1,3AC and 1,4AC MMMs, which can be explained in a similar manner as for gas selectivities of butanediol isomer MMMs.