Chapter 5

Results and Discussion

5.1 The Effect of Temperature on distribution coefficent

The performance of separation of aqueous solutions through silicone rubber membrane via pervaporation are related to the solubility of solute in polymer. The solubility of solutes in polymeric membrane can be shown in term of distribution coefficient. Distribution coefficient involves many complex interaction between the solute and polymeric membrane such as polarity, hydrogen bonding, and steric effects.[22] Figure 5.1 and 5.2 show the relations between distribution coefficient and feed temperature of acetone-butanol-ethanol-acetic acid-butyric acid-water mixtures and acetone-butanol fermentation broth. Distribution coefficients of butanol, acetone and ethanol were found to increase with temperature, whereas distribution coefficients of acetic acid, butyric acid and water were quite constant. The results were similar for both the synthetic mixtures and fermentation broth. However, distribution coefficients of butanol, acetone and ethanol were higher than other solutes. These results can be explained by a study of Tadashi Uragami, and et.al., that studied affinity between solvents and membrane.[23] Solvents that had high affinity force were preferentially incorporated into silicone rubber membrane.

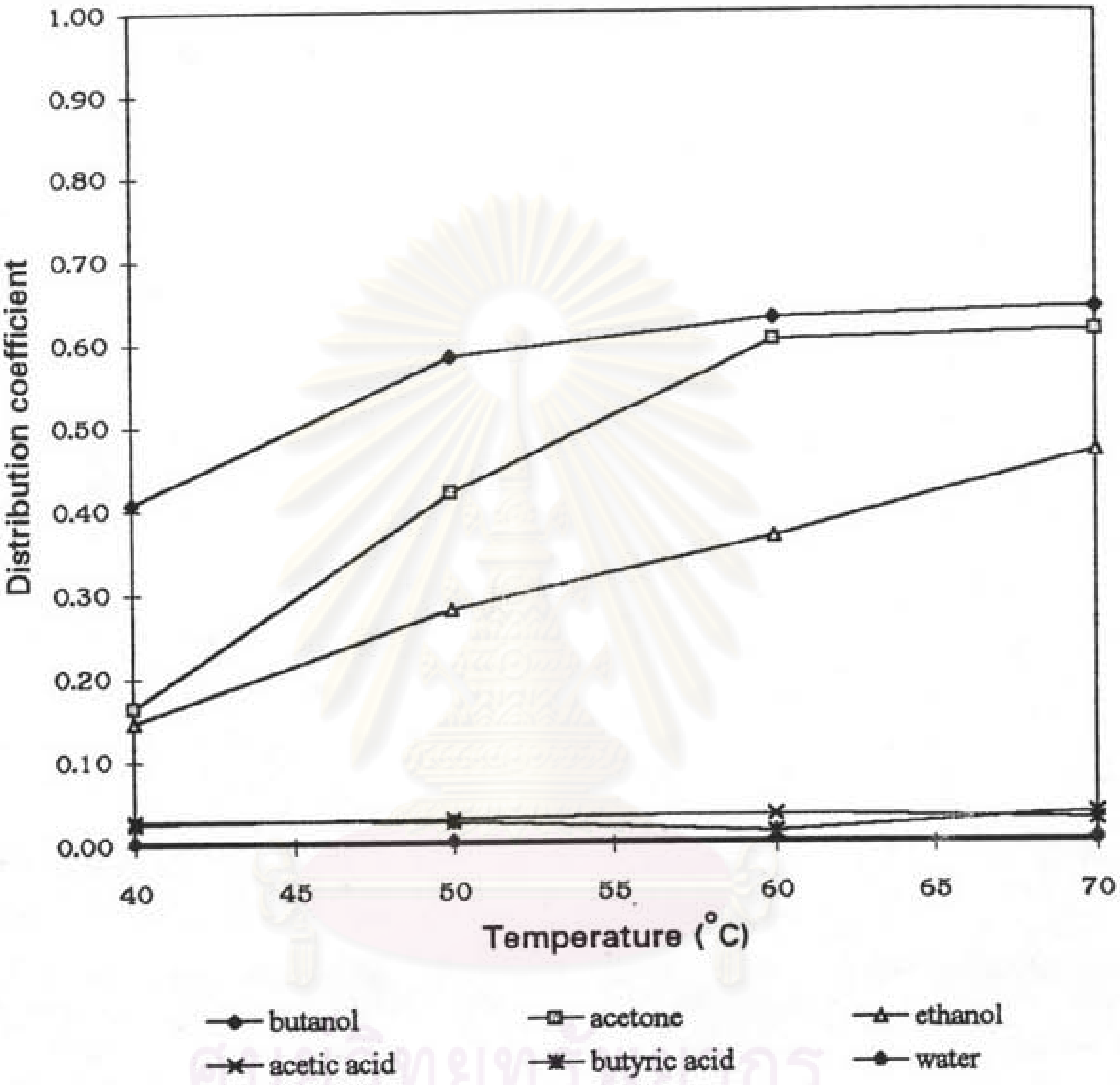

Figure 5.1 Correlation between temperature and distribution coefficient of synthetic mixtures

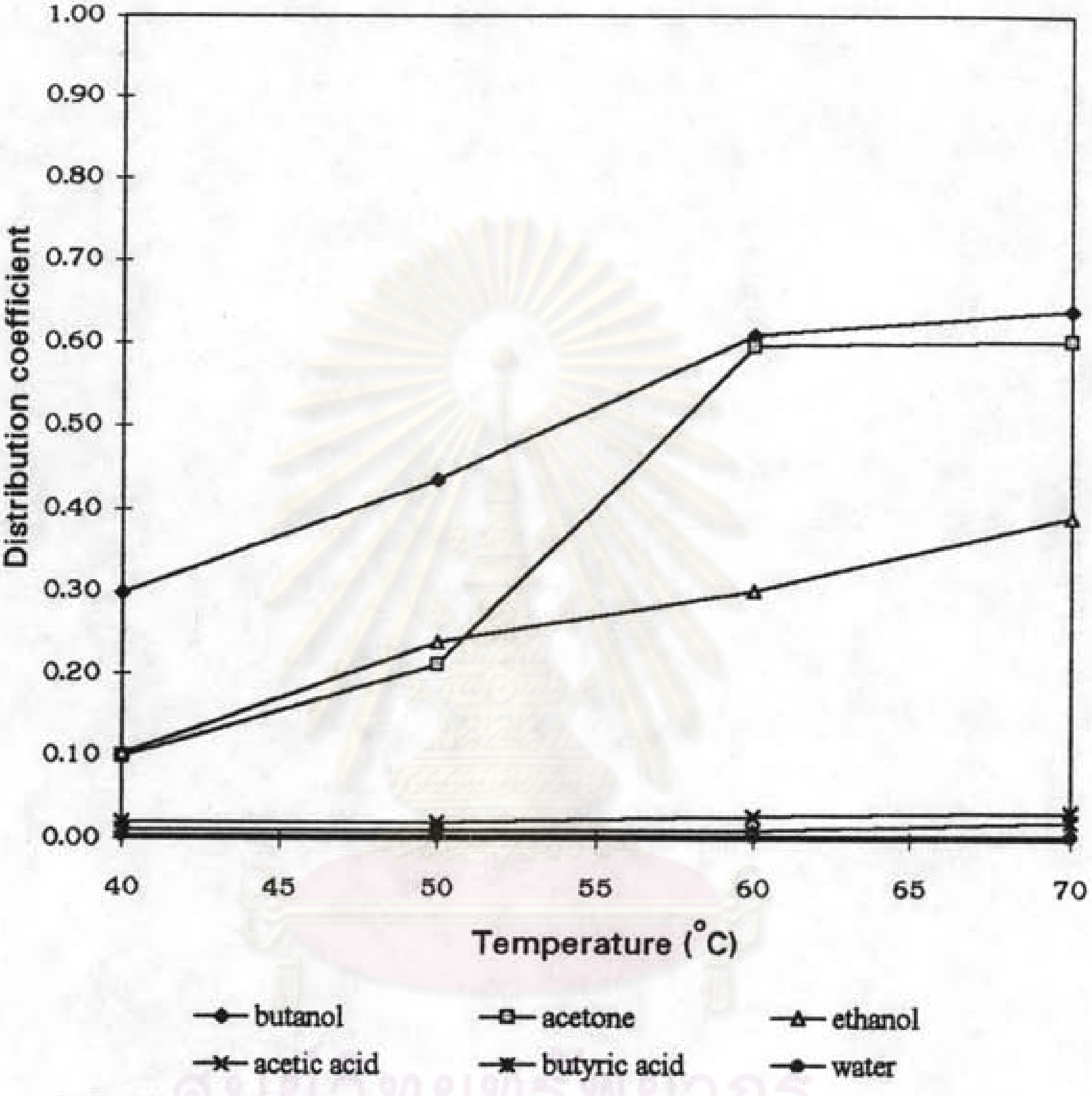

Figure 5.2 Correlation between temperature and distribution coefficient of acetone-butanol fermentation broth

5.2 The Effect of Feed Temperature on Pervaporation Process.

The effect of feed temperature on pervaporation at the permeation pressure of 2 torr, are shown in figure 5.3 and 5.4. It was found that permeation flux of all solutes in synthetic mixtures and fermentation broth increased as the feed temperature increased. Feed temperature affected every step of the pervaporation process such as sorption, membrane mass transfer, and desorption. The influence of feed temperature can be expressed by an Arrhenius exponential, that is shown in equation 3.26.

$$J_p = J_o\exp(E_p/RT) \qquad (3.26)$$

The permeation flux of butanol, acetone, ethanol, acetic acid, butyric acid, and water at the feed temperature of 60°C in synthetic mixtures were 11.29, 3.91, 0.39, 0.02, 0.02 and 29.70 $g/m^2.h$, respectively, and that in fermentation broth were 8.76, 3.04, 0.28, 0.01, 0.01 and 25.95 $g/m^2.h$, respectively. These results reflected that the permeation fluxes of acetic acid, and butyric acid were low because of their small distribution coefficients in sorption process Their high steric effects and high polarity due to the type of the molecules, whereas the permeation flux of water was high because of the driving force and its low steric effects.

Figure 5.5 to 5.7 show the effect of feed temperature on the permeate concentration and the membrane selectivity in synthetic mixtures. These values increased as temperature increased from of 40°C to 60°C. As the temperatures were higher than 60°C, the permeation concentration and the membrane selectivity decreased. This was because of the increase of permeation flux of water. The results of fermentation broth shown in figure 5.6 to 5.8 were similar to the results from synthetic mixtures, that .

At the feed temperature of 60°C, permeation concentration of acetone and ethanol in synthetic mixtures were 8.67, and 0.87 %wt., respectively, and that in fermentation broth were 8.00, and 0.74 %wt., respectively. Although acetone concentrations in permeation were higher than that of ethanol the membrane selectivity of ethanol are higher than the membrane selectivity of acetone. These results can be explained by the relation between feed concentration and membrane selectivity as shown in equation 5.1.

$$\alpha_{i/j} = \frac{y_i / y_j}{x_i / x_j} \qquad (5.1)$$

For alcoholic group, the membrane selectivity of the high molecular weight had higher membrane selectivity than the low molecular weight. These results were compatible to a study of J.M. Watson and P.A. Pyane.[24]

Thus, the best feed temperature for solvent separation in synthetic mixtures and fermentation broth was at 60 °C. This feed temperature could provide a high permeation flux, permeation concentration, and membrane selectivity of total solvent. The relation between permeation flux and feed temperature in synthetic mixtures and fermentation broth in other permeation pressure were similar to that of 2 torr.(See Appendix C)

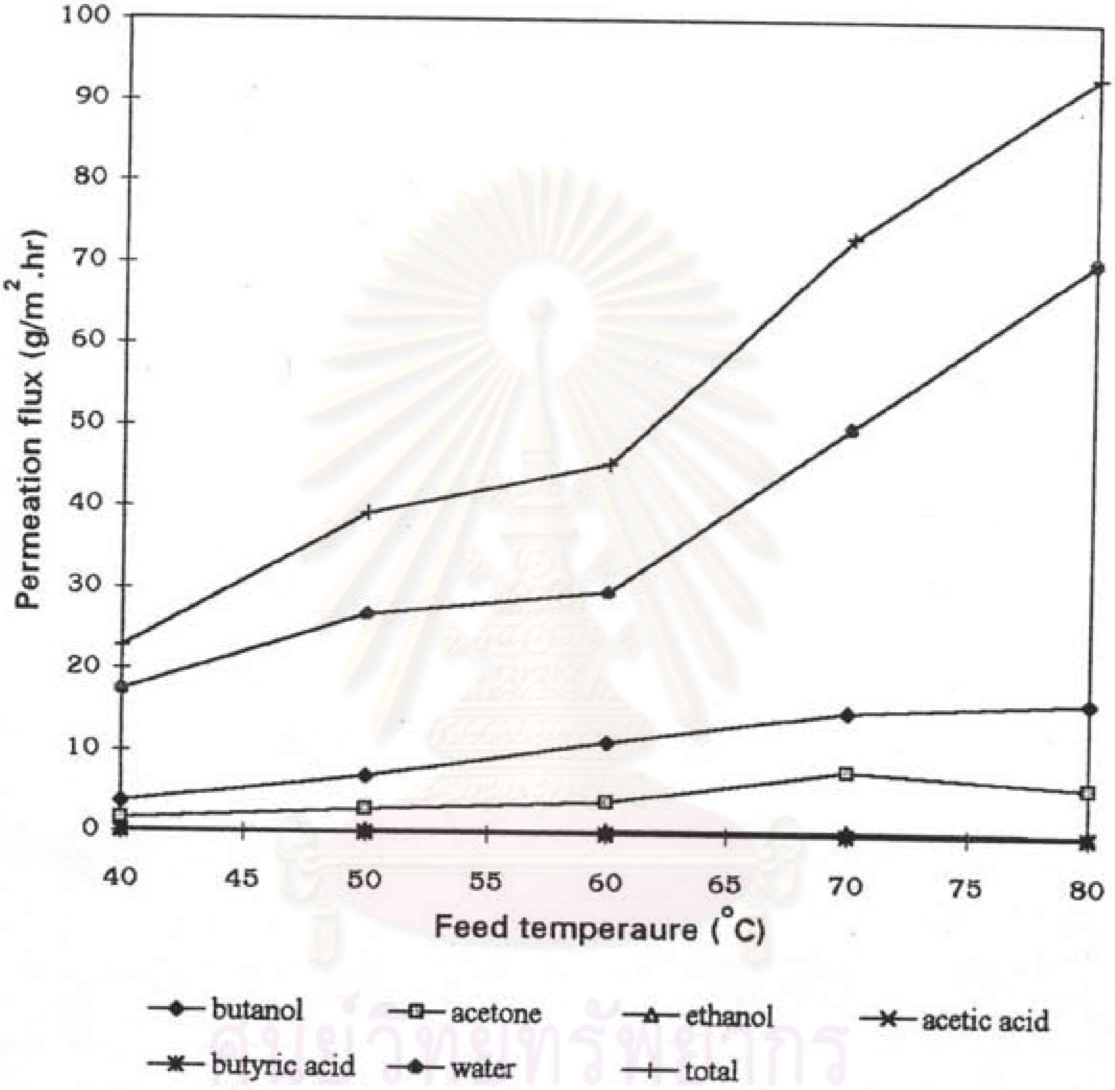

Figure 5.3 Correlation between feed temperature and permeation flux of synthetic mixtures at permeation pressure 2 torr and membrane thickness 0.25 mm.

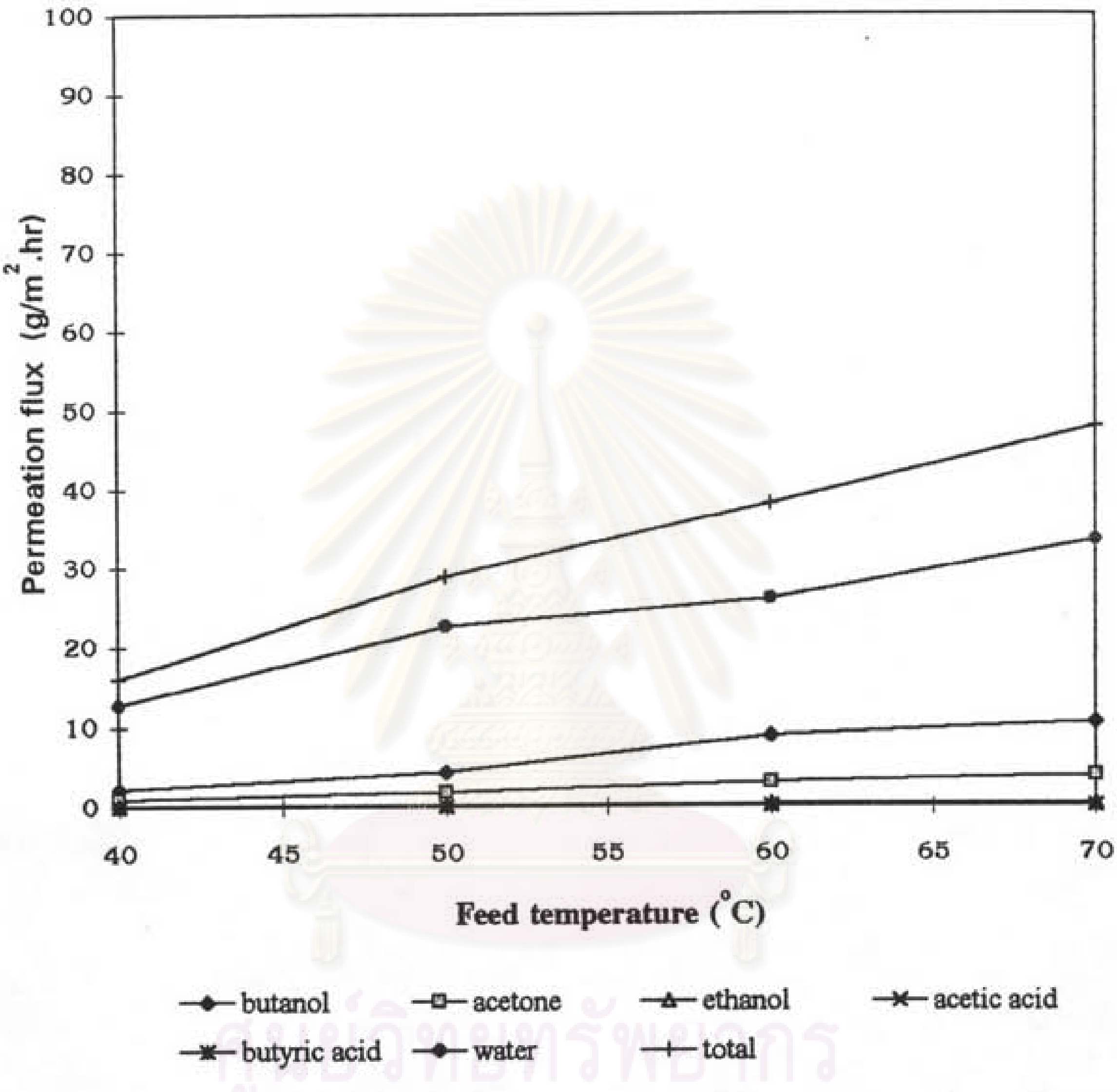

Figure 5.4 Correlation between feed temperature and permeation flux of acetone-butanol fermentation broth at permeation pressure 2 torr and membrane thickness 0.25 mm.

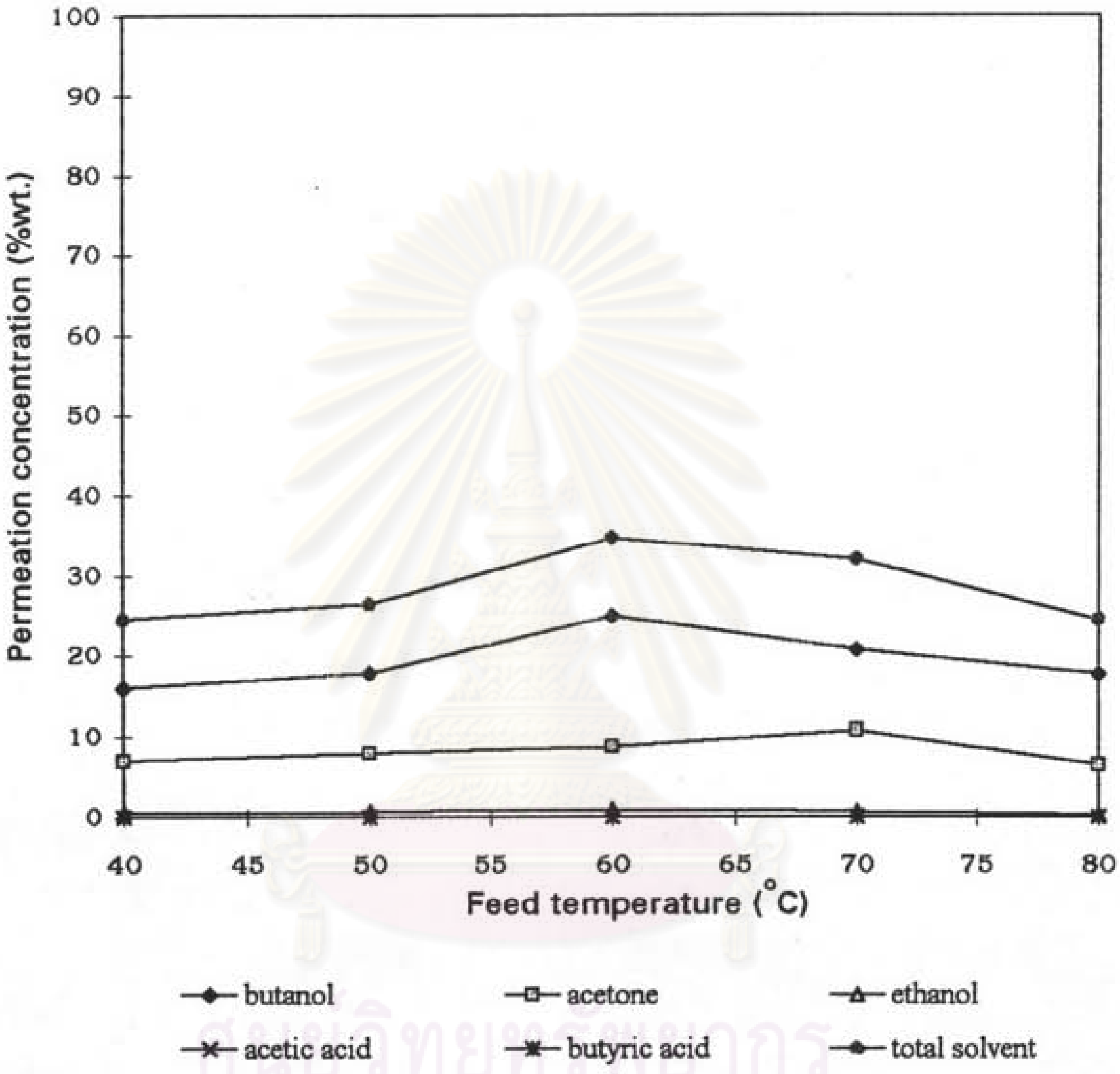

Figure 5.5 Correlation between feed temperature and permeation concentration of synthetic mixtures at permeation pressure 2 torr and membrane thickness 0.25 mm.

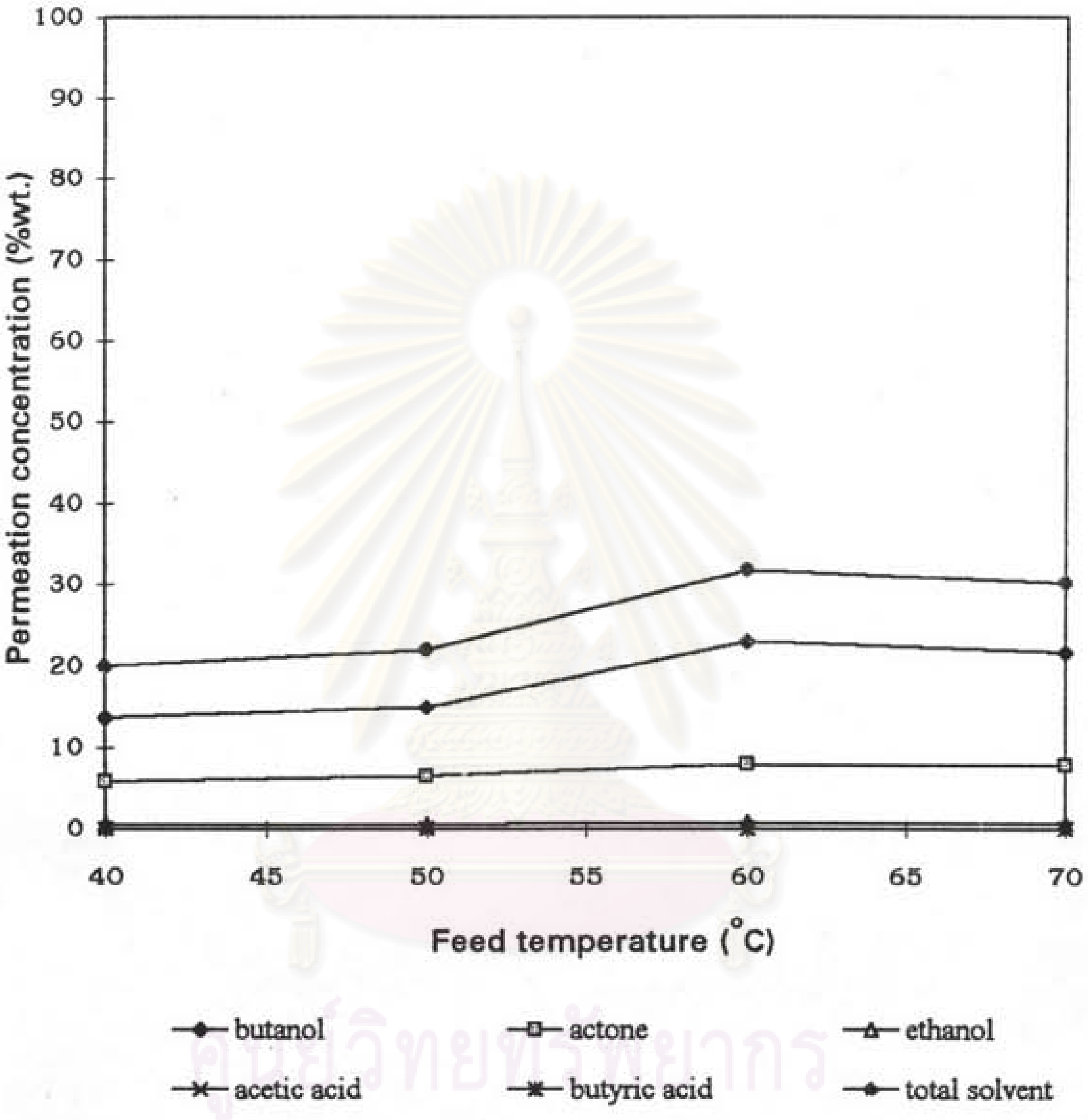

Figure 5.6 Correlation between feed temperature and permeation concentration of acetone-butanol fermentation broth at permeation pressure 2 torr and membrane thickness

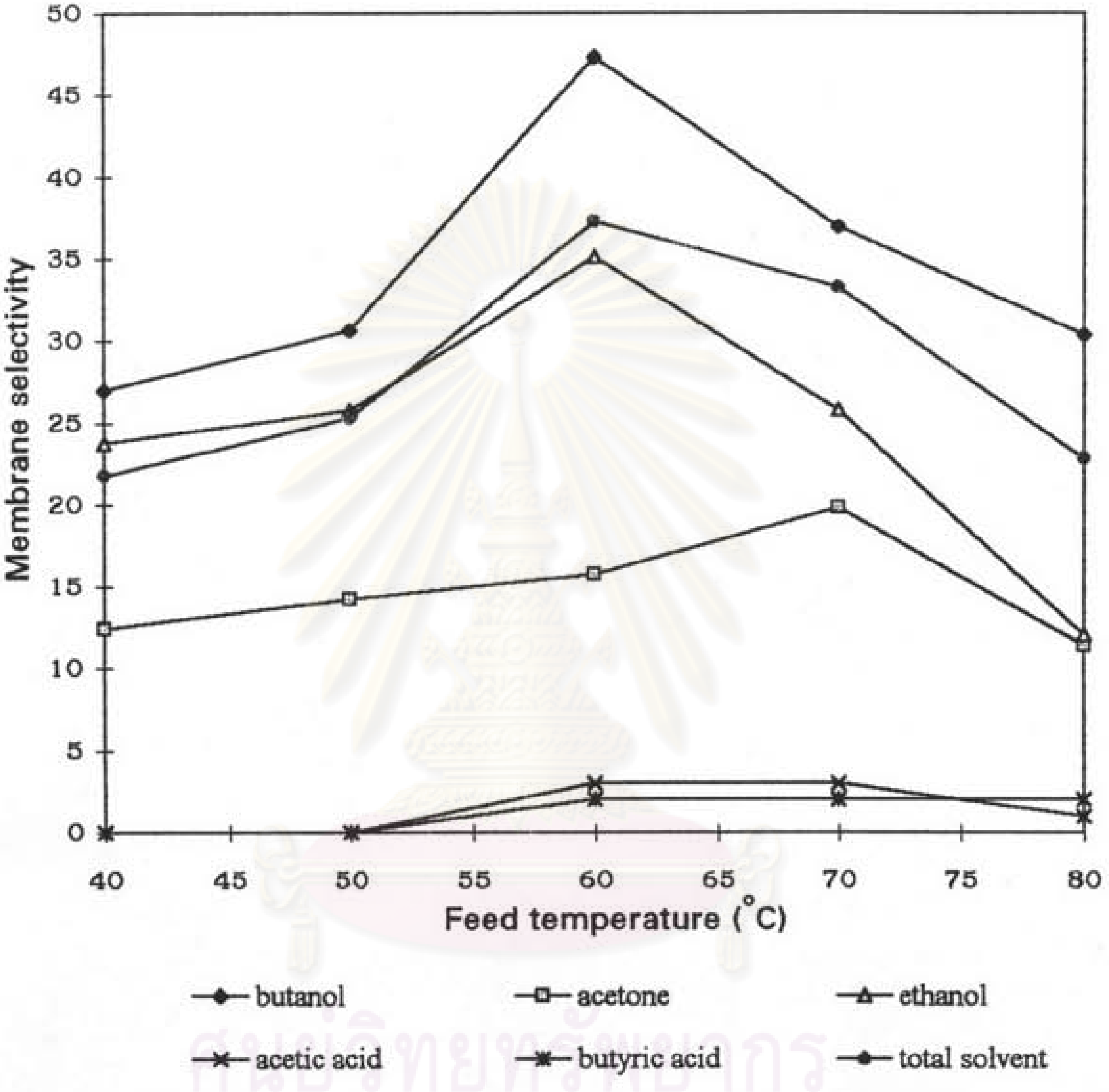

Figure 5.7 Correlation between feed temperature and membrane selectivity of synthetic mixtures at permeation pressure 2 torr and membrane thickness 0.25 mm.

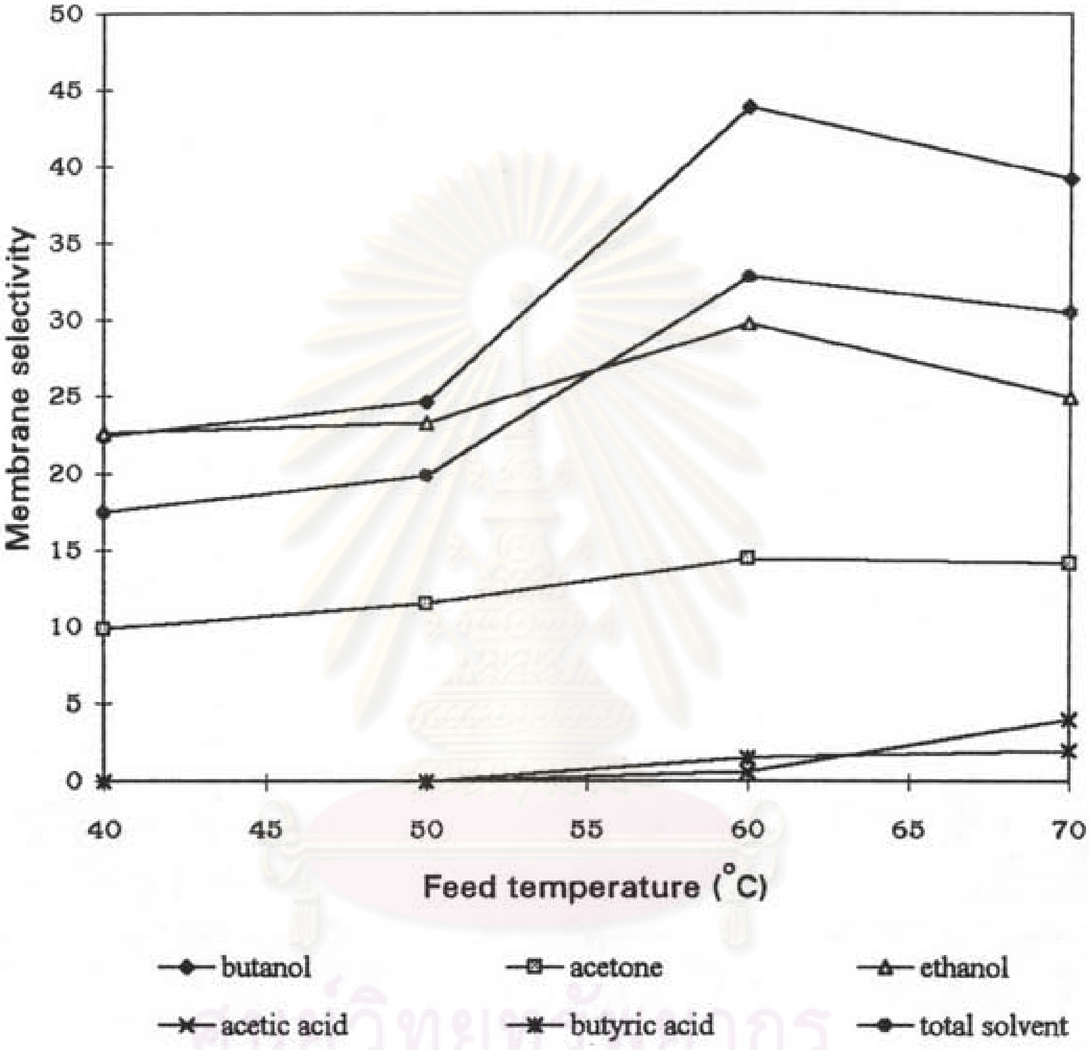

Figure 5.8 Correlation between feed temperature and membrane selectivity of acetone-butanol fermentation broth at permeation pressure 2 torr and membrane thickness 0.25 mm.

5.3 The Effect of Permeation Pressure.

From section 5.2, the suitable feed temperature was at 60°C. Therefore, in this section we are concerned about what is the most suitable permeation pressure for solvent separation by pervaporation. The effect of permeation pressure to the permeation flux at the feed temperature of 60°C of synthetic mixtures and fermentation broth are shown on figure 5.9 and 5.10. Generally, permeation pressure provides the driving force in pevaporation process. Therefore, as the permeation pressure increases and the difference in partial pressure between the feed and the permeate side of membrane decreases, the permeation flux also decreases. The total permeation flux of synthetic mixtures at the permeation pressures of 2, 10, and 30 torr were 45.34, 32.23 and 20.86 $g/m^2.h$, respectively and that of fermentation broth were 38.06, 20.01 and 16.42 $g/m^2.h$, respectively.

The effect of permeation pressure on the permeation concentration and the membrane selectivity are shown in figures 5.11 and 5.13 for synthetic mixtures, and figures 5.12 and 5.14 for fermentation broth. As the permeation pressure increases, the permeation concentration and the membrane selectivity are hardly decreased, whereas the permeation concentration and the membrane selectivity of solvents at the permeation pressure of 2 torr are higher than other permeate pressures. The silicone rubber was clearly much more selective to butanol than acetone and ethanol at all permeate pressures.

From these results, we can conclude that the best permeation pressure was 2 torr, because the permeation flux, the permeate concentration, and the membrane selectivity of all solvents were higher than these at other permeation pressures.

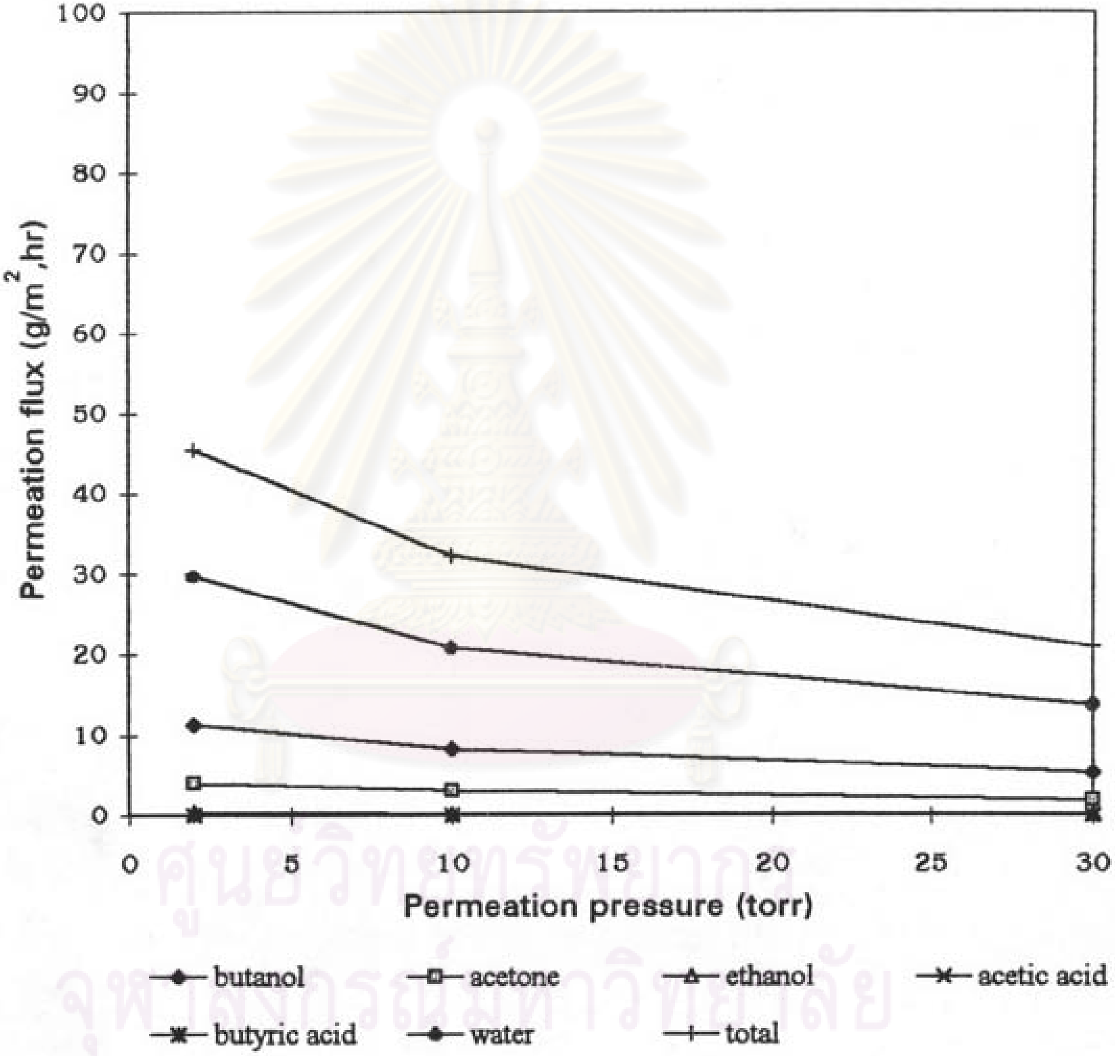

Figure 5.9 Correlation between permeation pressure and permeation flux of synthetic mixtures at feed temperature 60°C and membrane thickness 0.25 mm.

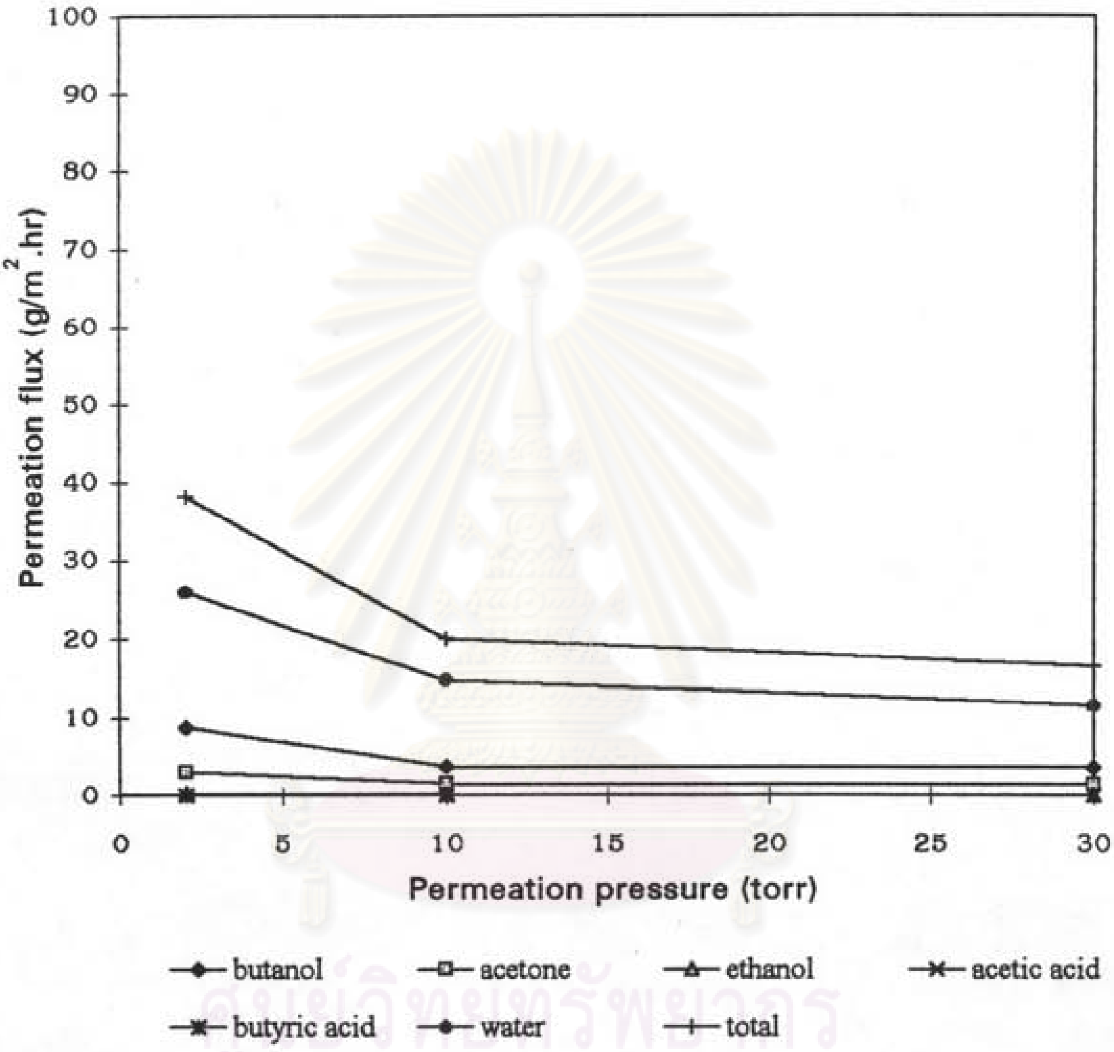

Figure 5.10 Correlation between permeation pressure and permeation flux of acetone-butanol fermentation broth at feed temperature 60°C and membrane thickness 0.25 mm.

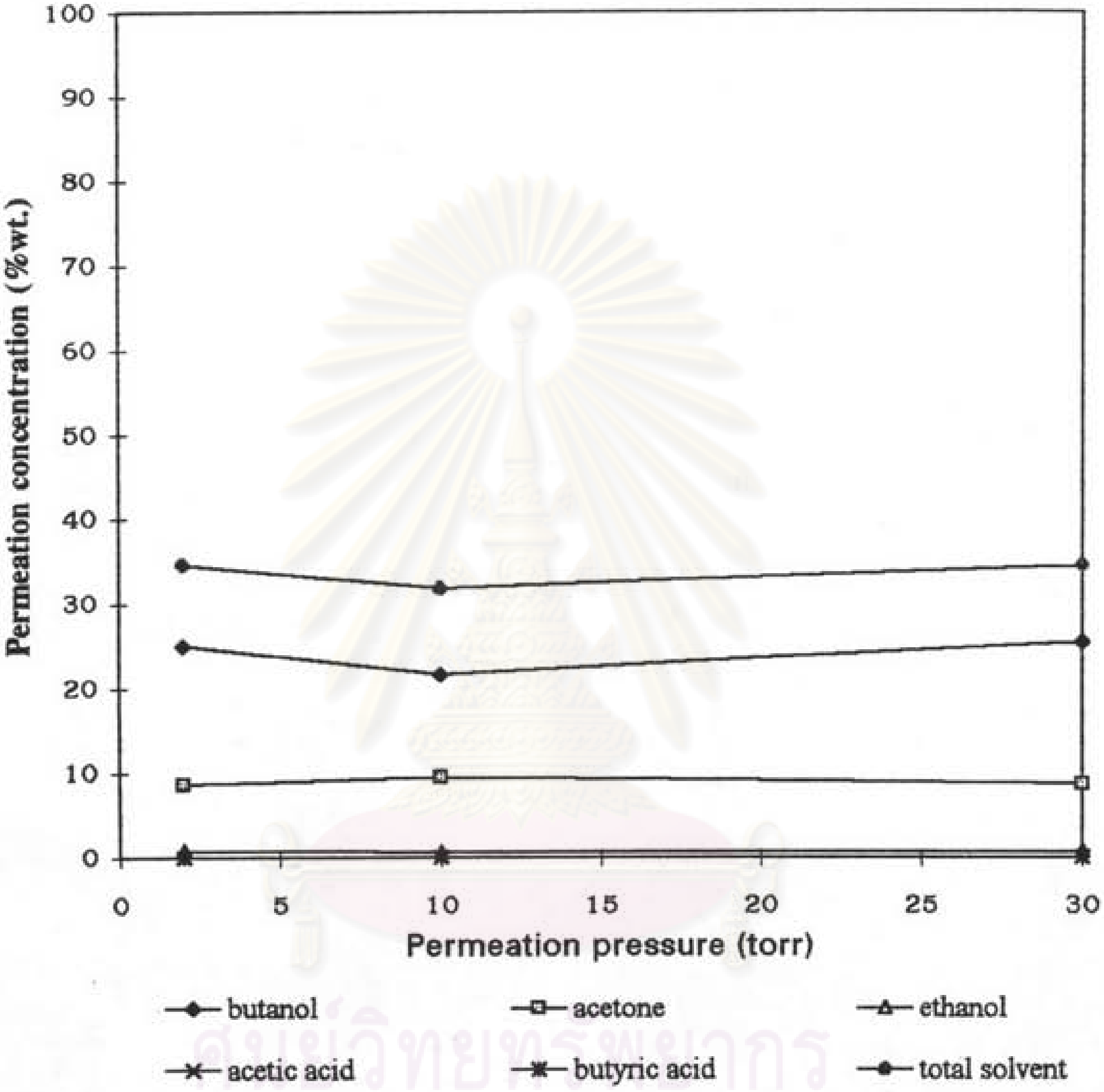

Figure 5.11 Correlation between permeation pressure and permeation concentration of synthetic mixtures at feed temperature 60°C and membrane thickness 0.25 mm.

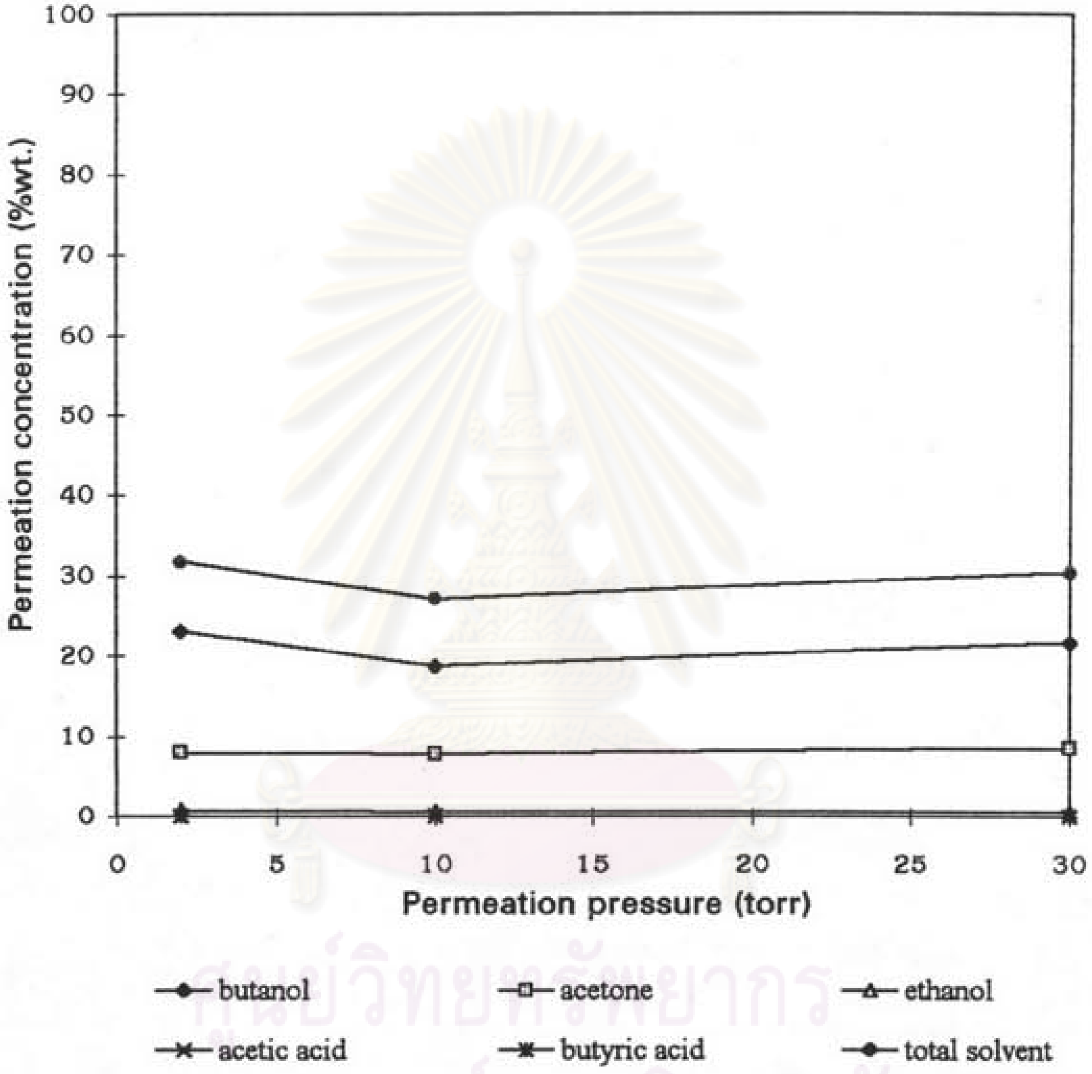

Figure 5.12 Correlation between permeation pressure and permeation concentration of acetone-butanol fermentation broth at feed temperature 60°C and membrane thickness 0.25 mm.

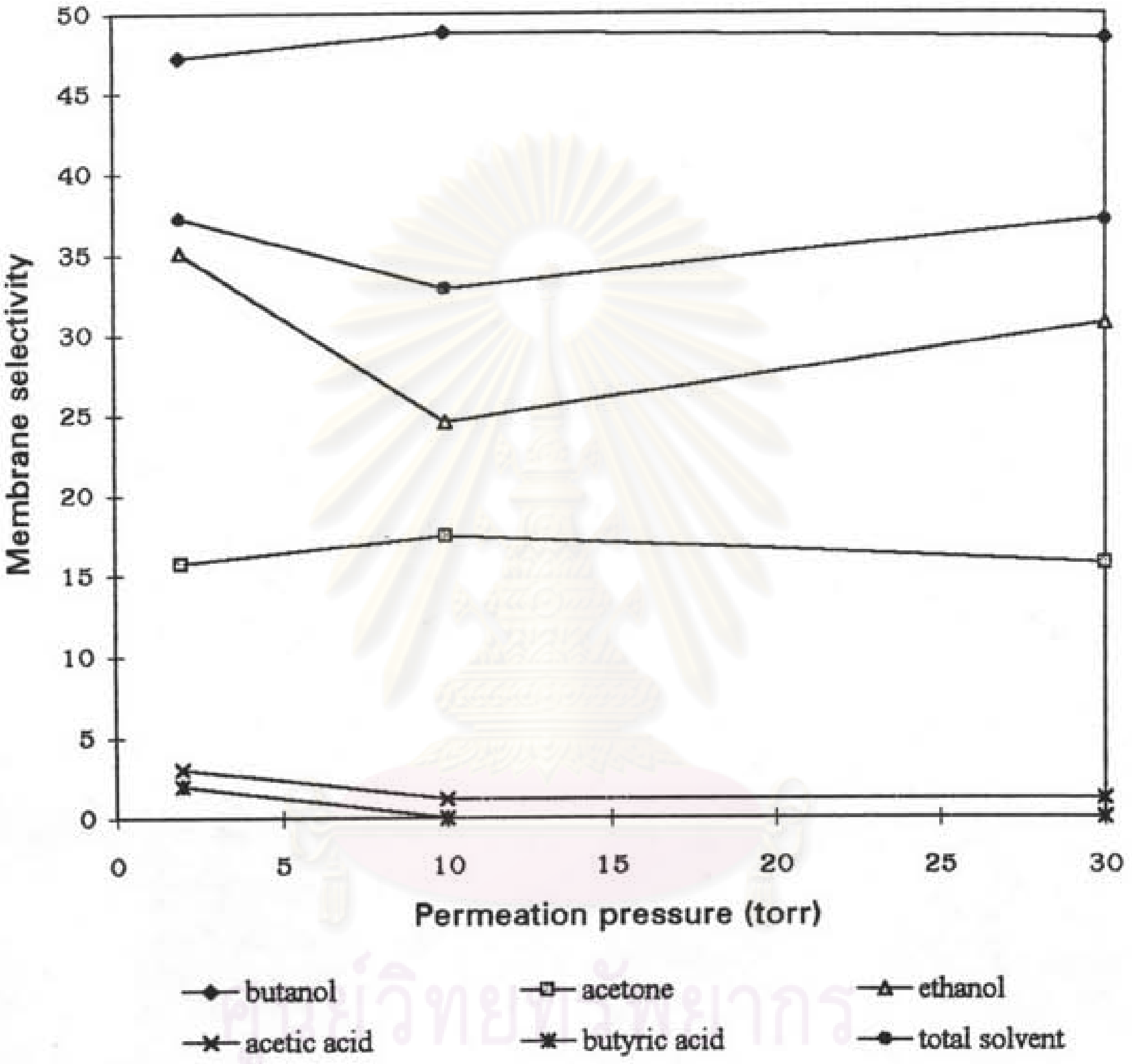

Figure 5.13 Correlation between permeation pressure and membrane selectivity of synthetic mixtures at feed temperature 60°C and membrane thickness 0.25 mm.

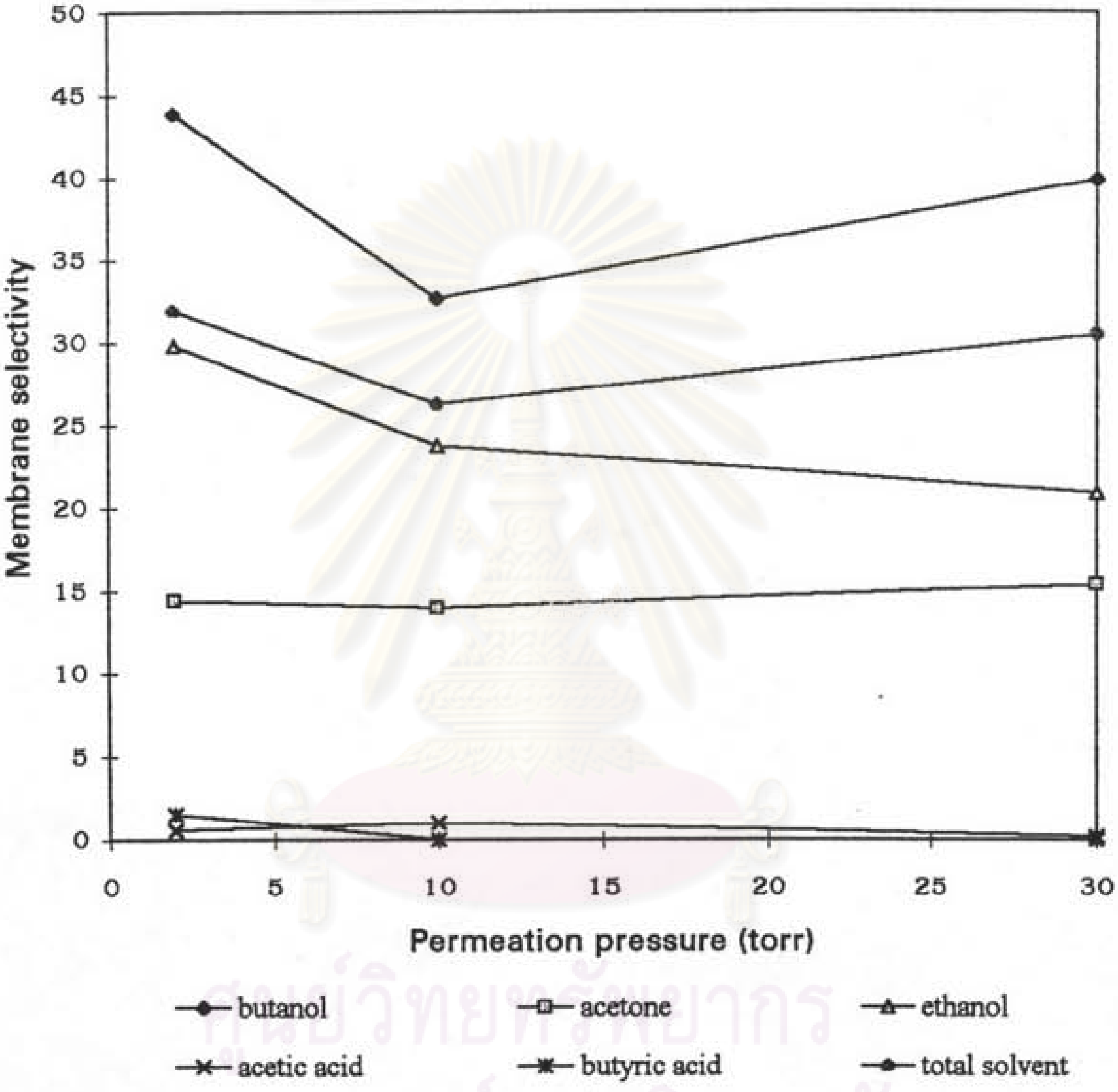

Figure 5.14 Correlation between permeation pressure and membrane selectivity of acetone-butanol fermentation broth at feed temperature 60°C and membrane thickness 0.25 mm.

5.4 The Effect of Membrane Thickness.

The effect of membrane thickness on permeation flux of synthetic mixtures and fermentation broth are shown in Figure 5.16 and 5.16, respectively. From both figures, it is notably shown that the permeation flux of all solutes were inversely correlated to membrane thickness. These effects can be described by Fick's law in equation 3.1.

$$J = -D\frac{dc}{dx} \qquad (3.1)$$

The total permeation fluxes of synthetic mixture were reduced from 45.34 to 16.66 $g/m^2.h$ as the membrane thickness increased from 0.25 mm. to 0.5 mm., and reduced to 7.06 $g/m^2.h$ as the membrane thickness increased to 1.0 mm.. Similarly, the relation between permeation flux of fermentation broth and membrane thickness were the same direction as synthetic mixtures. The influence of membrane thickness to the permeation concentration were shown in figure 5.17 and 5.18. The permeation concentration of total solvent for membrane thickness of 0.25, 0.5, and 1.0 mm. in synthetic mixtures were 34.53, 47.2, and 54.45%wt., respectively, and that in fermentation broth were 31.76, 42.89, and 50.13%wt., respectively. The permeate concentration of all solvents increased as membrane thickness decreased. The effect of membrane thickness on membrane selectivity was similar to what was found for permeation concentration. (Figure 5.19 and 5.20)

Although the permeation concentration and the membrane selectivity were increased with membrane thickness increased, the permeation flux were not suitable for solvent separation because of the low productivity and certainly high energy consumption.

From the effect of feed temperature, permeation pressure and membrane thickness on pervaporation that were demonstrated above, the experimental results had a similar trend with a study of Chompunut Pipoplapanant in water-butanol mixtures.[15] Butanol flux, butanol concentration and membrane selectivity of butanol increased as feed temperature increased , permeation pressure decreased and membrane thickness decreased.

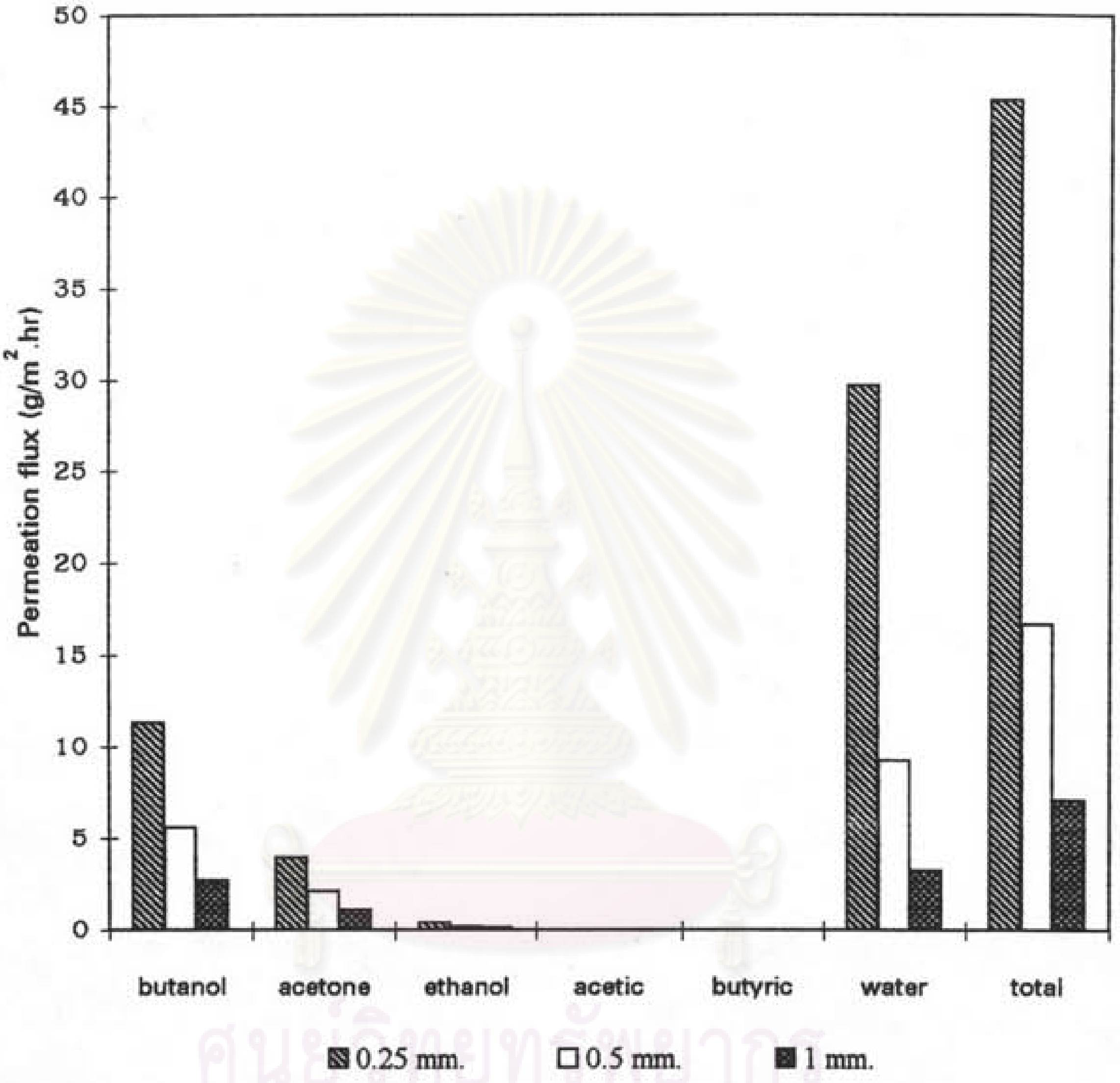

Figure 5.15 Correlation between membrane thickness and permeation flux of synthetic mixtures at permeation pressure 2 torr, and feed temperature 60°C

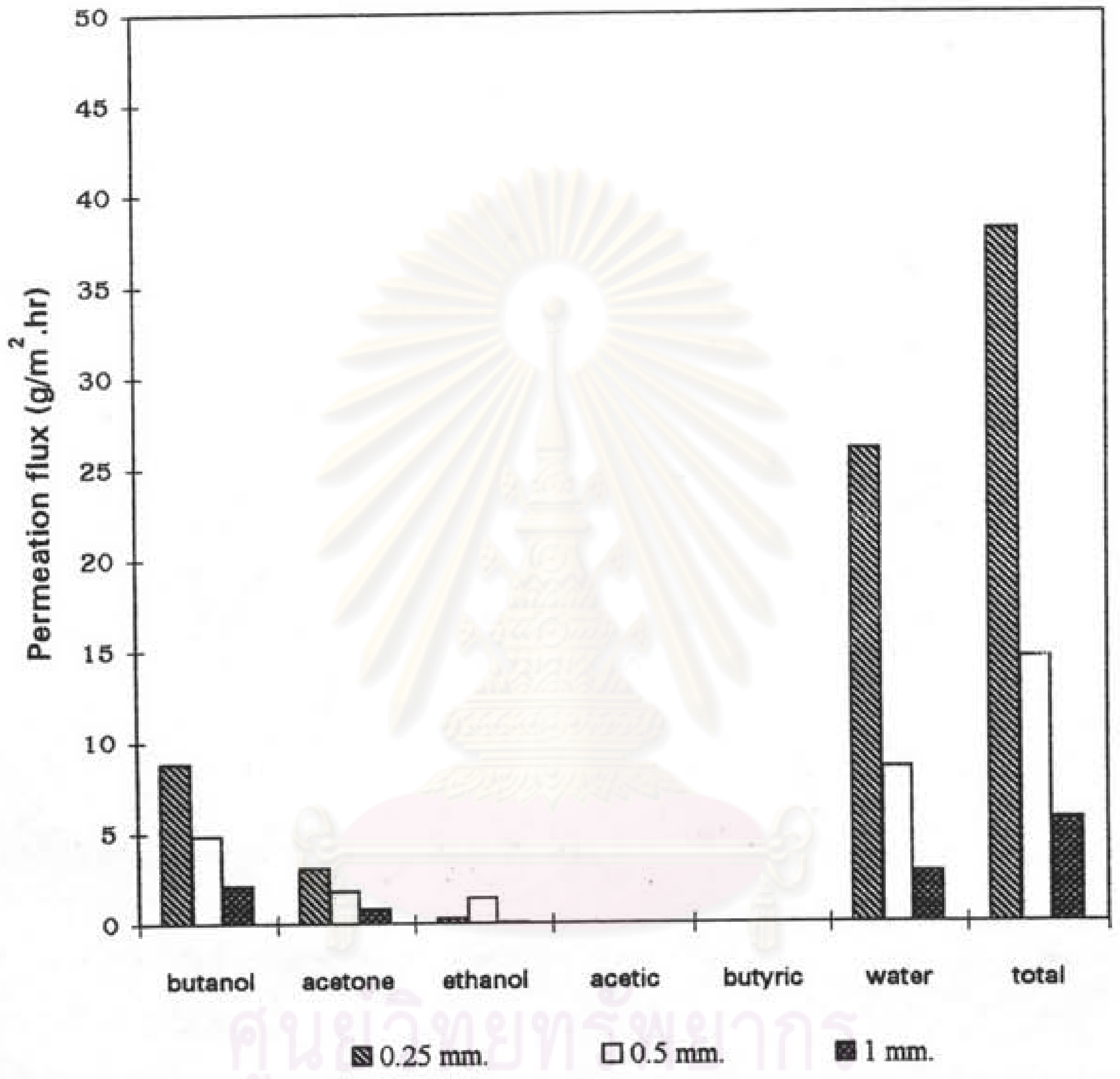

Figure 5.16 Correlation between membrane thickness and permeation flux of acetone-butanol fermentation broth at permeation pressure 2 torr, and feed temperature 60°C

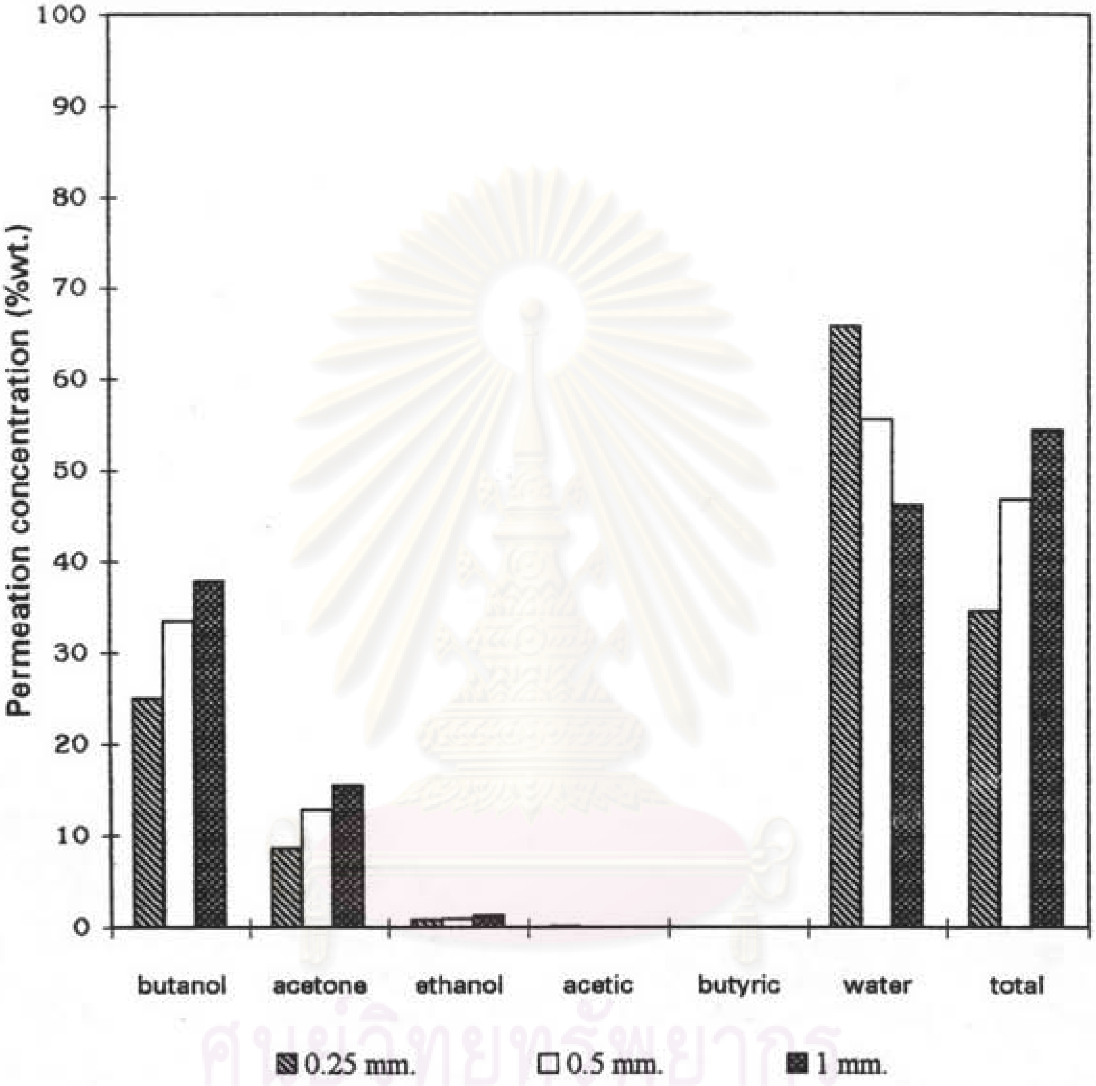

Figure 5.17 Correlation between membrane thickness and permeation concentration of synthetic mixtures at permeation pressure 2 torr, and feed temperature 60°C

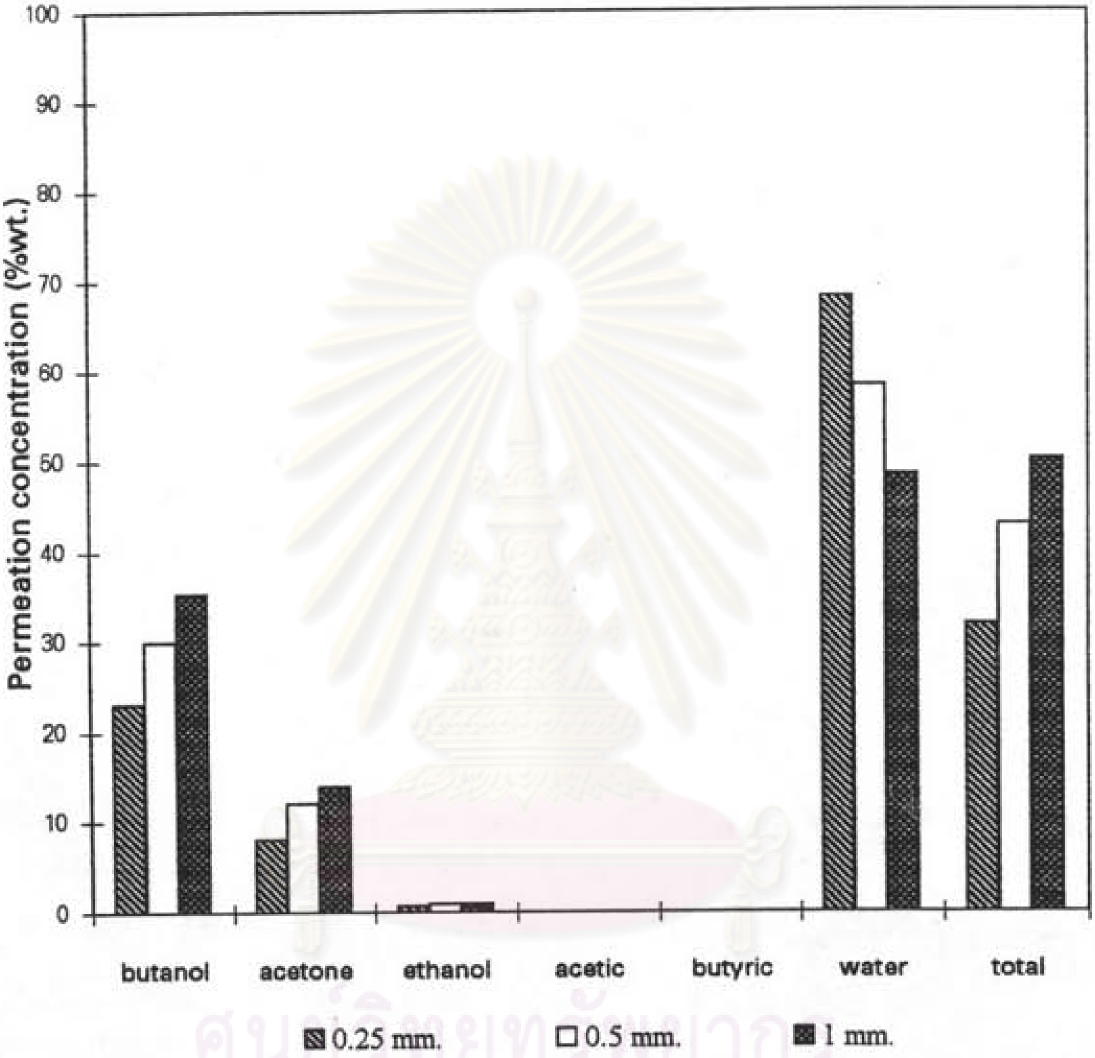

Figure 5.18 Correlation between membrane thickness and permeation concentration of acetone-butanol fermentation broth at permeation pressure 2 torr, and feed temperature 60°C

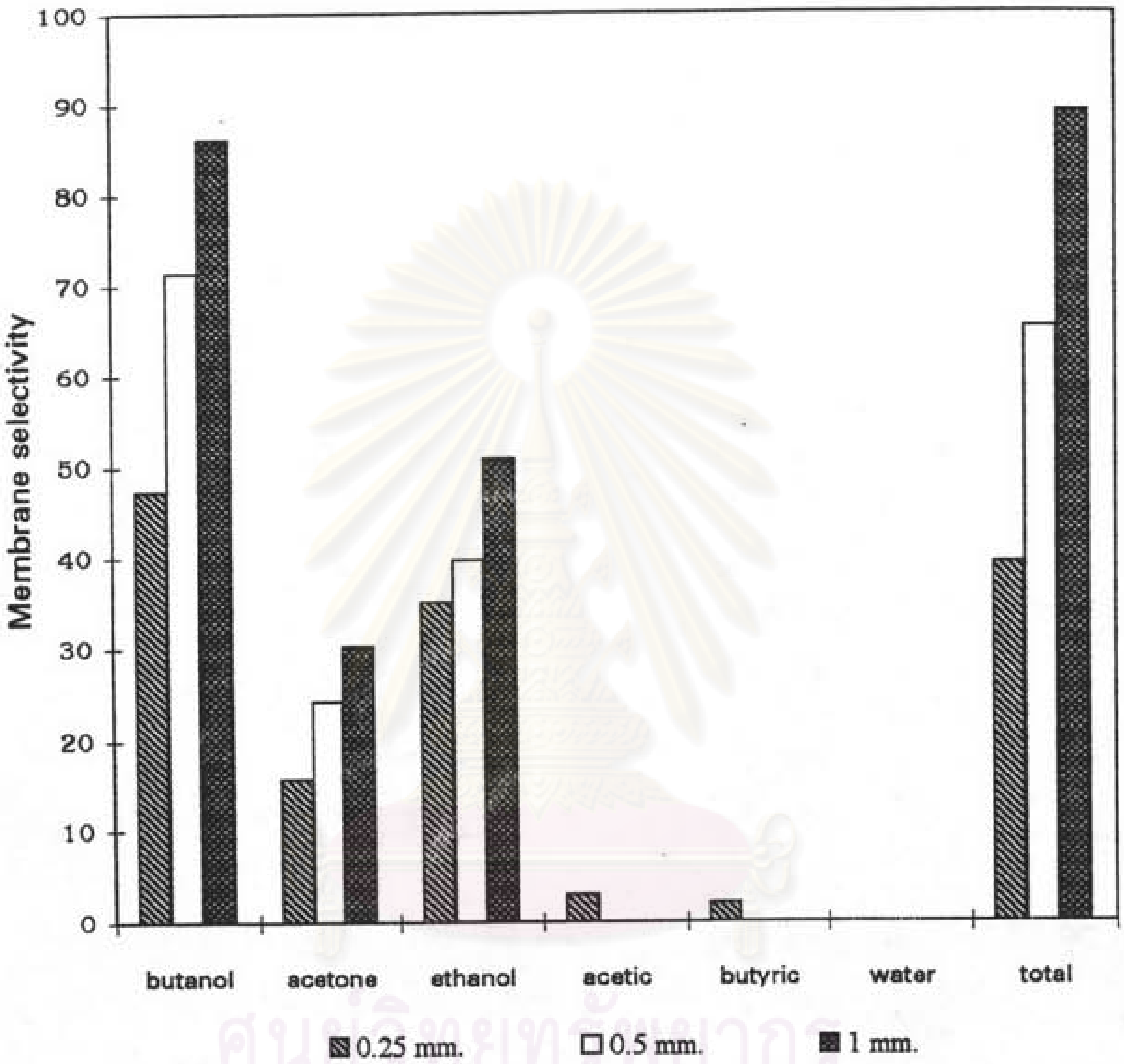

Figure5.19 Correlation between membrane thickness and membrane selectivity of synthetic mixtures at permeation pressure 2 torr, and feed temperature 60°C

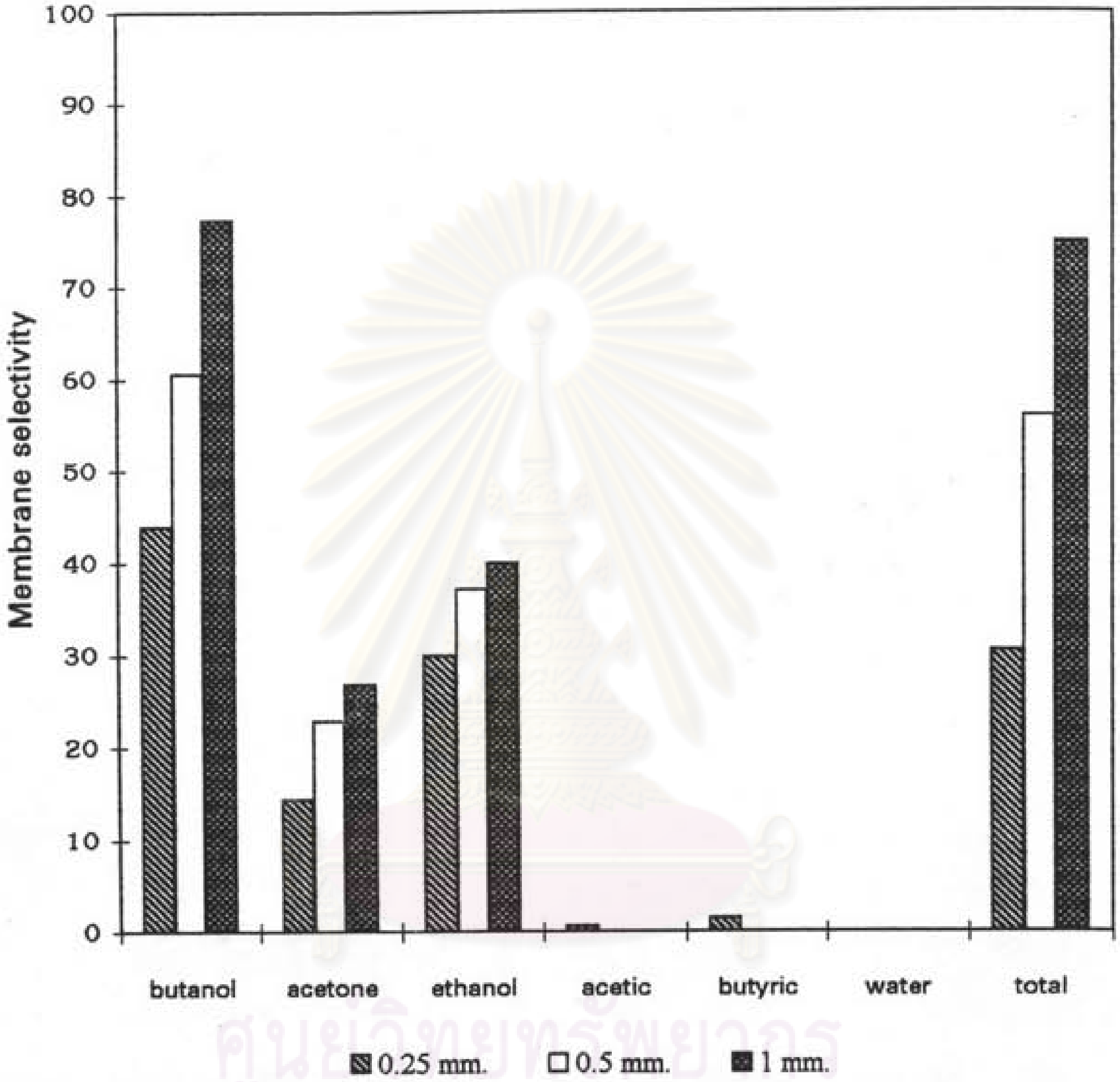

Figure 5.20 Correlation between membrane thickness and membrane selectivity of acetone-butanol fermentation broth at permeation pressure 2 torr and feed temperature 60°C

5.5 Permeability and Diffusivity of The Pervapertion Process.

Permeability and diffusivity are significant parameters indicating the performance of separation in pervaporation process. Solute with higher permeability can be separated more than other solutes by the pervaporation process, whereas diffusivity reflects an efficiency of solute movement in membrane. Permeability and diffusivity can be calculated from the solution-diffusion model. Permeability is given by the multiple value of distribution coefficient and diffusivity as shown in Appendix A. Table 5.1 show permeability and diffusivity of solutes in synthetic mixtures and fermentation broth. From Table 5.1 it was found that permeability of butanol was the highest among other solutes. This was because butanol had higher distribution coefficient than other solutes. In addition, permeability of solutes with same functional group increased with molecular weight. Morover, the diffusivity of small molecule were higher than these of bigger molecule. Water had higher diffusivity than other solutes. This results reflected that water can be separated by this process, although it had a low distribution coefficient.

Moreover, acetone had a lower diffusivity than ethanol, although it had a higher distribution coefficient. This result was caused by the molecular structure of acetone, which had more steric effect than ethanol.

The effect of feed temperature on permeability and diffusivity of synthetic mixtures and acetone-butanol fermentation broth were shown in Figures 5.21 to 5.24. These results were carried out of the permeation pressure of 2 torr and membrane thickness of 0.25 mm.. Permeability and diffusivity of all solutes increased as feed temperature increased because distribution coefficient and diffusivity were relevant to the change of feed temperature. Relation between feed temperature and diffusivity can be explained by equation 3.6.

$$D_{i,o} = D_{i,\infty}\exp(-E_p/RT) \qquad (3.6)$$

The effect of permeation pressure on permeability and diffusivity of synthetic mixtures and acetone-butanol fermentation broth were shown in Figure 5.25 to 5.28. The operating condition of these results were feed temperature of 60°c and membrane thickness of 0.25 mm. Permeability and diffusivity of all solutes were decreased as permeation pressure increased. Low permeation pressure provided high driving force between the two sides of the membrane which resulted in the faster movement of the solutes and thus higher diffusivity.

Membrane thickness did not have any effect on permeability and diffusivity as the results are shown in Figure 5.29 to 5.32. The operating conditions of these experiments were permeation pressure of 2 torr and feed temperature of 60°C. Permeability of butanol at membrane thickness 0.25, 0.5 and 1.0 mm. of synthetic mixtures were 4.03, 3.98 and 3.80 ($\times 10^{7}$, m^{2}/h), respectively, and that of acetone-butanol fermentation broth were 3.13, 3.11 and 2.96 ($\times 10^{7}$, m^{2}/h), respectively. Similarly, diffusivity of butanol of synthetic mixtures and that in acetone-butanol fermentation broth were rarely constant.

Permeability and diffusivity of solutes in the fermentation broth were lower than that in the synthetic mixtures at all operating condition. These results will be discussed in section 5.7 (The pervaporation process in comparison between synthetic mixtures and acetone-butanol fermentation broth).

Table 5.1 Permeability and diffusivity of synthetic mixtures and acetone-butanol fermentation broth at permeation pressure 2 torr, feed temperature 60°c and membrane thickness 0.25 mm.

Solute	Synthetic Mixtures		Acetone-Butanol Fermentation Broth	
	Permeability (*10^7, m^2/h)	Diffusivity (*10^7, m^2/h)	Permeability (*10^7, m^2/h)	Diffusivity(*10^7, m^2/h)
Butanol	4.0325	6.4007	3.1302	5.1315
Acetone	1.6325	3.2248	1.2695	2.7068
Ethanol	3.9040	10.6376	2.8120	9.3421
Acetic Acid	0.1170	3.5450	0.0570	2.5221
Butyric Acid	0.2287	3.1158	0.1537	2.3941
Water	0.0753	16.7380	0.0657	16.424

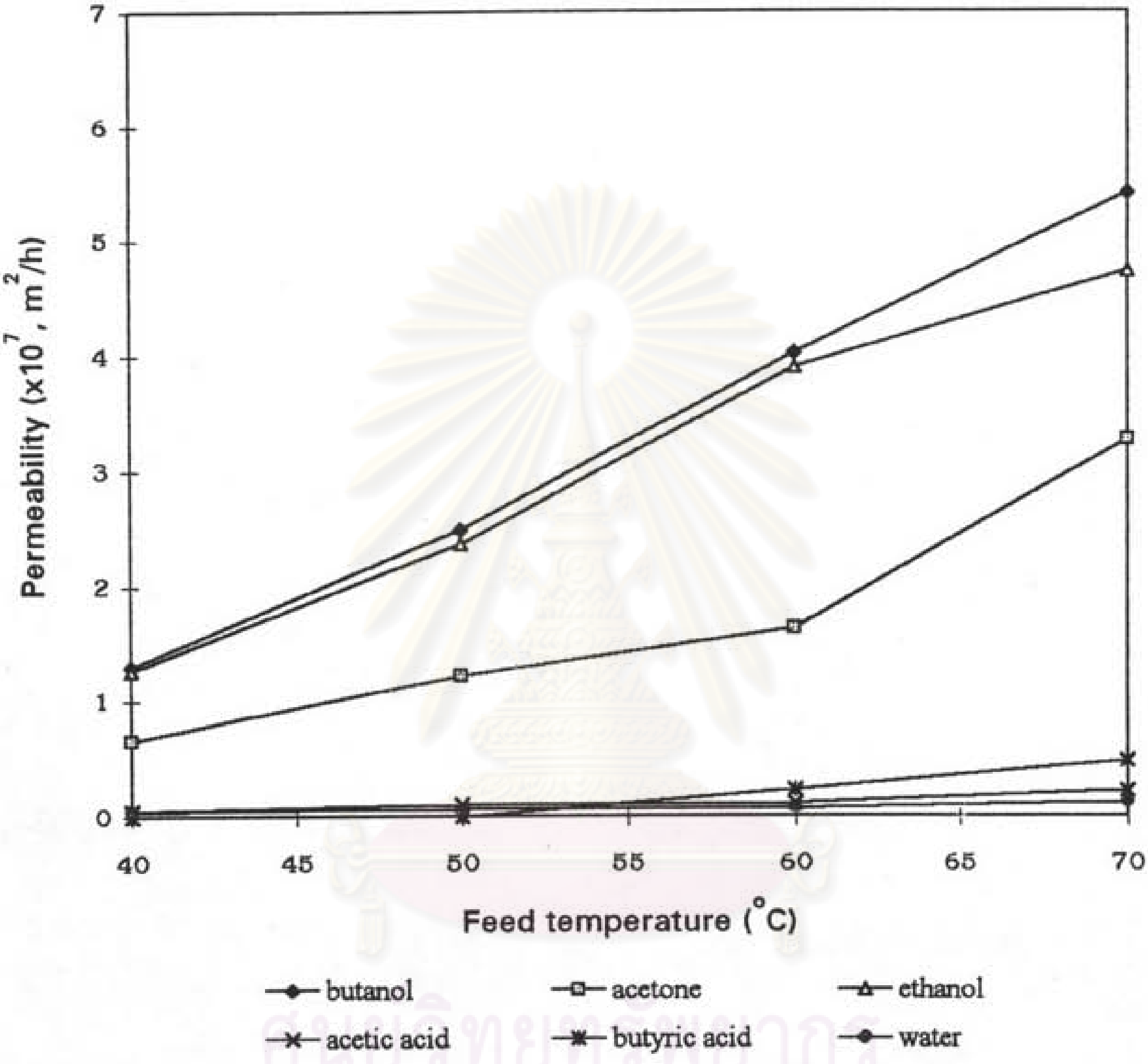

Figure 5.21 Correlation between feed temperature and permeability of synthetic mixtures at permeation pressure 2 torr and membrane thickness 0.25 mm.

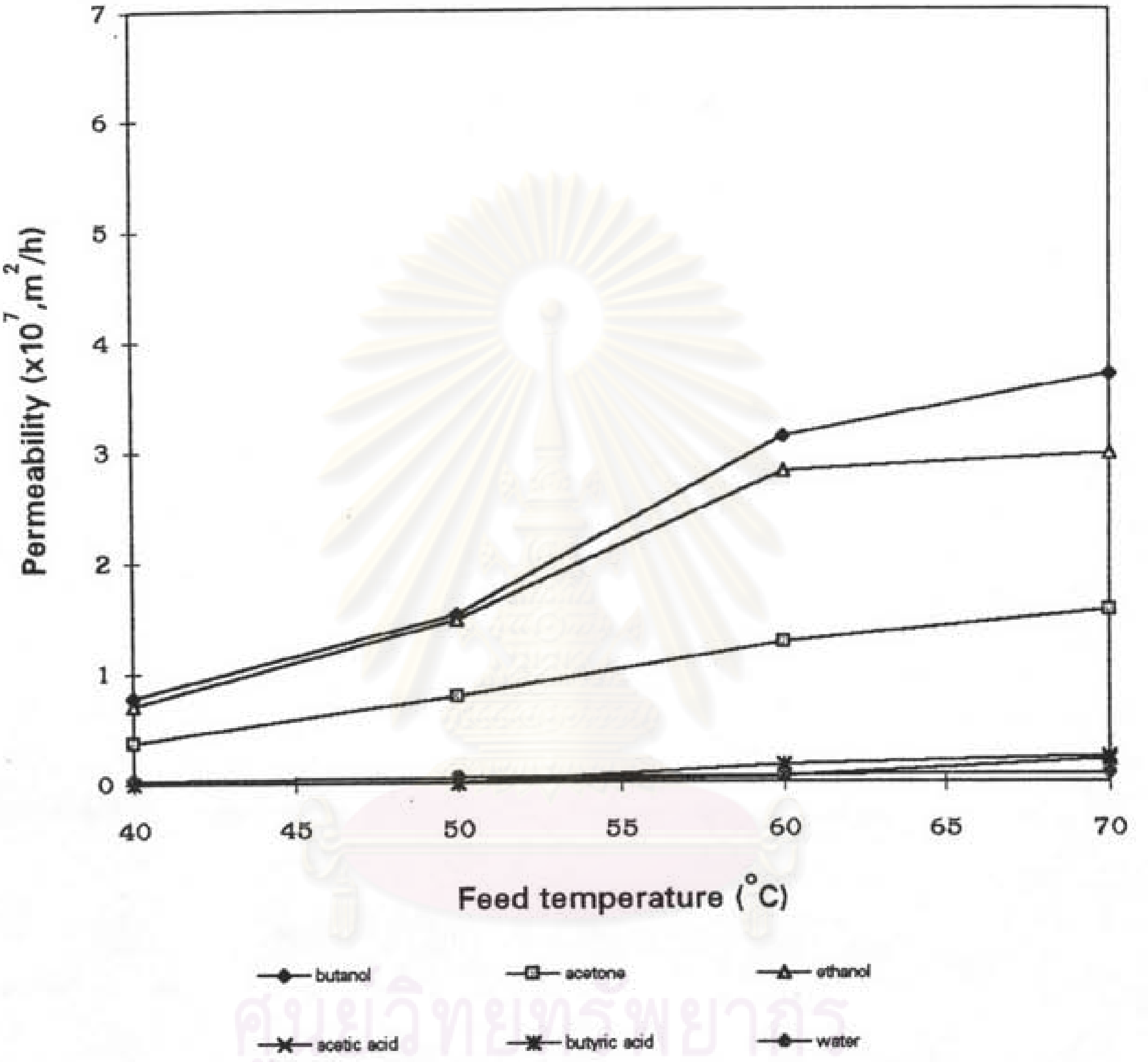

Figure 5.22 Correlation between feed temperature and permeability of acetone-butanol fermentation broth at permeation pressure 2 torr and membrane thickness 0.25 mm.

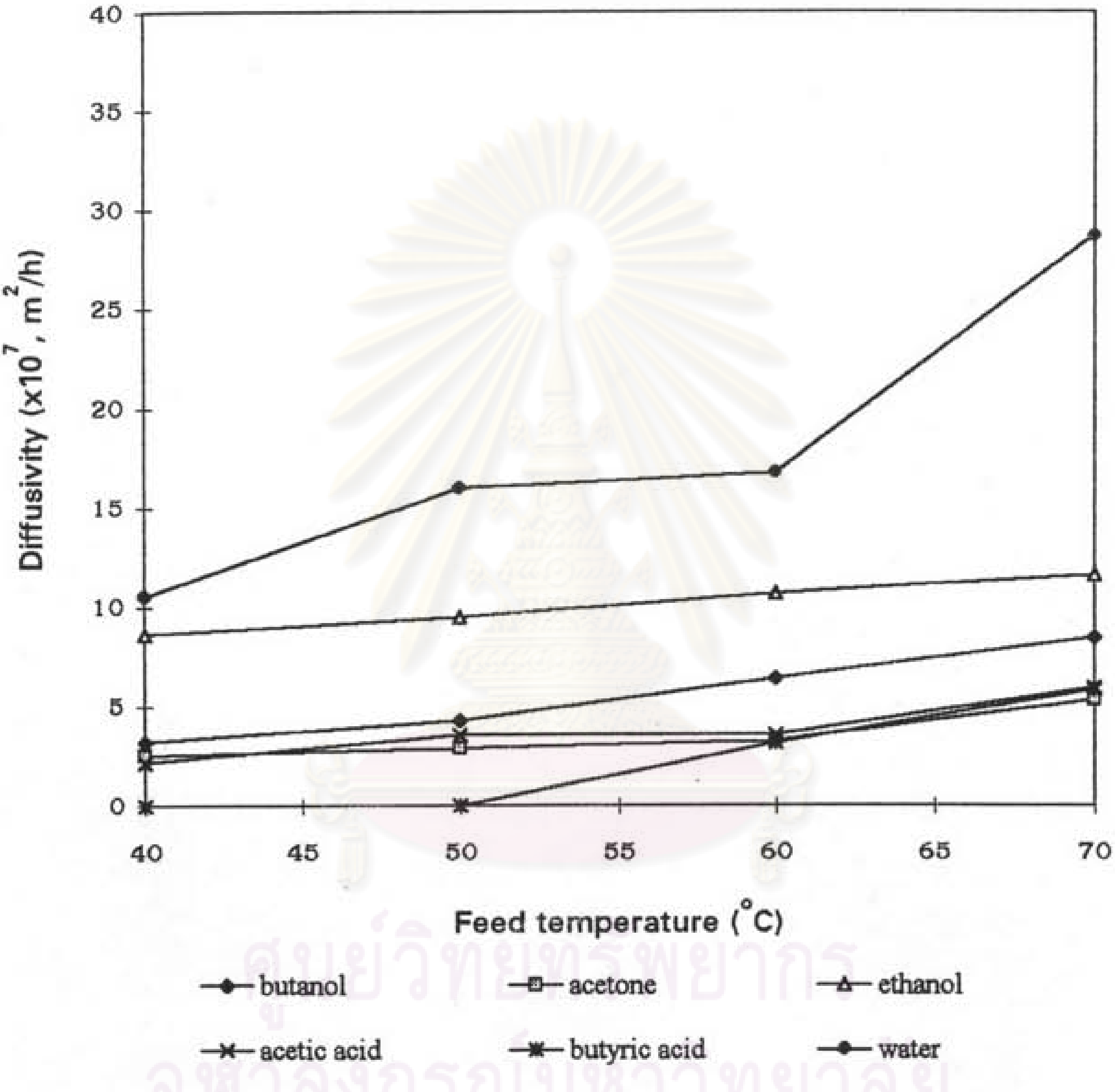

Figure 5.23 Correlation between feed temperature and diffusivity of synthetic mixtures at permeation pressure 2 torr and membrane thickness 0.25 mm.

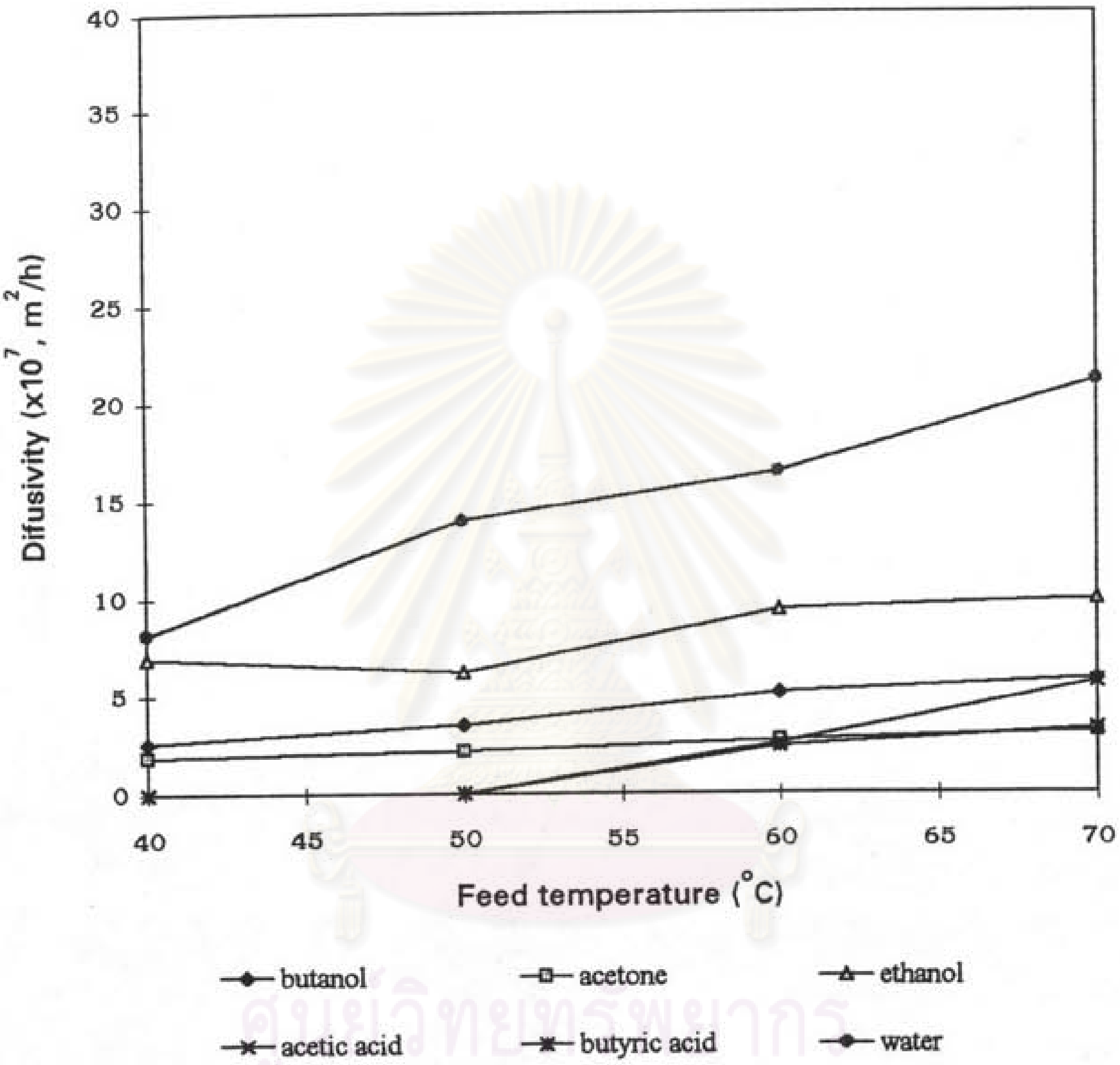

Figure 5.24 Correlation between feed temperature and diffusivity of acetone-butanol fermentation broth at permeation pressure 2 torr and membrane thickness 0.25 mm.

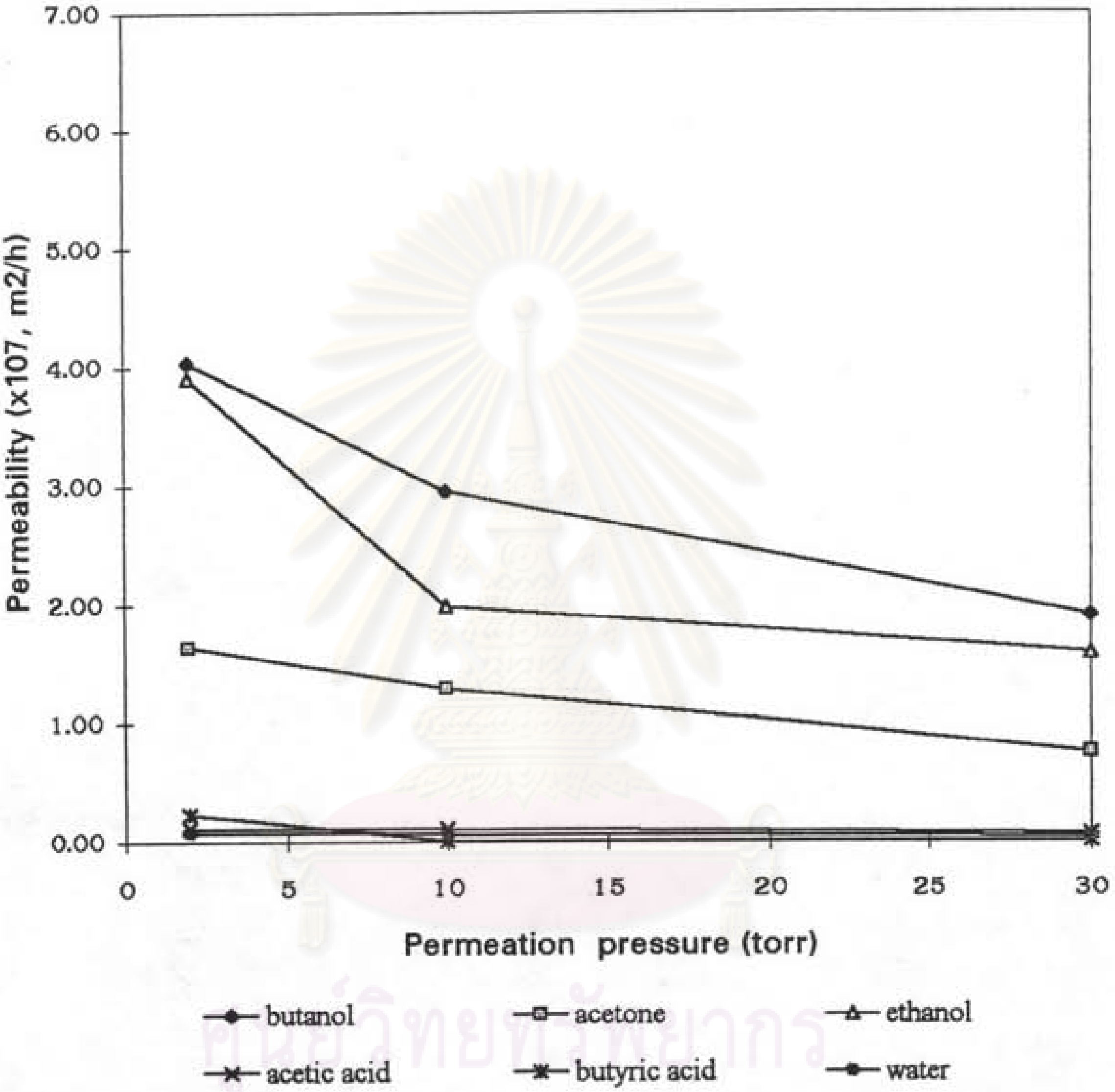

Figure 5.25 Correlation between permeation pressure and permeability of synthetic mixtures at feed temperature 60°C and membrane thickness 0.25 mm.

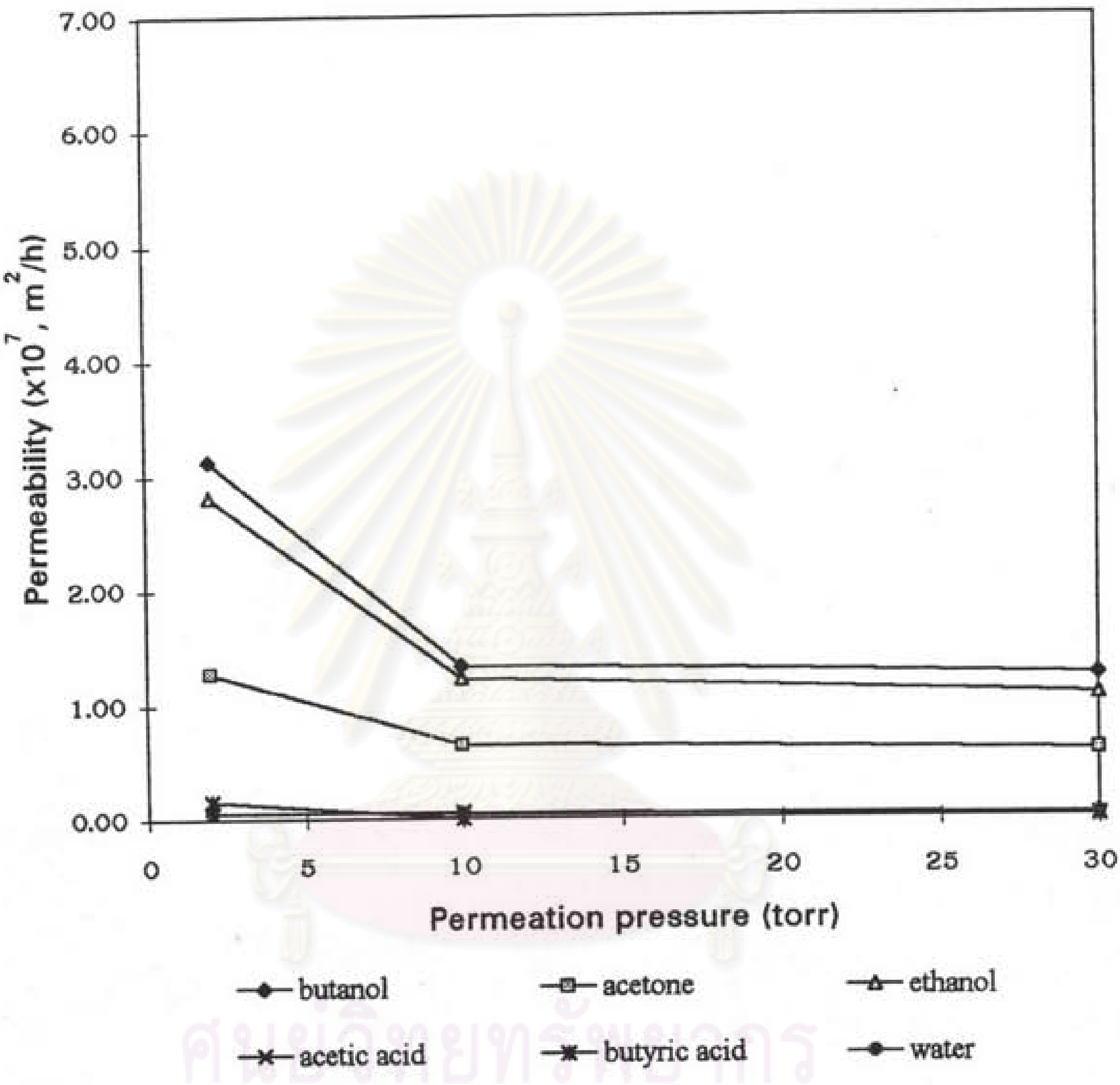

Figure 5.26 Correlation between permeation pressure and permeability of acetone-butanol fermentation broth at feed temperature 60°C and membrane thickness 0.25 mm.

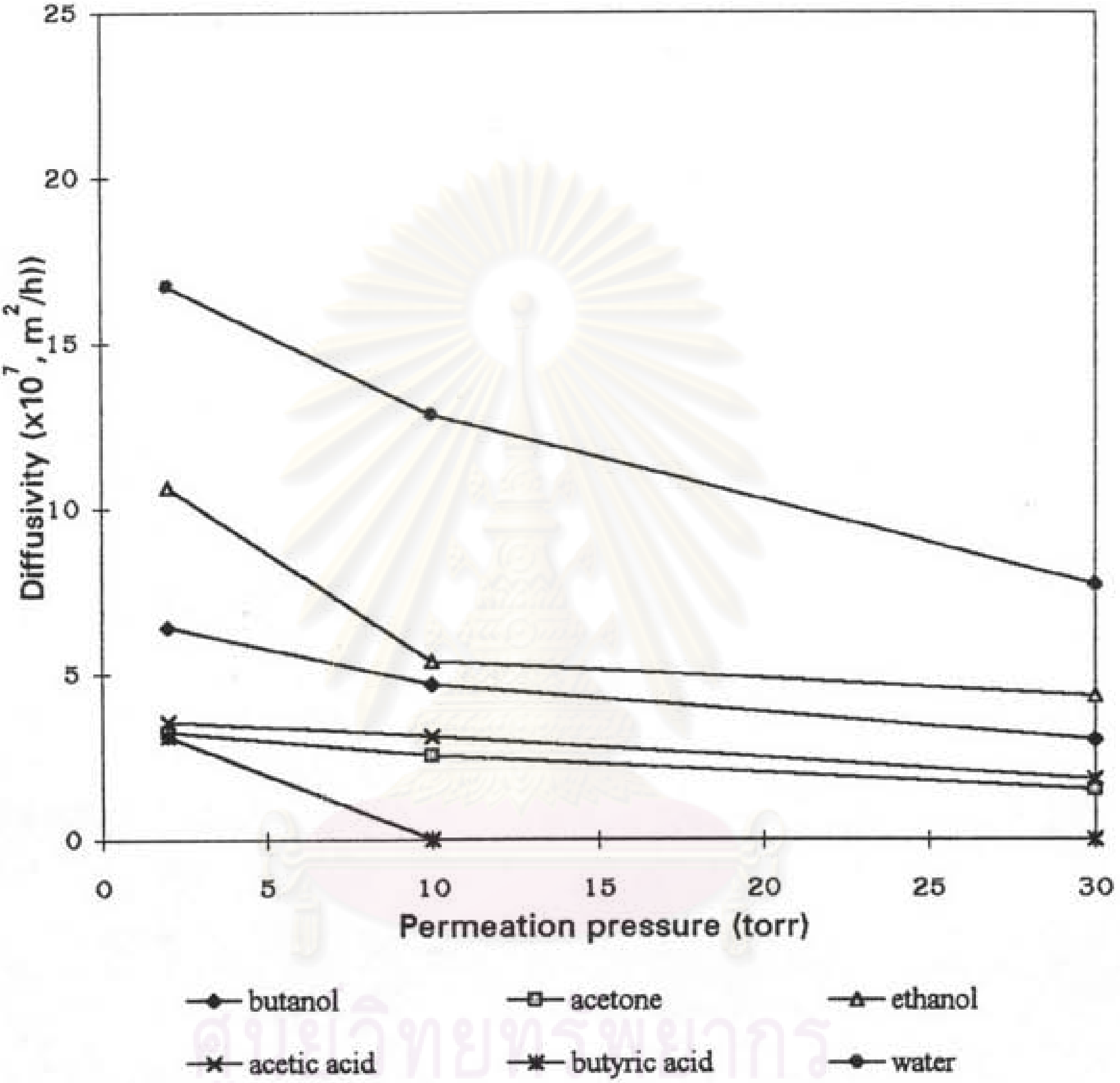

Figure 5.27 Correlation between permeation pressure and diffusivity of synthetic mixtures at feed temperature 60°C and membrane thickness 0.25 mm.

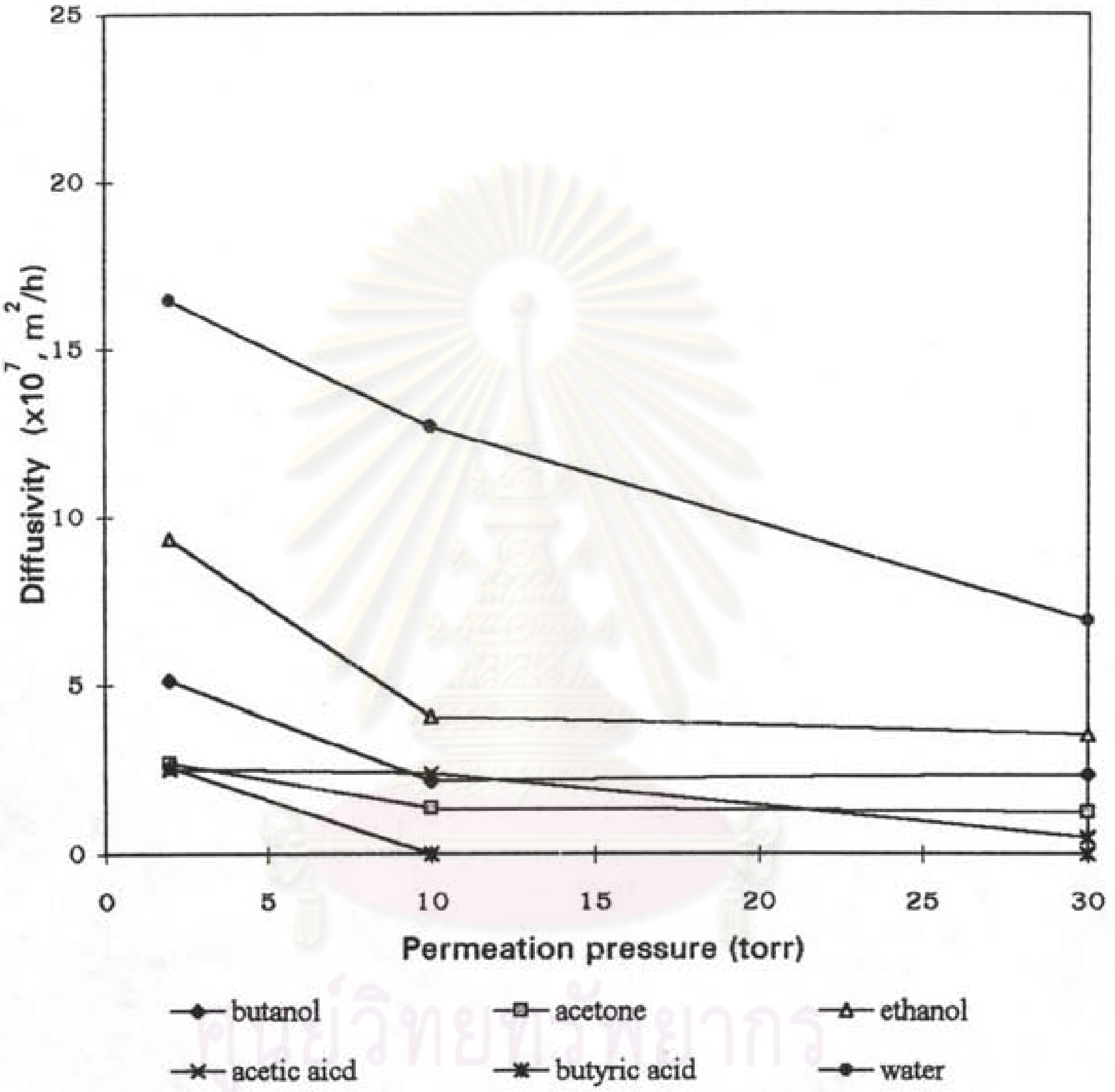

Figure 5.28 Correlation between permeation pressure and diffusivity of acetone-butanol fermentation broth at feed temperature 60°C and membrane thickness 0.25 mm.

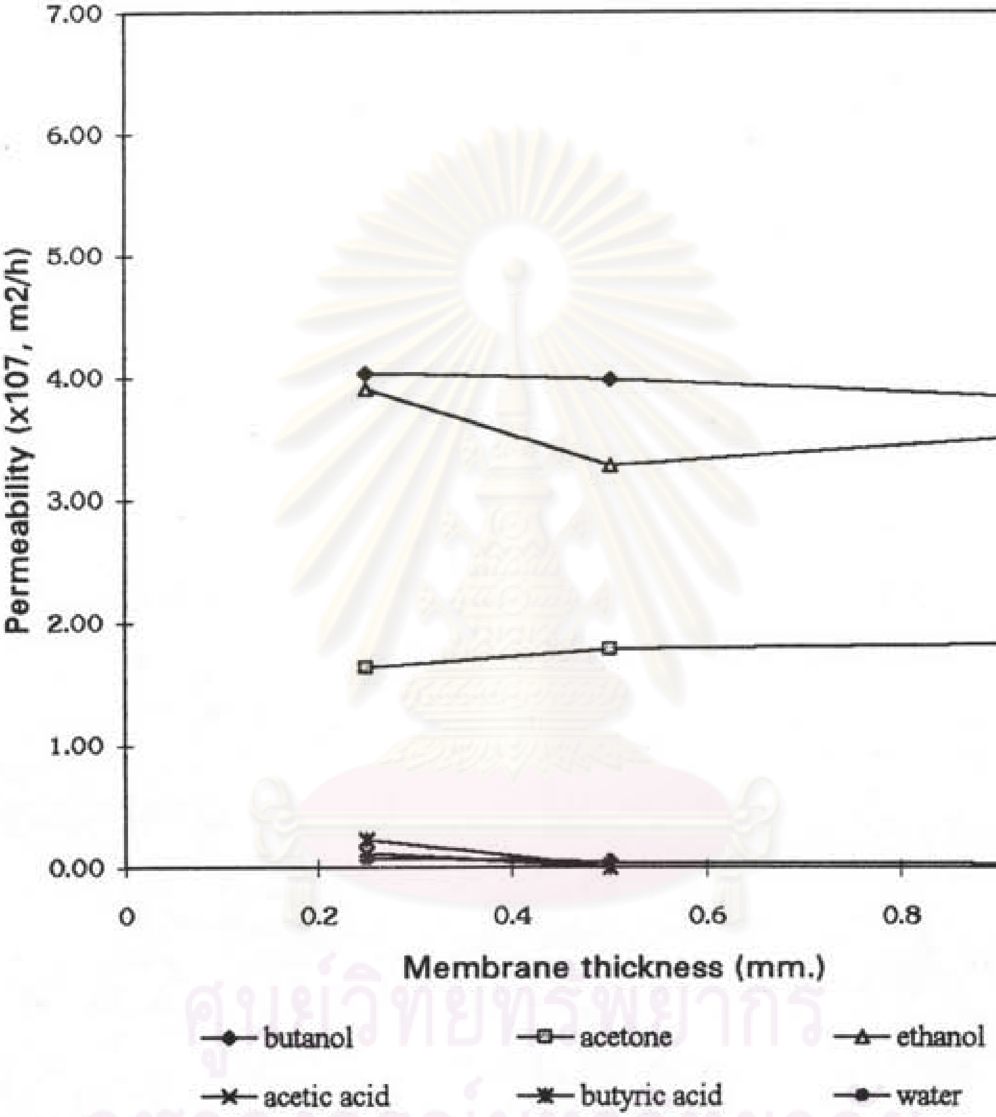

Figure 5.29 Correlation between membrane thickness and permeability of synthetic mixtures at permeation pressure 2 torr and feed temperature 60°C.

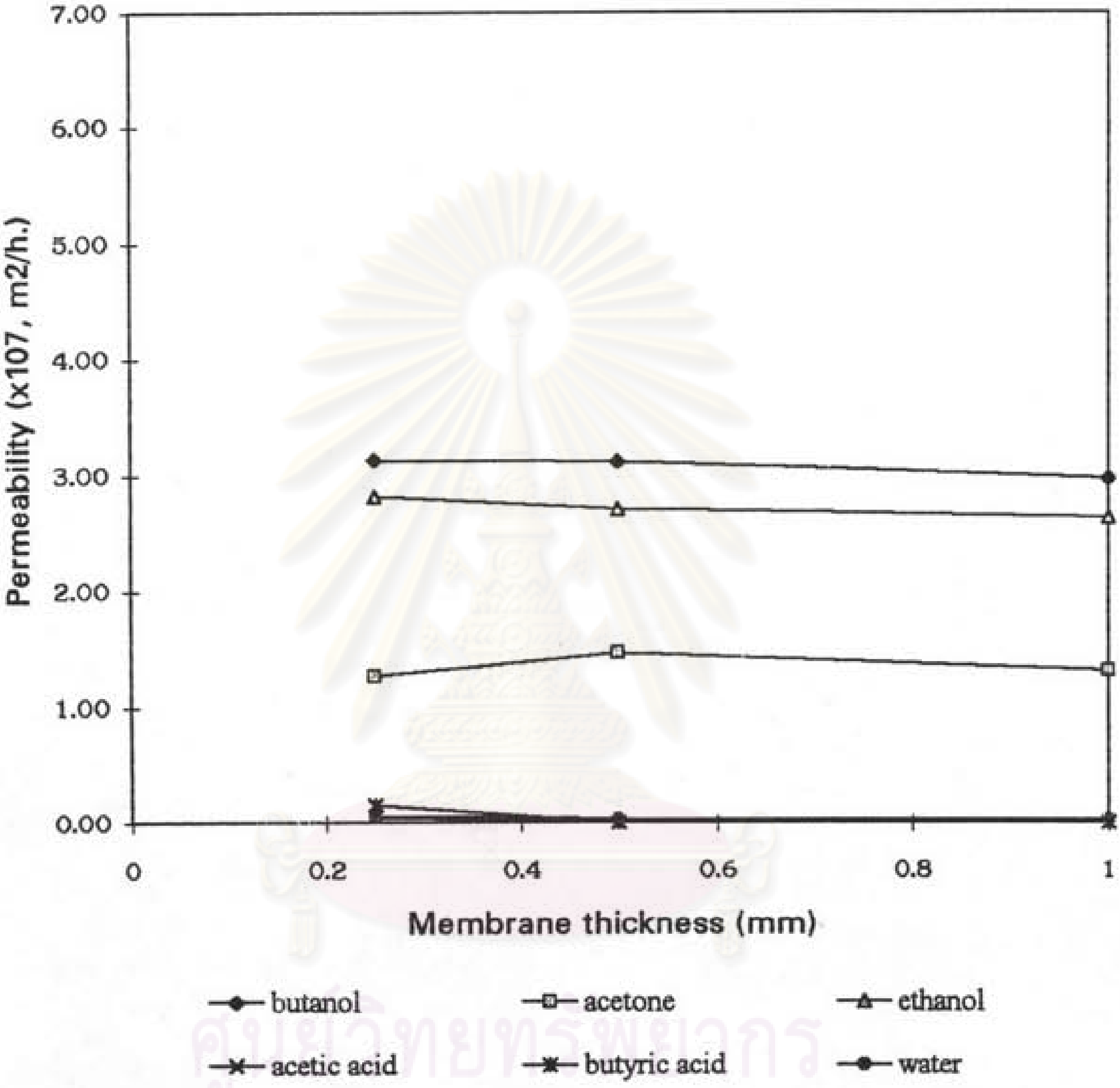

Figure 5.30 Correlation between membrane thickness and permeability of acetone-butanol fermentation broth at permeation pressure 2 torr and fee temperature 60°C.

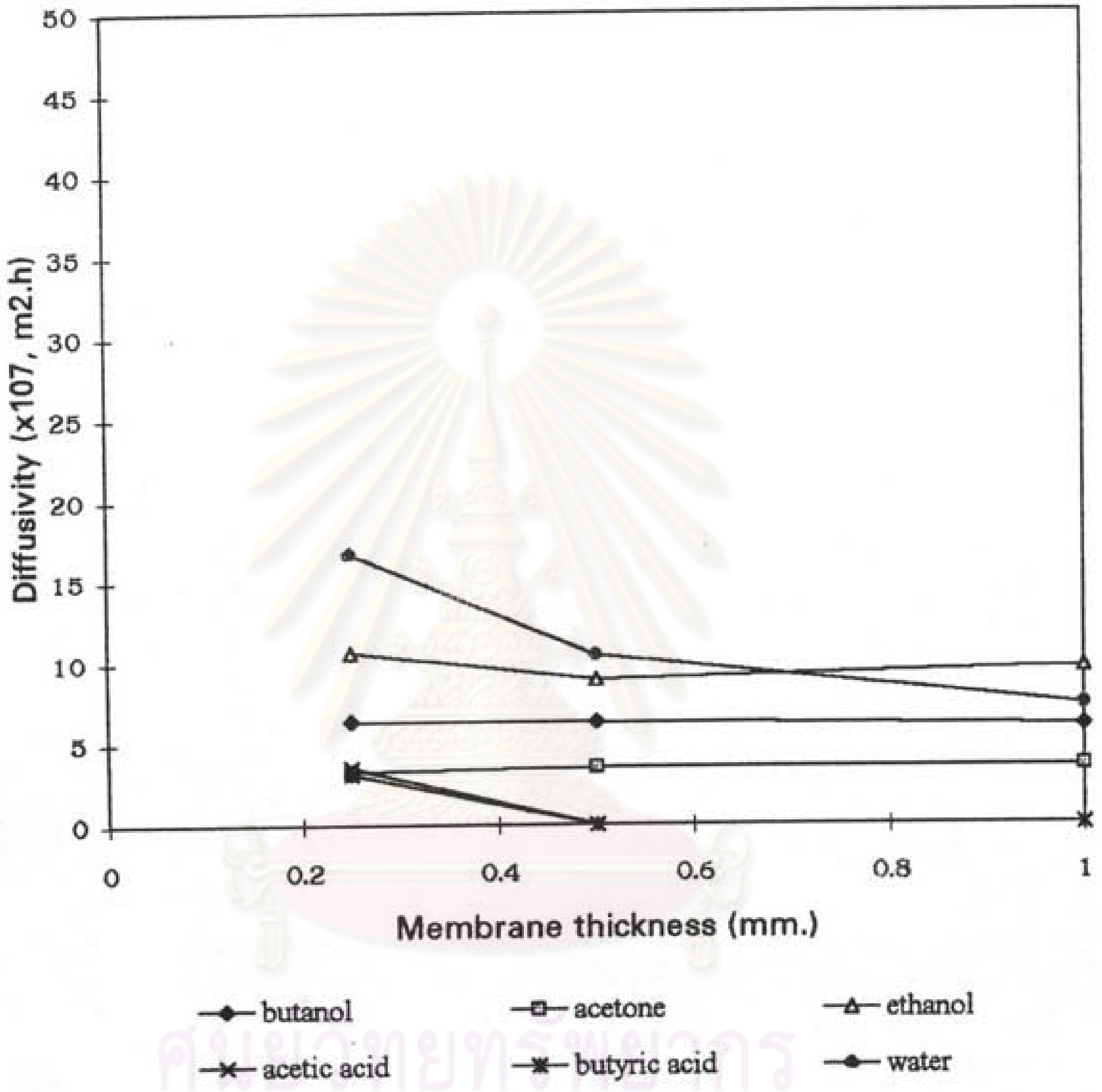

Figure 5.31 Correlation between membrane thickness and diffusivity of synthetic mixtures at permeation pressure 2 torr and feed temperature 60°C.

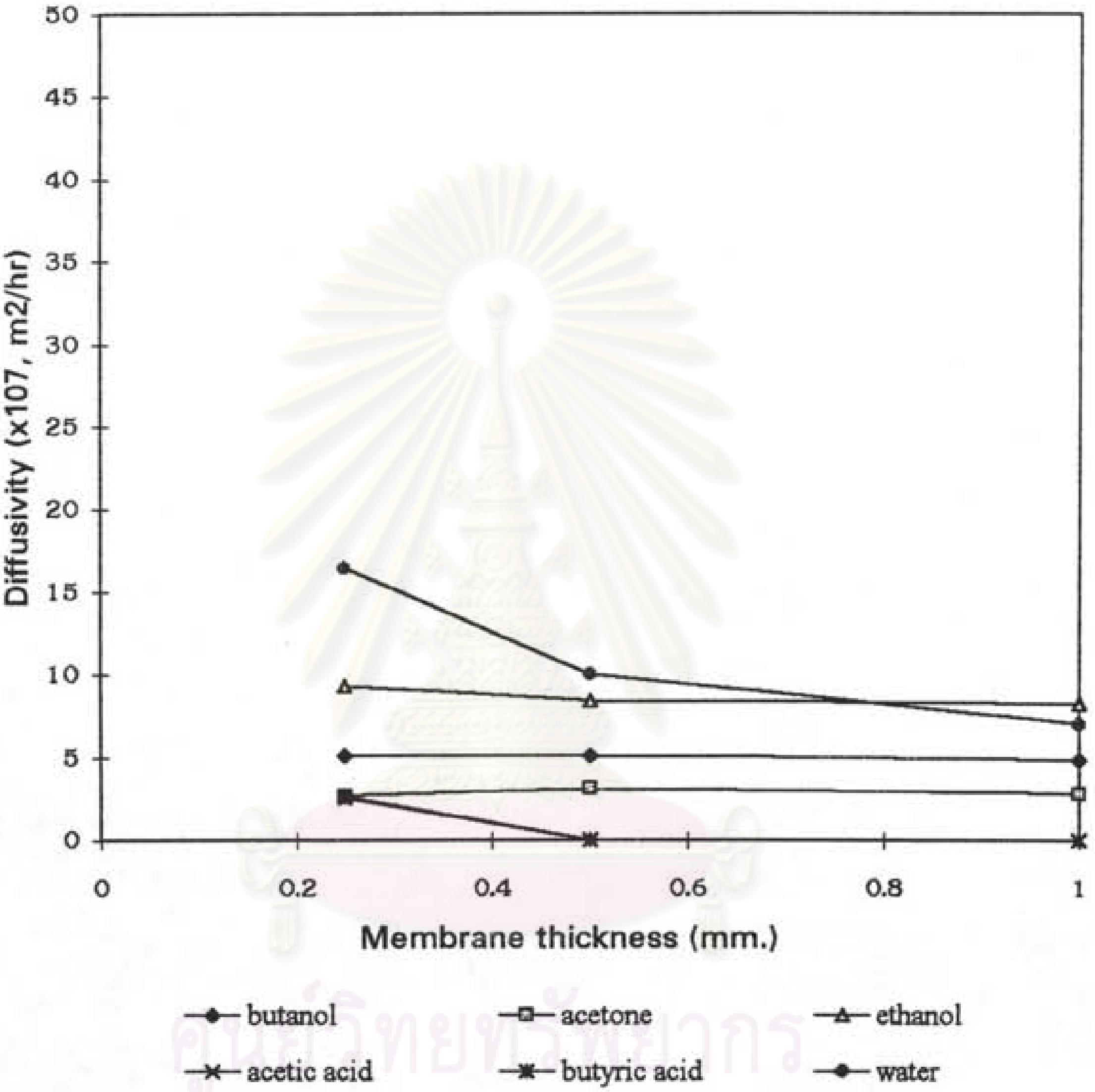

Figure 5.32 Correlation between membrane thickness and diffusivity of acetone-butanol fermentation broth at permeation pressure 2 torr and feed temperature 60°C.

5.6 Pervaporation of binary components and multicomponents.

In this section, we will discuss about the effects of other solutes on the pervaporation process of butanol and the results are shown in Figure 5.33 to 5.38. Other solutes can be seen in Appendix C. The acidic group was not studied because had only little effect on all the steps of pervaporation process. As a result, mixtures that were studied were water-butanol mixtures, water-acetone-butanol mixtures and acetone-butanol-ethanol mixtures and the operating conditions were: the permeation perssure of 2 torr, the feed temperature of 60°C and the membrane thickness of 0.25 mm.. The results indicated that distribution coefficient, permeation flux, permeation concentration, membrane selectivity, permeability and diffusivity of butanol in water-butanol were higher than other mixtures and decreased as the number components increased. Moreover, the effect of acetone addition was higher than that of ethanol addition. From these results, it showed that molecules with higher distribution coefficient were had higher effect on pervaporation of butanol than molecules with lower distribution coefficients.

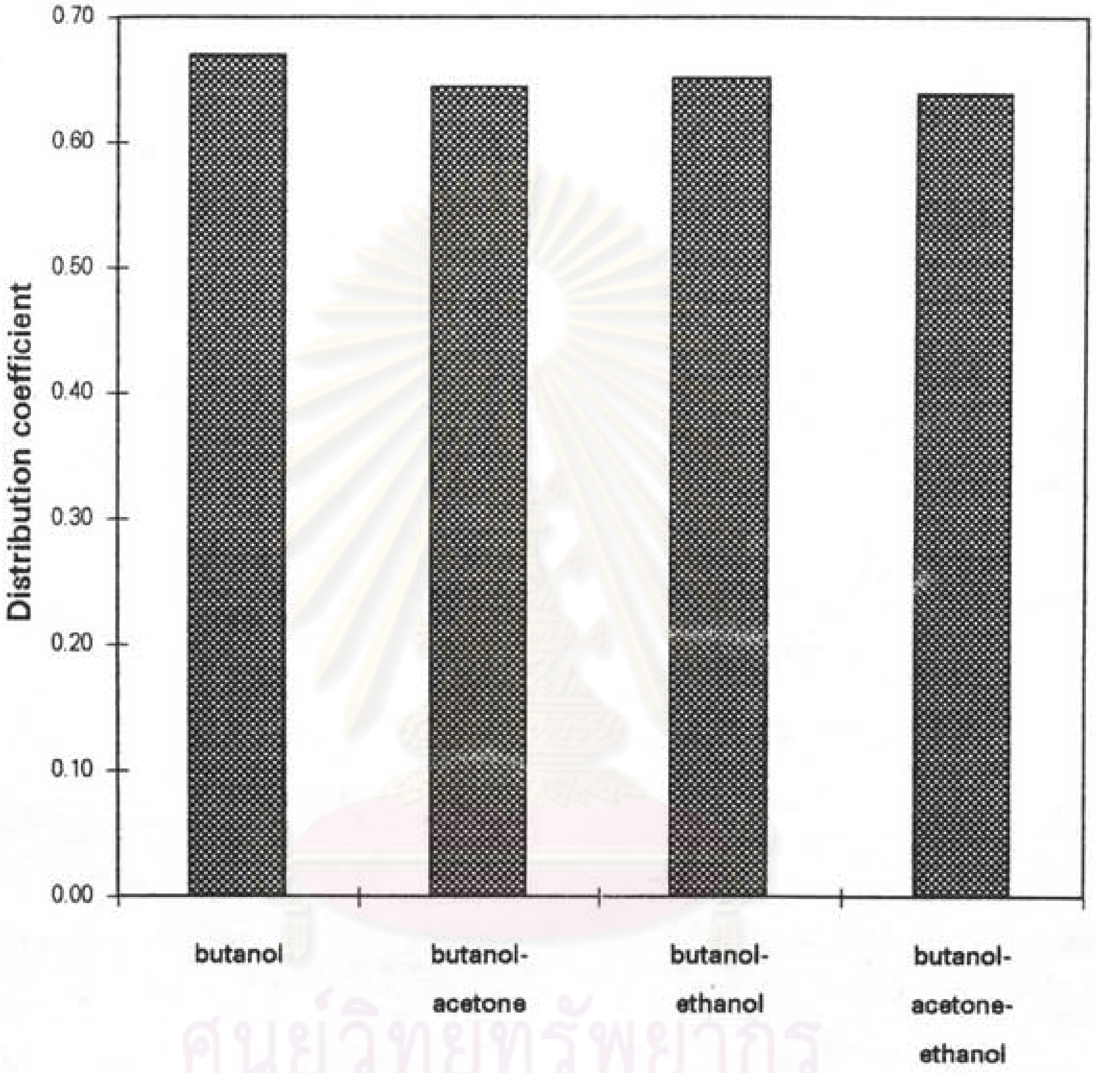

Figure 5.33 Distribution coefficient of butanol in various mixtures.

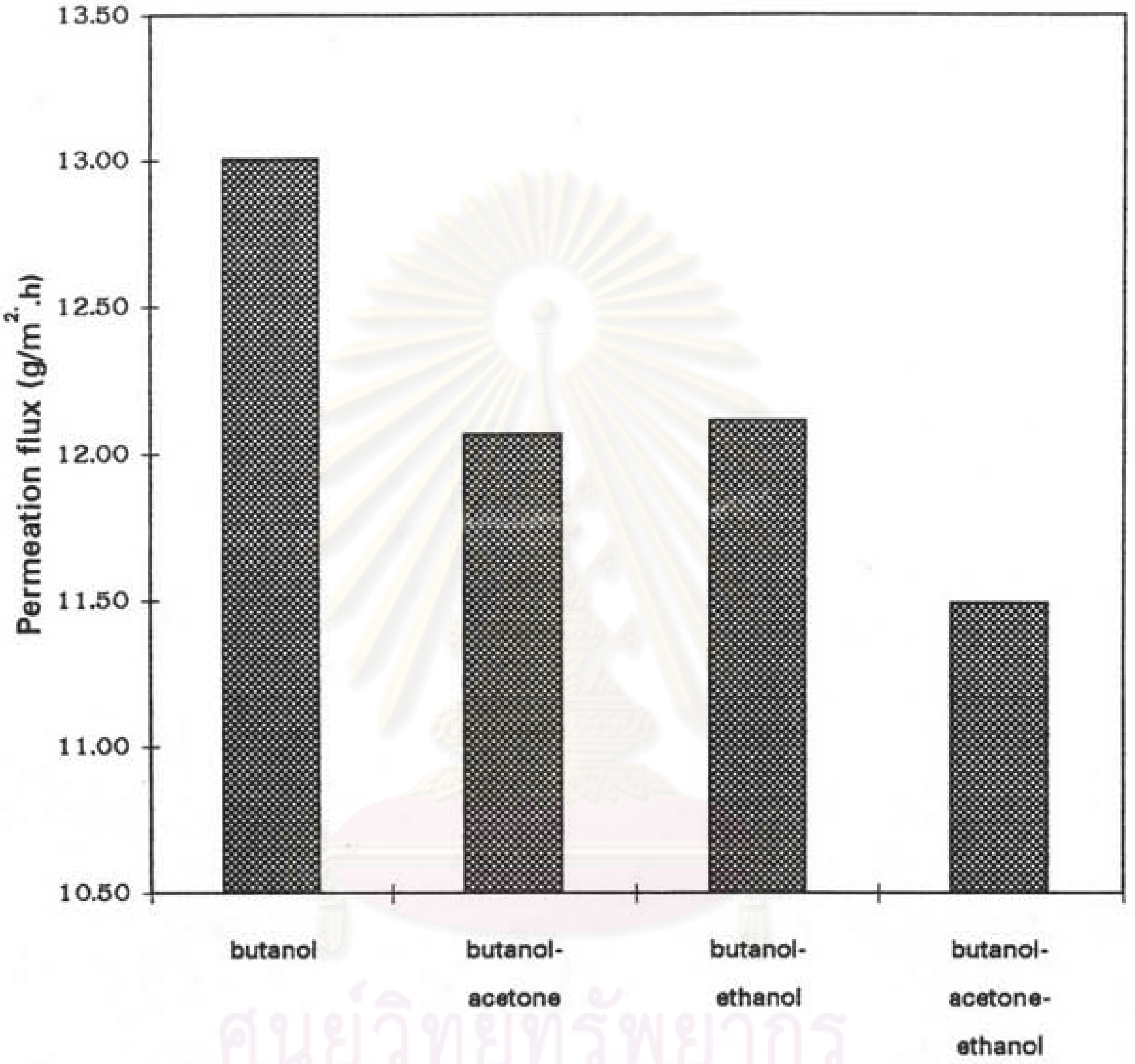

Figure 5.34 Permeation flux of butanol in various mixtures at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

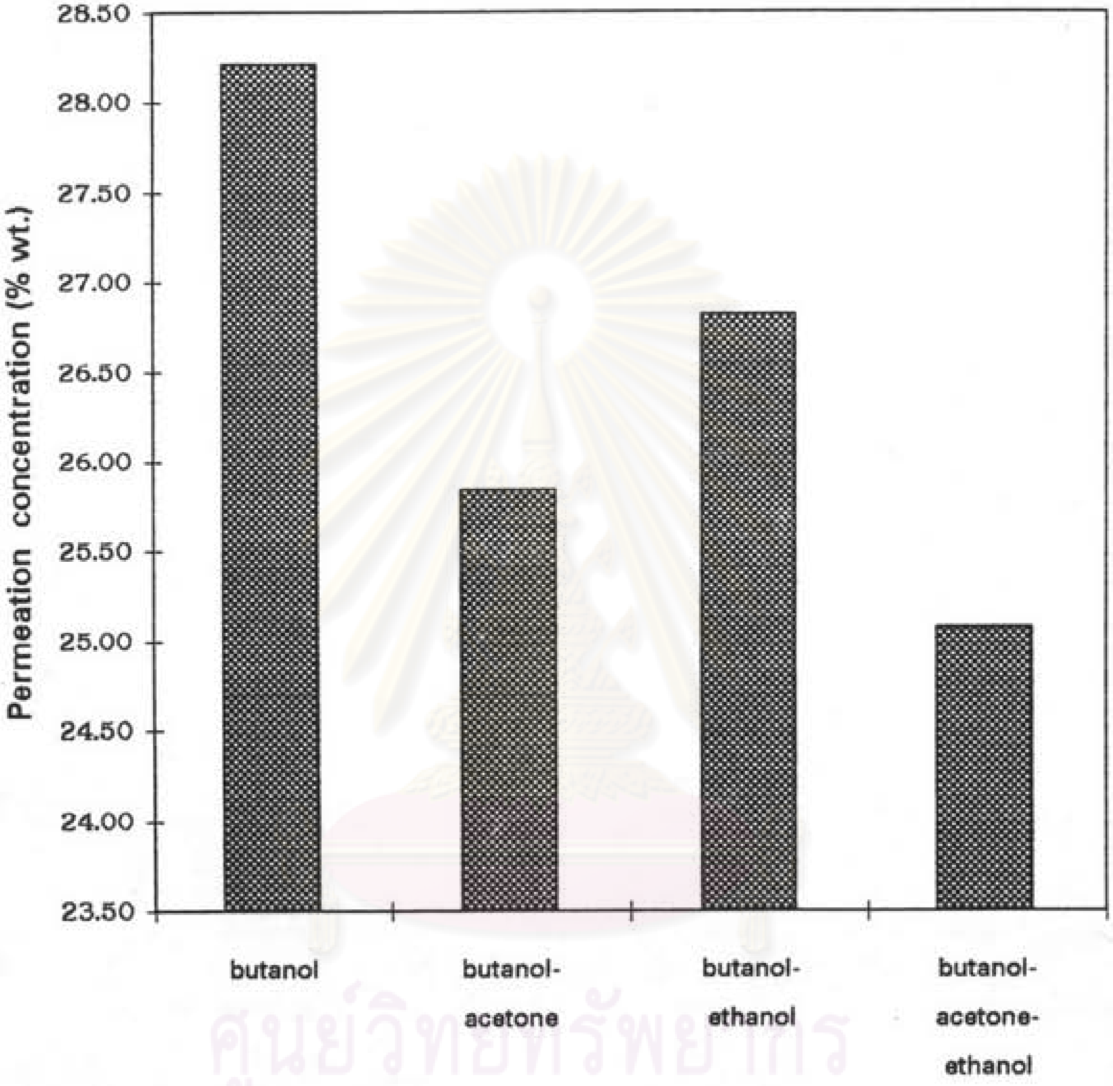

Figure 5.35 Permeation concentration of butanol in various mixtures at permeation pressure 2 torr, feed temperature 60 °C and membrane thickness 0.25 mm.

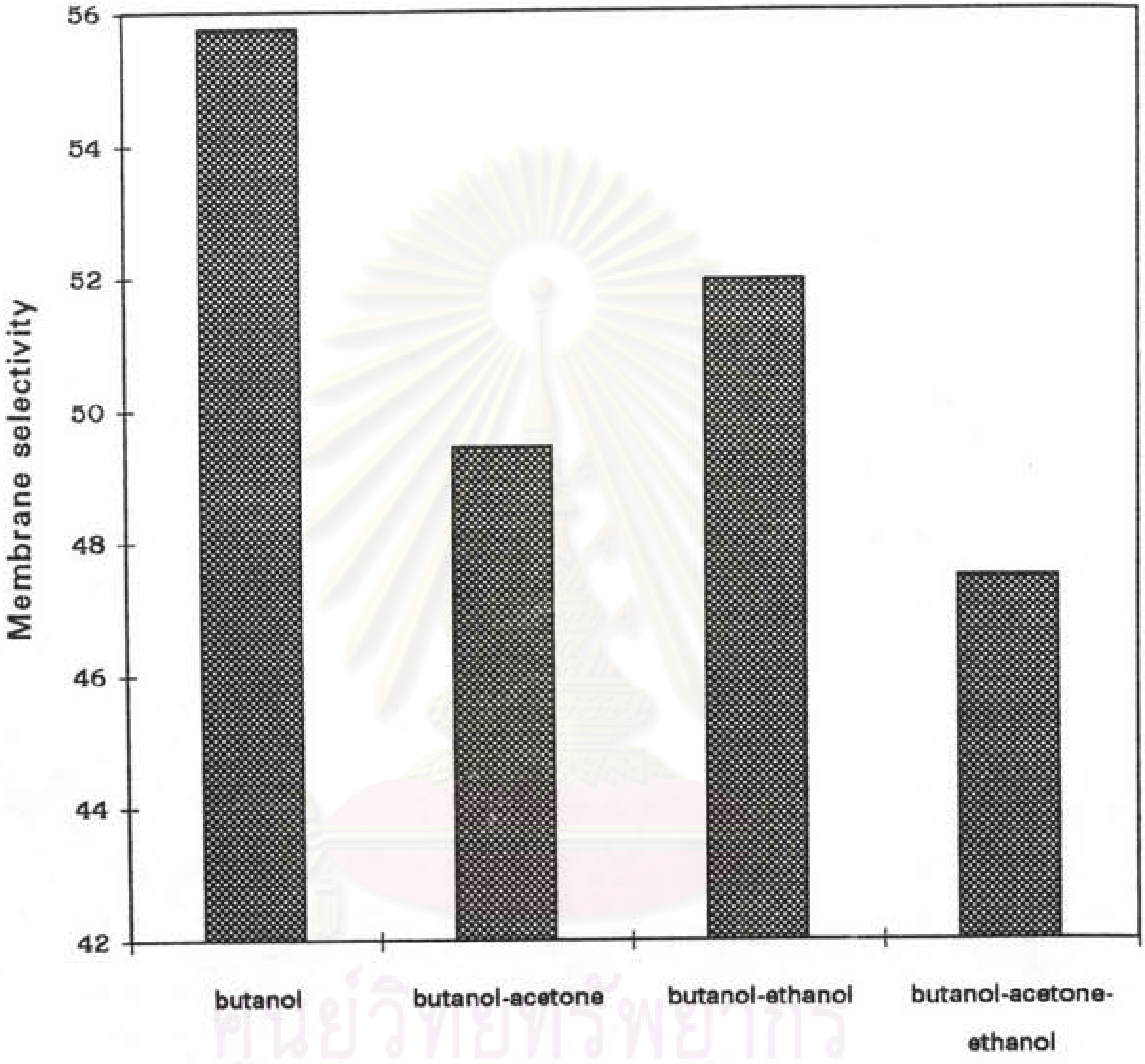

Figure 5.36 Membrane selectivity of butanol in various mixtures at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

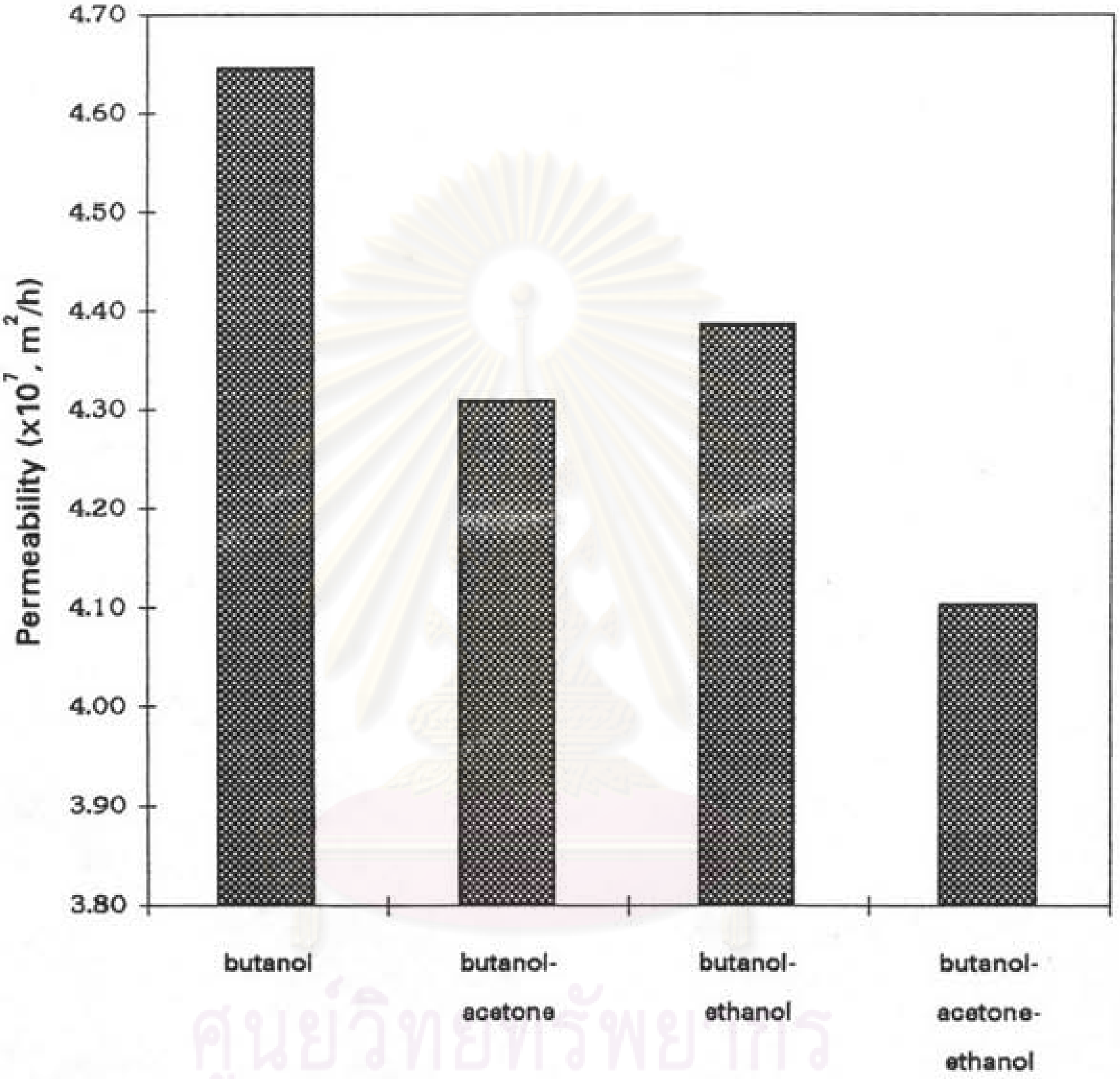

Figure 5.37 Permeability of of butanol in various mixtures at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

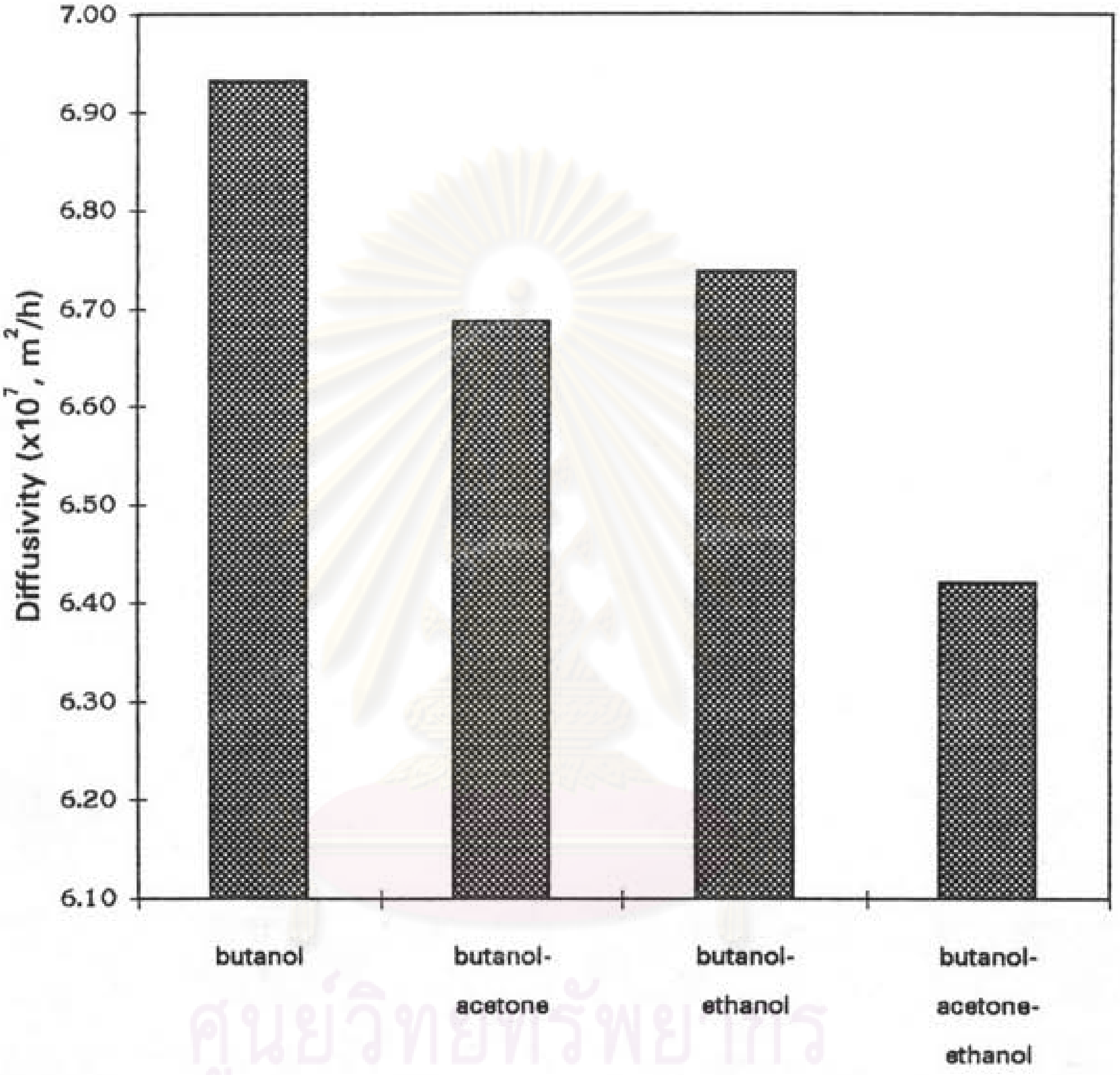

Figure 5.38 Diffusivity of butanol of butanol in various mixtures at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

5.7 The Pervaporation Process: The Comparison between Synthetic Mixtures and Acetone-Butanol Fermentation Broth.

The comparisons of the results of the permeation flux and distribution coefficient in synthetic mixtures and fermentation broth are shown in figures 5.35 and 5.36, respectively. The permeation fluxes of butanol in synthetic mixtures and fermentation broth were 11.2911, and 8.7646 $g/m^2.hr$, respectively. The permeation fluxes of all solutes in the synthetic mixtures are higher than that in the fermentation broth. Similarly, the results of permeate concentration, membrane selectivity, one pass mass recovery, permeability, and diffusivity of butanol in synthetic mixtures were higher than that in fermentation broth. (Figure 5.41-5.45) From these results it appeared that, an effect of other solutes in fermentation broth occurred, which can be seen from the reduction values of distribution coefficient, permeation flux, permeation concentration, membrane selectivity, one pass mass recovery, permeability and diffusivity. These molecules were hard to identify what types of molecules and mechanisms of competion occurred. However, we show the result in supporting this reduction by performing sorption experiments in various mixtures in section 5.6 and Appendix C. From these results, we concluded that parameter reduction found in the fermentation broth depended upon the adsorptive molecules in sorption process that were not found in synthetic mixtures. In addition, the residual glucose in the fermentation broth might also cause same reduction.

At the same membrane thickness, feed temperature, permeation pressure, permeability and diffusivity of all solutes in the synthetic mixtures were higher than that found in the fermentation broth.

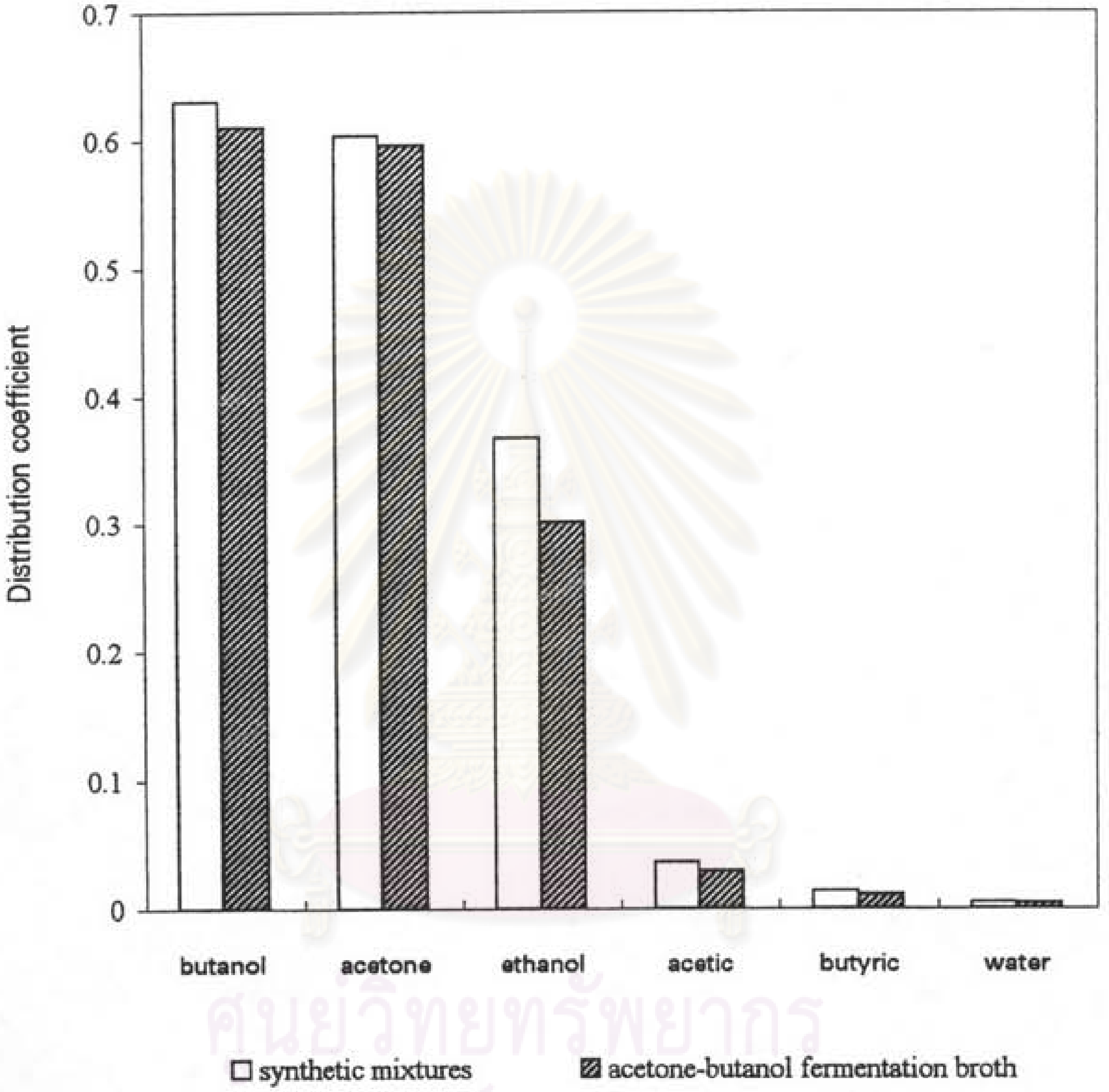

Figure 5.39 Comparison of distribution coefficient between synthetic mixtures and acetone-butanol fermentation broth at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

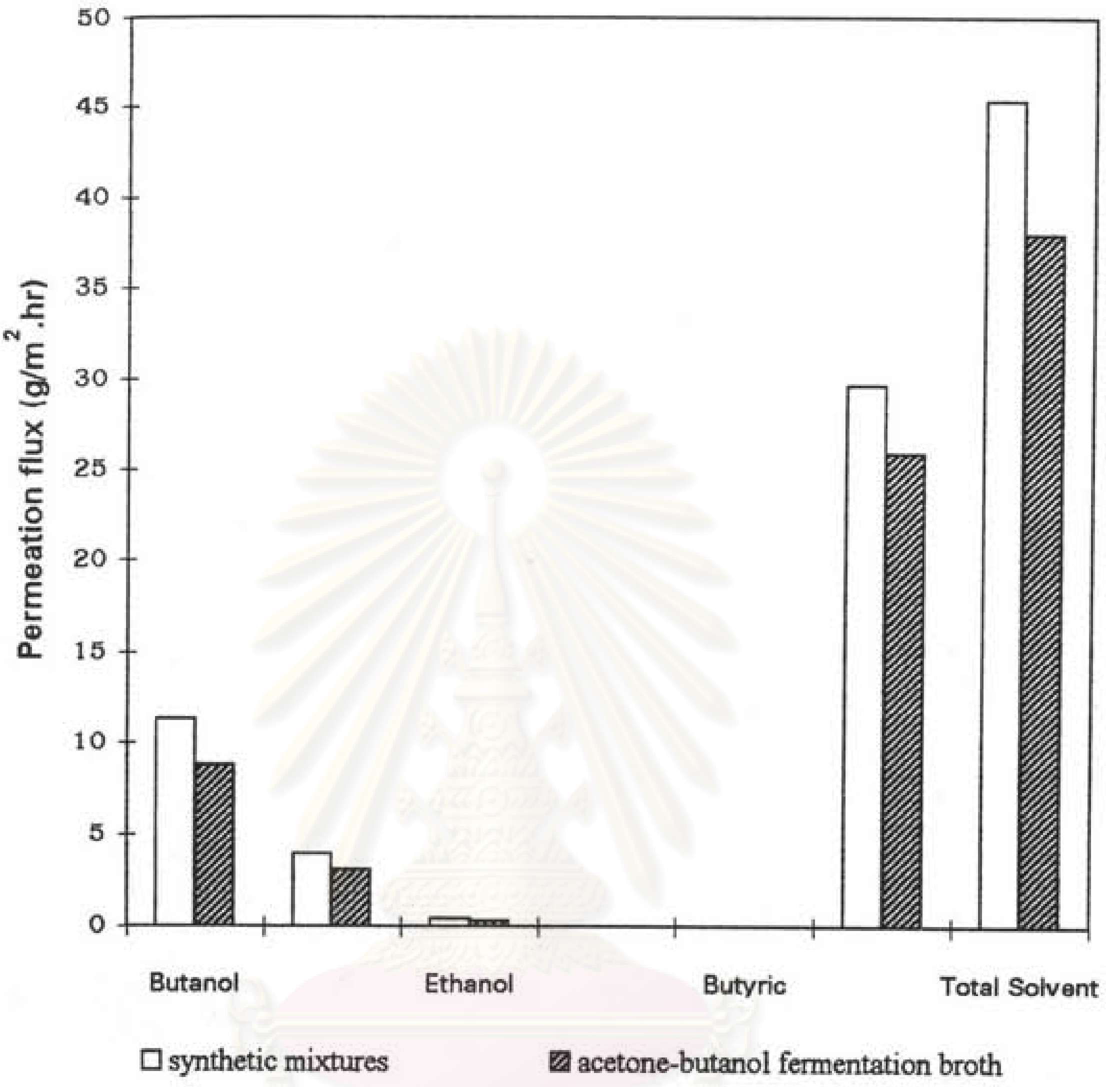

Figure 5.40 Comparison of permeation flux between synthetic mixtures and acetone-butanol fermentation broth at permeate pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

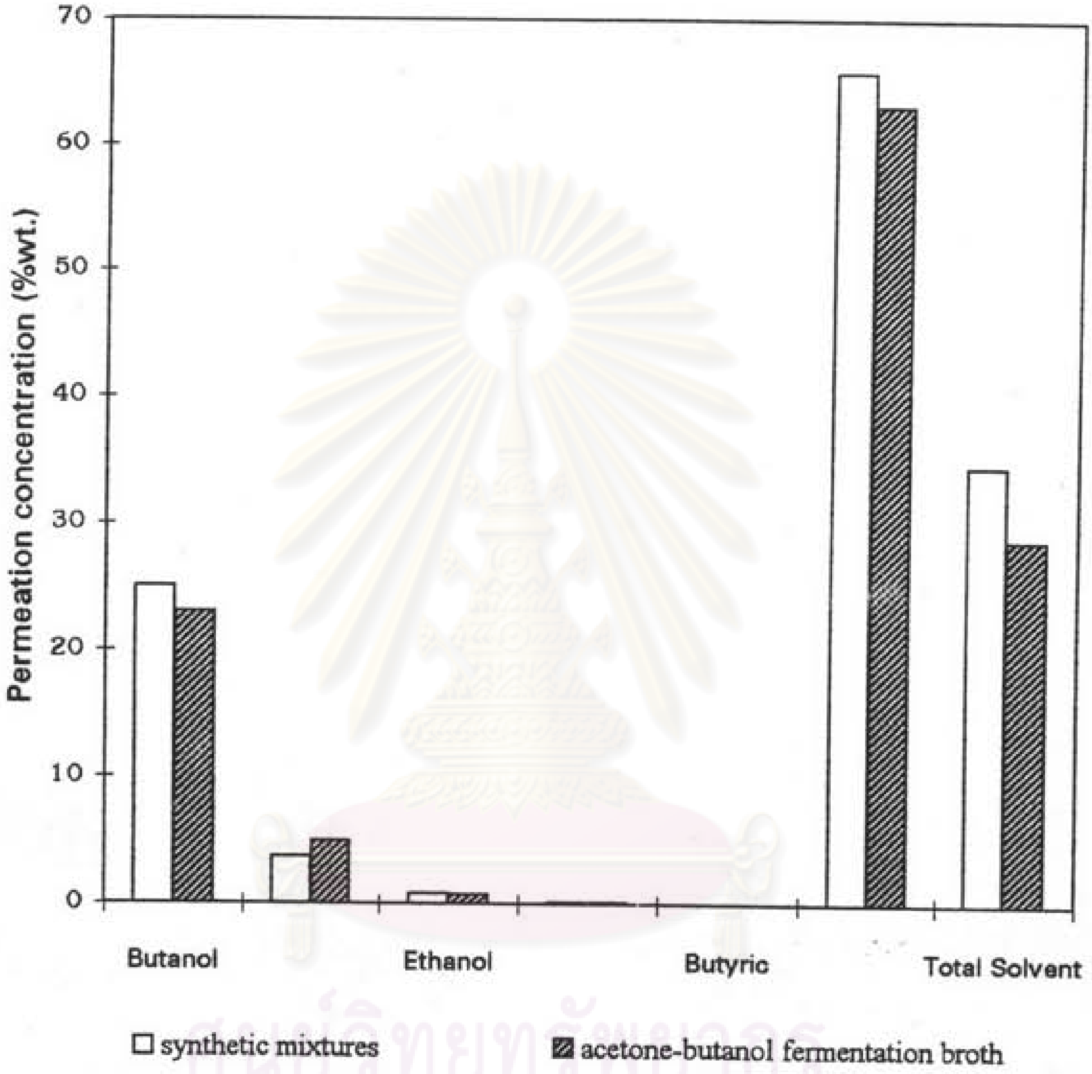

Figure 5.41 Comparison of permeate concentration between synthetic mixtures and acetone-butanol fermentation broth at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

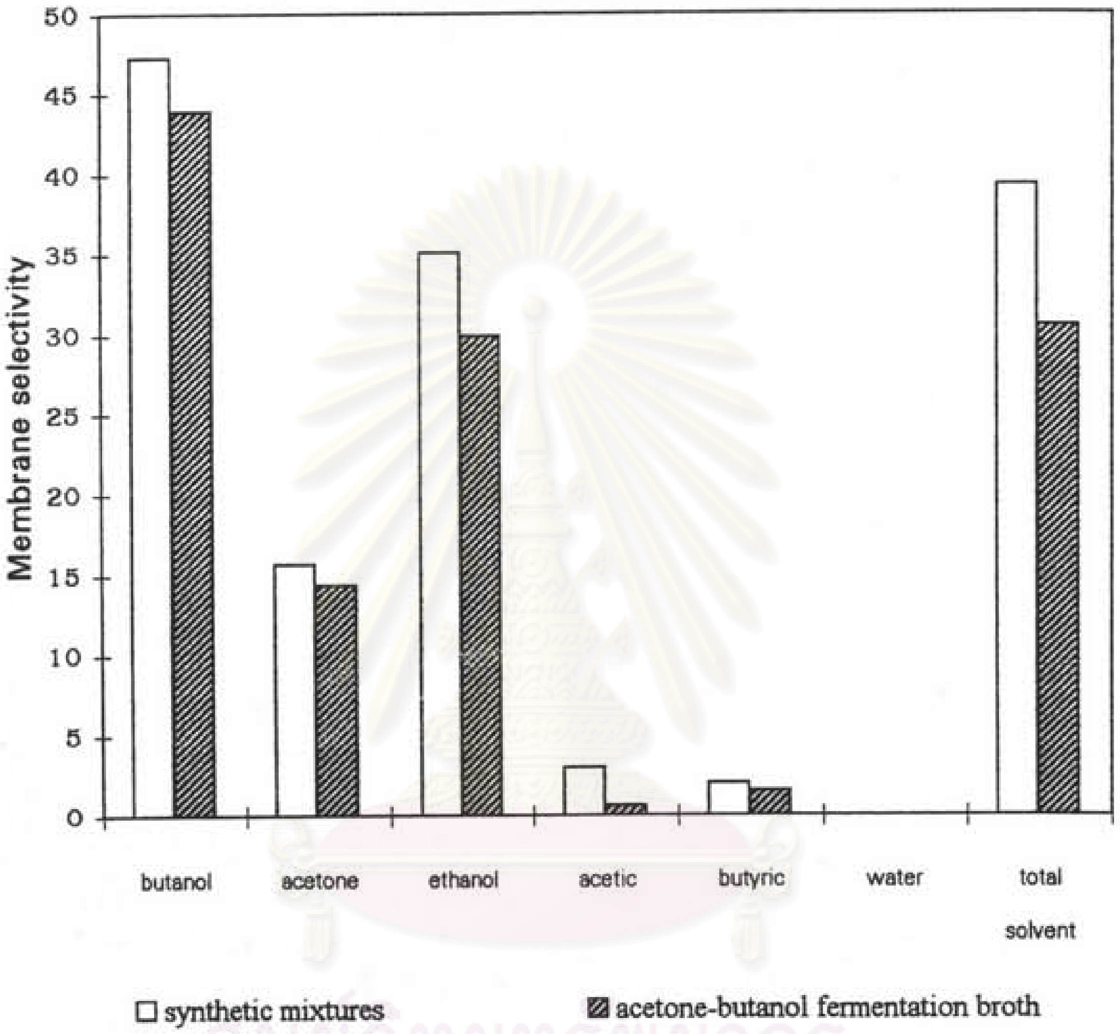

Figure 5.42 Comparison of membrane selectivity between synthetic mixtures and acetone-butanol fermentation broth at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

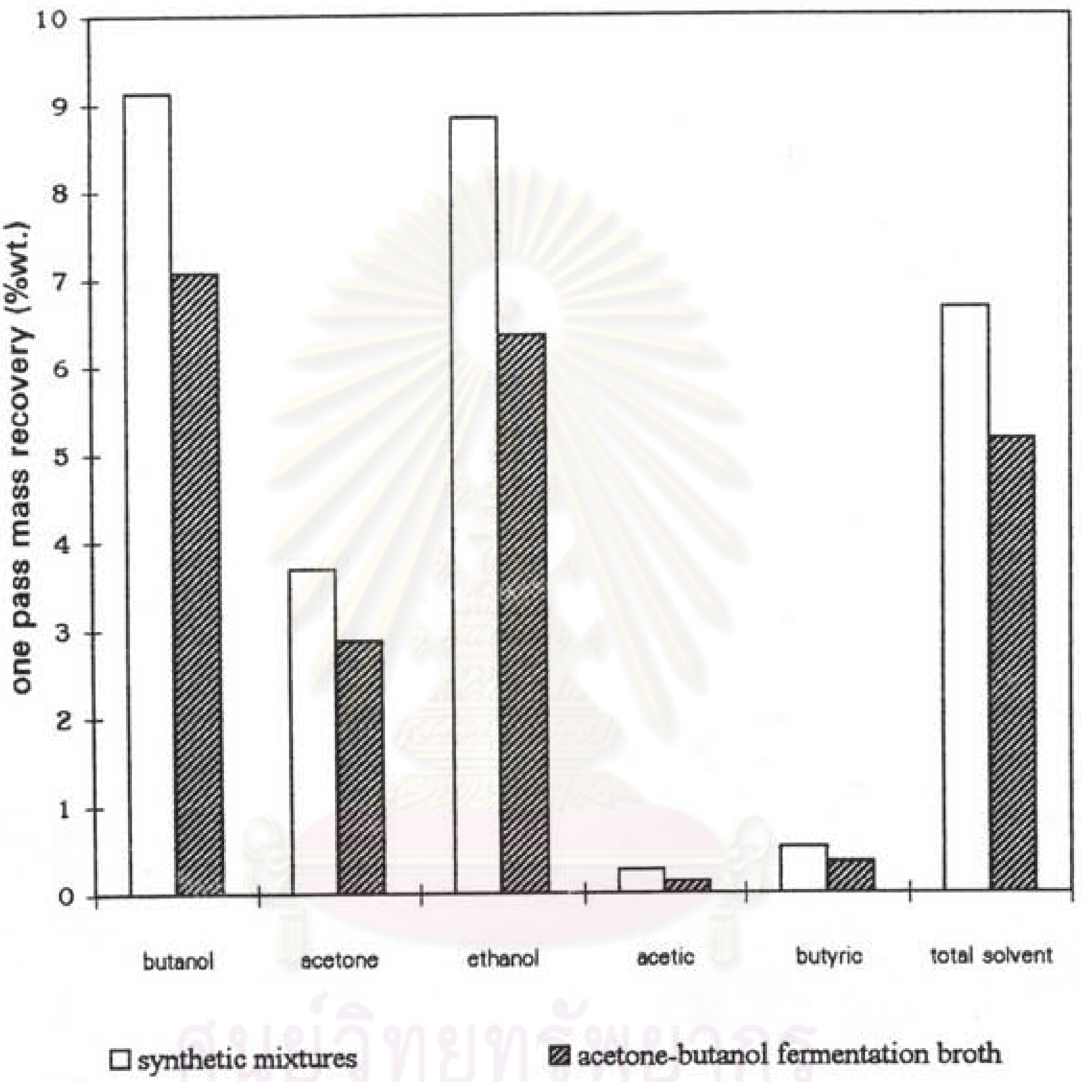

Figure 5.43 Comparison of permeability between synthetic mixtures and acetone-butanol fermentation broth at permeate pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

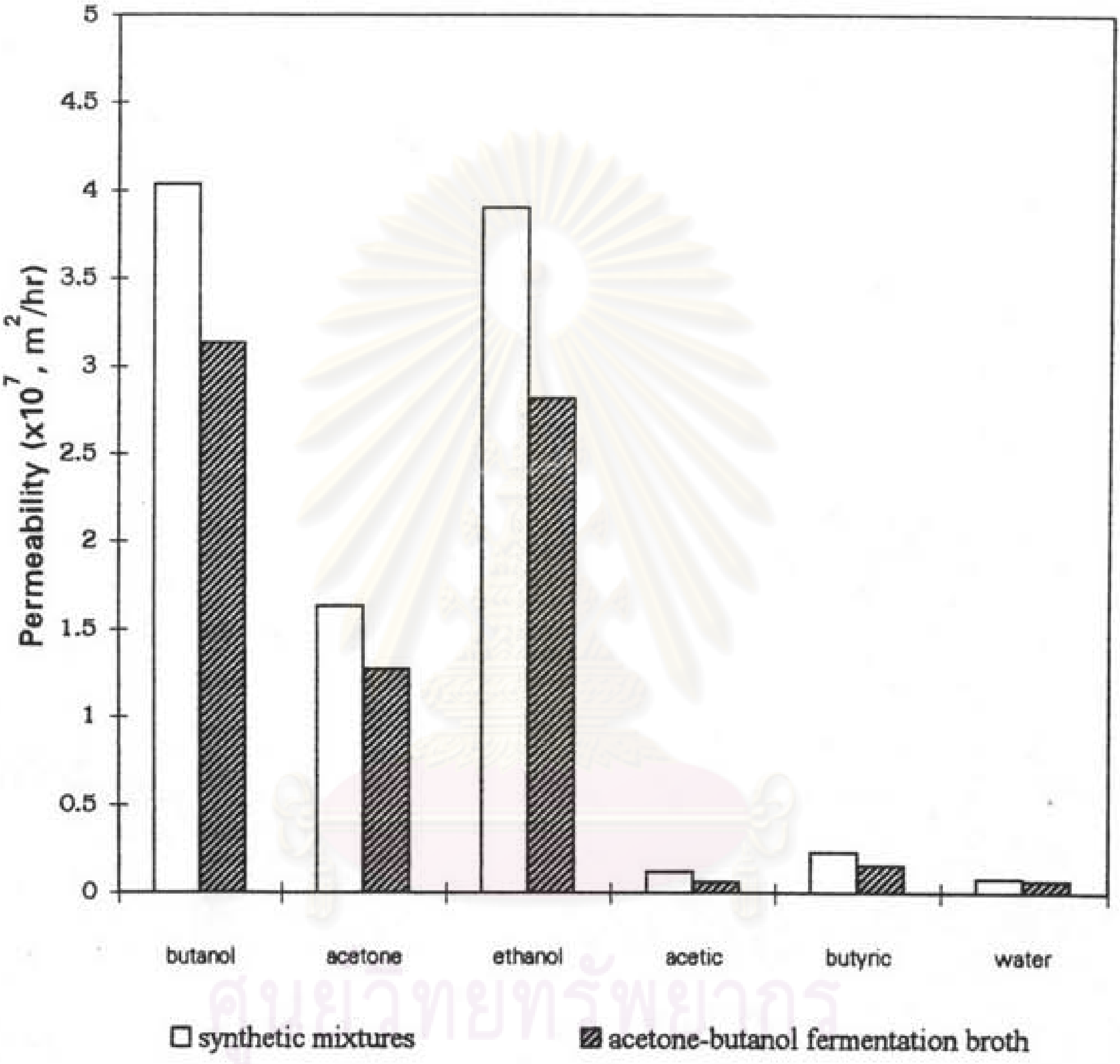

Figure 5.44 Comparison of diffusivity between synthetic mixtures and acetone-butanol fermentation broth at permeation pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

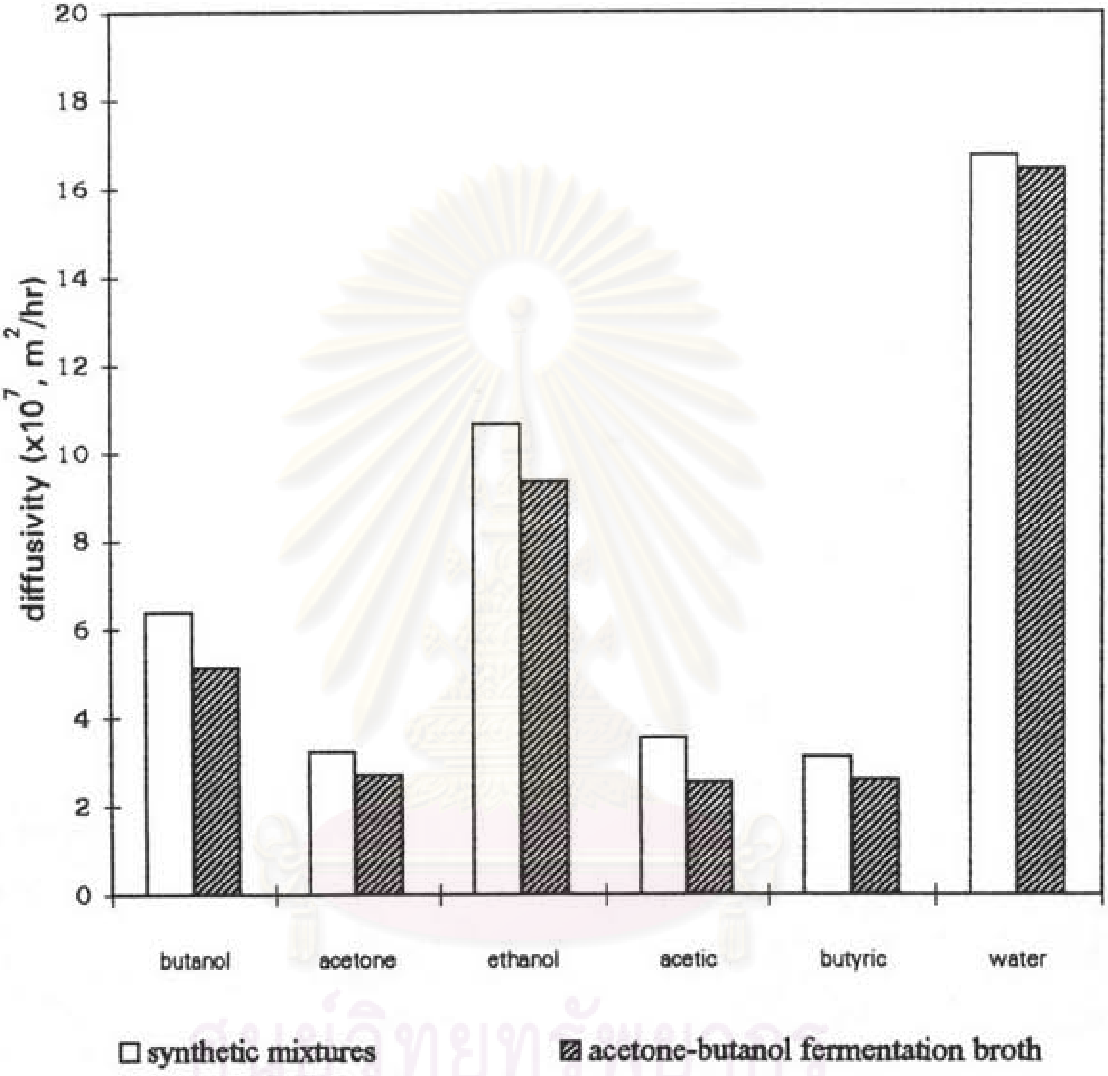

Figure 5.45 Comparison of distribution coefficient between synthetic mixtures and acetone-butanol fermentation broth at permeate pressure 2 torr, feed temperature 60°C and membrane thickness 0.25 mm.

5.8 Extractive fermentation through the pervaporation process.

In this project, the pervaporation process can be coupled with acetone-butanol fermentation as was earlier studied by Satida Krailas[25] on "solvent productivity improvement in acetone-butanol fermentation by two-stage continuous system". It was found from this study that two-stage continuous system coupled by microfiltration can provide high productivity of butanol, and solvent. The operating condition of extractive fermentation are shown in table 5.2. Figure 5.42 shows the schematic of extractive acetone-butanol fermentation through the pervaporation process. Product per hour of one pass through pervaporation unit, was 2.1503 g. ,which contained butanol 24.99%wt., acetone 8.67%wt. and ethanol 0.87%wt..

The Comparisons of these results with the extractive fermentation without microfiltration that was studied by M.A. Larrayoz and L. Puigjaner[8], are shown in table 5.3. From this comparing, the extractive fermentation with microfiltration was suitable for solvent separation and concentration than that without microfiltration. This was because permeation flux and production index of butanol were higher, although permeation concentration and membrane selectivity of butanol in the extractive fermentation without microfiltration were higher than that with microfiltration. The result of high permeation concentration and membrane selectivity of butanol in extractive fermentation without microfiltration may be caused by the difference of silicone rubber. For a low permeation flux of butanol in extractive fermentation without microfiltration, cell concentration in fermentor highly influenced the butanol separation.

Table 5.2 Operating condition of extractive acetone-butanol fermentation through the pervaporation process.

Two-Stage Coupled by Microfiltration	Pervaporation with Silicone Rubber Hollow Fiber Membrane
First Stage Dilution Rate = $0.17h^{-1}$ Working Volume 1 L Second Stage Dilution Rate = $0.55\ h^{-1}$ Working Volume 1.27L Feed Rate of Medium = 1.232 L/h Microfiltration Area = $0.2030\ m^2$ Velocity 0.465 m/s Permeation Rate 1.495 l/h	Feed Flow Rate 1 l/h Feed Temperature 60°C Permeate Pressure 2 torr Membrane Thickness 0.25 mm. Area = $0.065485835\ m^2$ Permeation Flux = $45.37\ g/m^2.h$

Table 5.3 Comparison between extractive fermentation with pervaporation

	M.A. Larrayoz et.al.	Present Study
Butanol		
concentration in feed	1.6 %wt.	0.7 %wt.
concentration in permeate	46 %wt.	23.02 %wt.
permeation flux	$6.63\ g/m^2.h$	$8.76\ g/m^2.h$
selectivity	52	43.8
production index	$183.9825\ g/m^2.h$	$279.3188\ g/m^2.h$
Vacuum System	Gas weeping	Vacuum pump

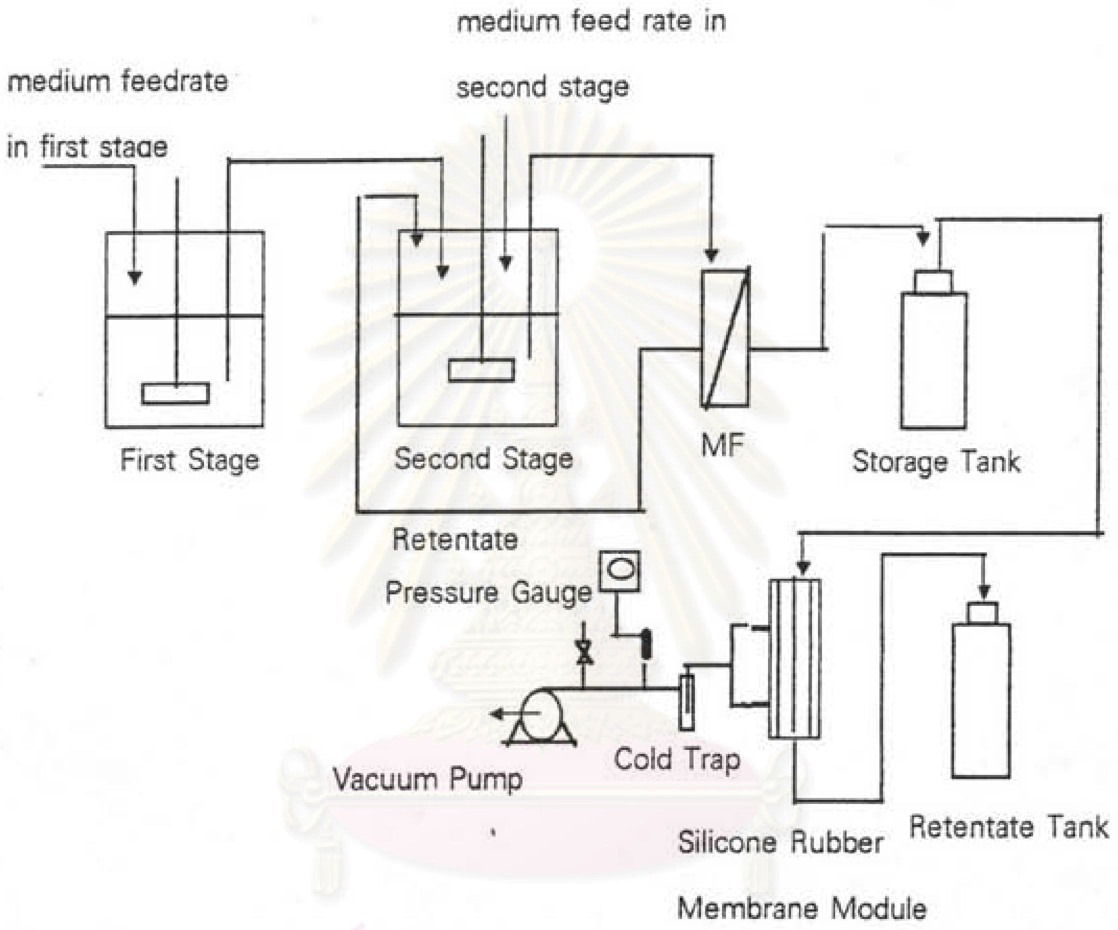

Figure 5.46 Extractive fermentation with microfiltration by pervaporation process.