

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Membrane Selection

For the separation of liquid hydrocarbon using a polymeric membrane, the membrane-selection step is important. The stability of the membrane in all liquid components has to be taken in to account. In this work, n-olefins, n-paraffins and C₈-aromatics were used in the experiment; therefore, appropriate membranes must be resistant to aliphatic and aromatic hydrocarbon.

The membrane-resistance test was straight forward. A membrane was cast and cut into small pieces. Then, it was soak in liquid solution comprising n-olefms, n-paraffins and C₈-aromatics. After a few minutes, the change of the membrane can be observed. Three membranes made of silicone rubber, polysulfone and polyimide membranes were tested. A silicone rubber membrane swelled after soaking in the solution. Furthermore, the membrane was tested in the extractor and found that the edge of the membrane was easily torn. Moreover, the leakage of the membrane was detected. Another membrane made of polysulfone was tested. After soaking in the solution, the membrane was immediately dissolved. Lastly, a polyimide membrane tested, unlike the previous two membranes, was stable and possessed enough strength to remain in the extractor for a long period without any damage. Thus, polyimide membrane was selected for further study.

Silicone rubber or polysiloxanes have an outstanding resistance to high and low temperatures as well as aliphatic solvents, oils, and greases (Green and Maloney, 1997). Although silicone rubber can resist to the aliphatic hydrocarbon, it is susceptible to aromatics. So, the swell after soaking in the solution was possibly caused by the aromatics. For polysulfone, it is resistant to high temperature, which can be used up to 170°C, mineral acid, alkali, and salt solutions as well as to detergents, oils, and alcohols. But, it is not so to organic solvents such as ketones, chlorinated hydrocarbons, and aromatic hydrocarbon (Green and Maloney, 1997). From these polymers' properties and the results from the experiments, it was

suggested that both silicone rubber and polysulfone are not appropriate to be used as membranes in this work.

Polyimides are characterized by the presence of aromatic rings and heterocyclic rings containing nitrogen and attached oxygen (Anderson *et al.*, 1998). The structure (Ultem 1000) shown in Figure 4.1 is the one used in this study. Polyimide is resistant to aliphatic, aromatic, and chlorinated or fluorinated hydrocarbons as well as to many acidic and basic systems but are degraded by high-temperature caustic exposures (Green and Maloney, 1997). So, the properties of polyimide can support the result from the experiment that it was stable in the olefins, paraffin and C₈-aromatics.

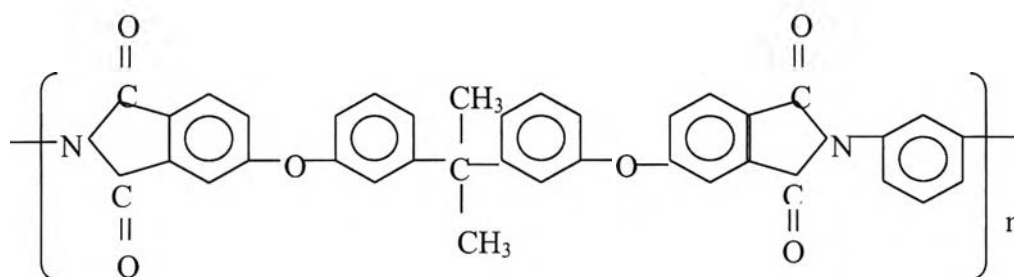


Figure 4.1 Polyetherimide (ULTEM 1000).

4.2 Extraction Experiments

In this part, polyimide membrane and polyimide-based MMM were tested in the extractor. A feed mixture consisted of n-C₉:EB:PX:OX:MX = 1:1:1:1:1 and i-octane as the desorbent. The experiments were conducted at 20°C and 15 psi. Concentrations of all components in the retentate were plotted versus time. Figure 4.2 shows concentration of ethylbenzene, p-xylene, o-xylene and m-xylene in the retentate side while Figure 4.3 shows concentration of n-nonane in the same side. The results show that the concentration of ethylbenzene, p-xylene, and m-xylene

decreases while that of n-nonane increases. That means the C₈-aromatics can pass through the membrane faster than n-nonane or the polyimide membrane is selective for the C₈-aromatics over n-paraffin. Furthermore, considering among the C₈-aromatics, ethylbenzene, p-xylene, and m-xylene can pass through the membrane faster than o-xylene. This result is consistent to that from Schleiffelder and Staudt-Bickel (2001) who reported that the separation factor of p-/o-xylene for pure polyimide membrane is 1.15-1.47.

A polyimide-based MMM was also subject to the same condition. In this study, 20 wt% silicalite/polyimide MMM was used. The results are shown in Figures 4.4 and 4.5. It can be observed that the silicalite/polyimide MMM has the same performance as the polyimide membrane.

A possible reason for the results is the interaction of the membrane and the molecular structure of the species present in the feed. Since the polyimide structure contains aromatic rings as shown in Figure 4.1, the C₈-aromatics prefer to permeate through the membrane than n-paraffin. The preference of p-xylene, ethylbenzene, and m-xylene than o-xylene may be due to the different molecular shape of these isomers. For the polyimide-based MMM, it can be explained by the same reason. However, the separation among C₈-aromatics is still low.

4.3 Pervaporation Experiments

In the extraction test, which is a batch system, the back diffusion can occur and reach the equilibrium easily. And that may pose the problem of low C₈-aromatics selectivity. So, a continuous system has been set up to investigate this issue. Besides its continuous operation mode nature, the pervaporation technique is attractive due to a high-pressure difference between the retentate and a permeate sides, which increases the driving force of the species in the unit. Liquid components are also vaporized to the permeate side meaning that there is no need of a desorbent. In other words, the pervaporation system seems to be less complex than the extraction system.

A polyimide membrane was tested with the feed composition of octane:octene:n-C₉:EB:PX:MX:OX = 2:2:1:1:1:1:1 (weight ratio) at 21, 40 and 70 °C and 1200 psi. Selectivity was calculated with respect to n-octane. The results in Figure 4.6 show that at all studied temperatures, this membrane is more selective for the C₈-aromatics and n-octane than n-octene ($\alpha_{C_8\text{-aromatics}/n\text{-octane}}$ and $\alpha_{n\text{-octane}/n\text{-octene}} > 1$). Considering between the C₈-aromatics and n-octane, the membrane is selective for the aromatics because the selectivity of all C₈-aromatics to n-octane is slightly higher than 1 (1.01-1.04). This is consistent to the result from the extraction unit, i.e., all membranes are selective to aromatics over n-paraffin. For the separation among C₈-aromatics, it indicates that the separation is still low.

For the effect of temperature, Figure 4.6 shows that the increase in the temperature hardly affects the selectivity of the C₈-aromatics to n-octane but the selectivity of n-octene to n-octane decreases. However, with the temperature higher than 70°C, the membrane was damaged. From these results, it can be concluded that the polyimide membrane is selective for the C₈-aromatics and n-paraffins. The temperature does not play a significant role on the separation. Further study about the internal mechanism of the membrane is needed to understand and explain these membrane performances.

Since each C₈-aromatic cannot be separated, the next study focuses on the separation among C₈-aromatics, n-olefins, and n-paraffins. In this experiment, p-xylene, n-octene, and n-octane were chosen as the representative of the C₈-aromatics, n-olefin, and n-paraffin, respectively. The feed composition of octane:octene:PX = 1:1:1 (weight ratio). A polyimide membrane, 20 wt% NaY/polyimide and 20 wt% silicalite/polyimide were tested in the pervaporation unit. The results are shown in Figure 4.7. All membranes show approximately the same result that is they are selective for n-octane over n-octene. The selectivity of n-octane to n-octene of polyimide membrane, 20 wt% NaY/Polyimide, and 20 wt% silicalite/polyimide is 1.276, 1.210, and 1.280, respectively. The polyimide membrane is selective for n-paraffin, which is consistent to the previous results as shown in Figure 4.6. The incorporation of NaY or silicalite into the polyimide membrane does not affect the selectivity of n-octane to n-octene.

In addition to the above experiments, another experiment was carried out to confirm the results. For this purpose, 20 wt% silicalite/polyimide was tested with a mixture of 50 wt% n-hexane in n-hexene, and the selectivity of n-hexane to n-hexene is 1.617. This further supports the above-mentioned results. It can be concluded that both polyimide membrane and polyimide-based MMM's are selective for n-paraffin over n-olefin.

Selectivity of p-xylene to n-octane was considered to substantiate the polyimide-based MMM selectivity towards the C₈-aromatics. Here, polyimide, 20 wt% NaY/polyimide, 20 wt% silicalite/polyimide, and 20 wt% AC/polyimide were used to cast membranes. Figure 4.8 shows that all membranes are selective for p-xylene over n-octane. The selectivity of p-xylene to n-octane for polyimide membrane, 20 wt% NaY/polyimide MMM, 20 wt% silicalite/polyimide MMM, and 20 wt% AC/polyimide MMM were 1.744, 1.786, 1.777 and 1.006, respectively. As mentioned before, the polyimide membrane prefers to interact with aromatics, so it is not surprising that the polyimide membrane is selective for p-xylene. Again, NaY and silicalite show that there is no significant improvement in the selectivity. These results are consistent to the results from the extraction unit, which conclude that polyimide membrane and polyimide-based MMM were selective for C₈-aromatic over n-paraffin. However, the AC/polyimide membrane is not preferentially selective to either p-xylene or n-octane.

From the membranes test results, it can be implied that the selectivity of the membranes are affected by the interaction between the membrane and the interested species. And this correlation depends on both molecular structure of the feed species and the hydrophobic-hydrophilic property of the adsorbent.

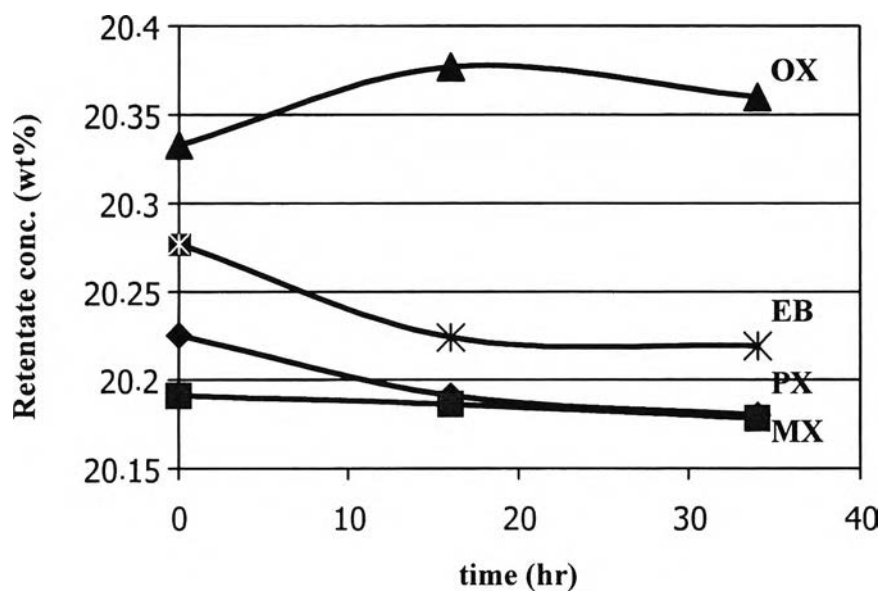


Figure 4.2 Retentate concentration of C₈-aromatics from the extraction unit equipped with polyimide membrane. Feed composition of n-C₉:EB:PX:OX:MX = 1:1:1:1:1 (wt ratio).

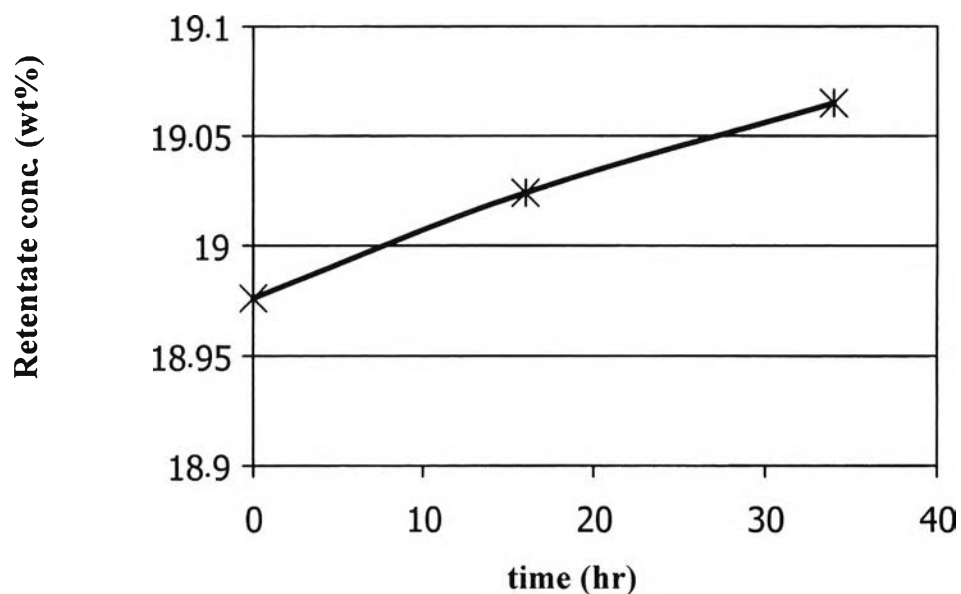


Figure 4.3 Retentate concentration of n-nonane from the extraction unit equipped with polyimide membrane. Feed composition of n- C₉:EB:PX:OX:MX = 1:1:1:1:1 (wt ratio).

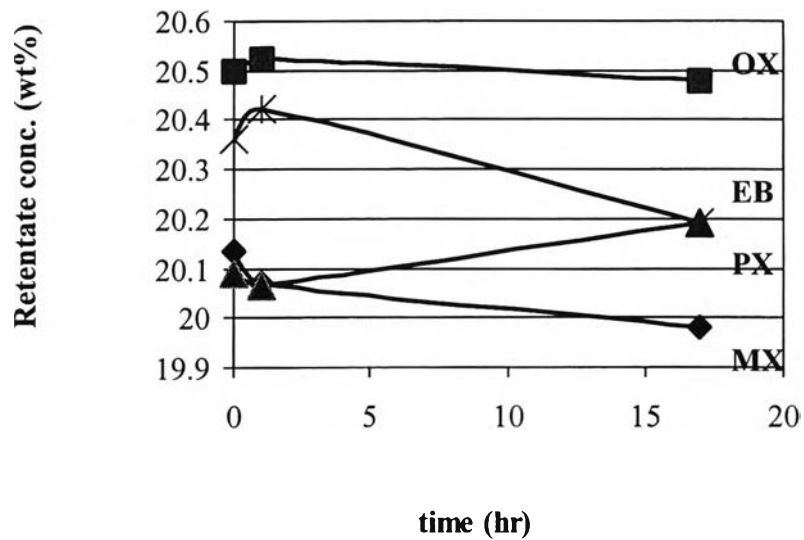


Figure 4.4 Retentate concentration of C₈-aromatics from the extraction unit equipped with 20 wt% silicalite /polyimide membrane. Feed composition of n-C₉:EB:PX:OX :MX= 1:1:1:1:1 (wt ratio).

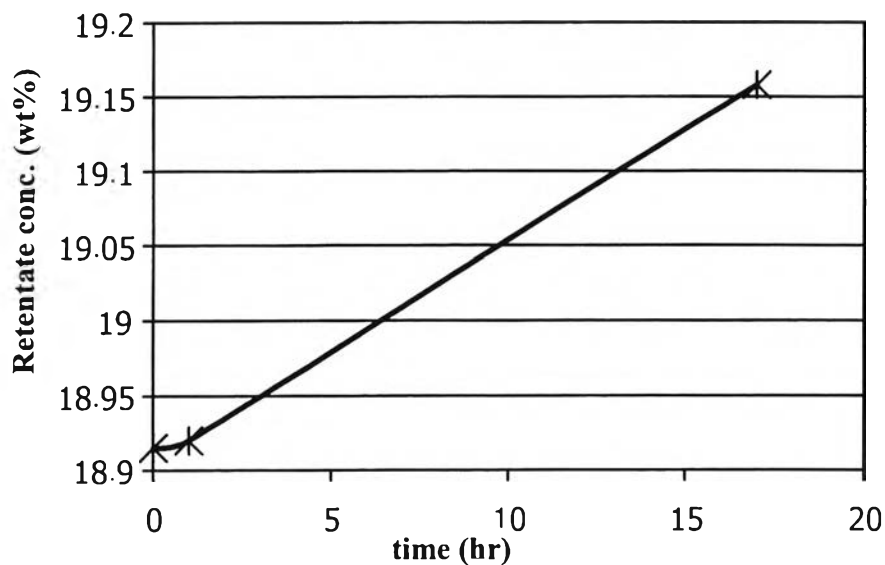


Figure 4.5 Retentate concentration of n-nonane from the extraction unit equipped with 20 wt% silicalite /polyimide membrane. Feed composition of n- C₉:EB:PX:OX :MX = 1:1:1:1:1 (wt ratio).

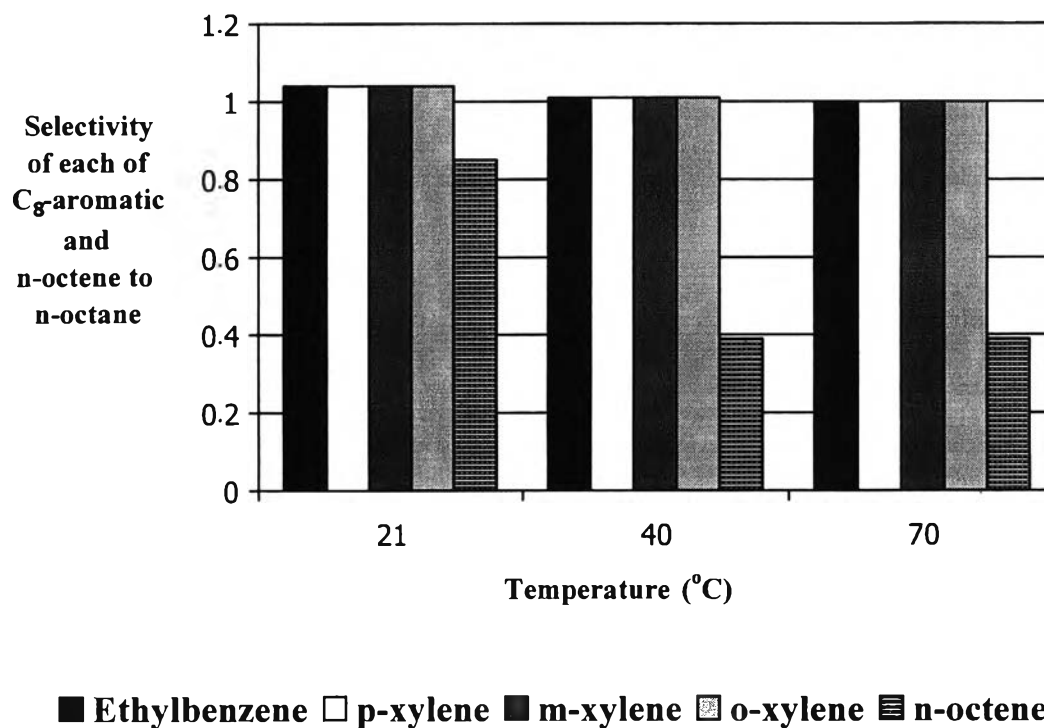


Figure 4.6 Selectivity of each C₈-aromatic and n-octene with respect to n-octane from the pervaporation unit using polyimide membrane. Feed composition of octane:octene:n-C₉:EB:PX:MX:OX = 2:2:1:1:1:1:1 (wt. ratio).

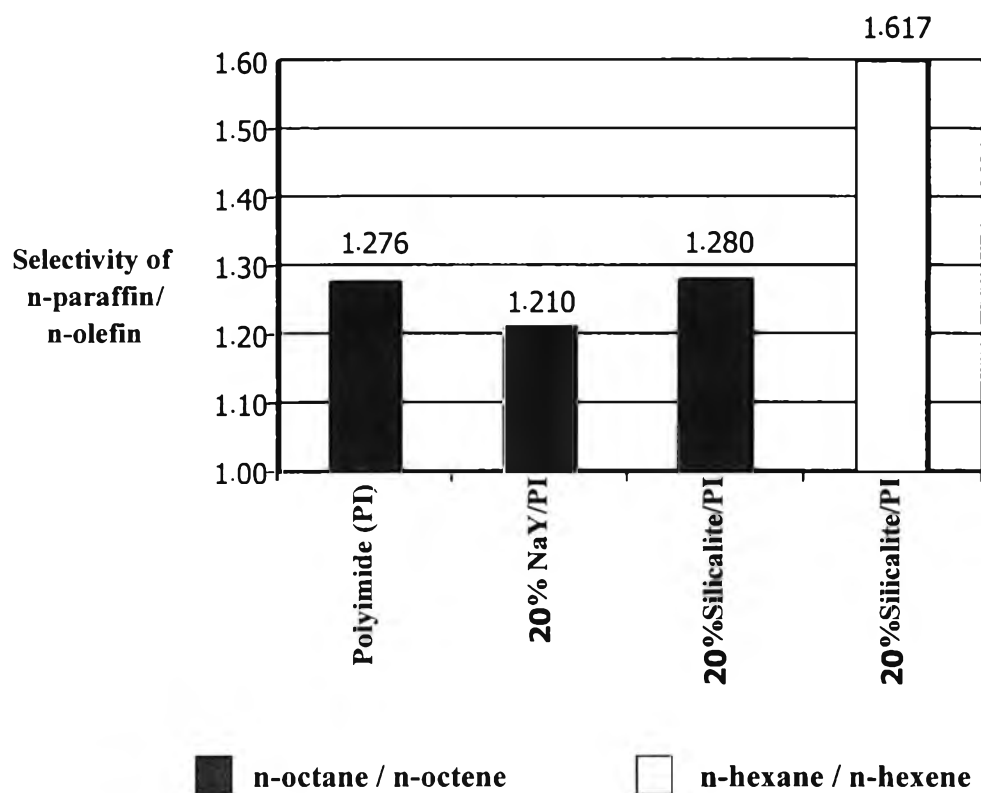


Figure 4.7 Selectivity of n-paraffin with respect to n-octane from the pervaporation unit using polyimide membrane and MMM. Feed composition of octane:octene:PX = 1:1:1 (wt. ratio).

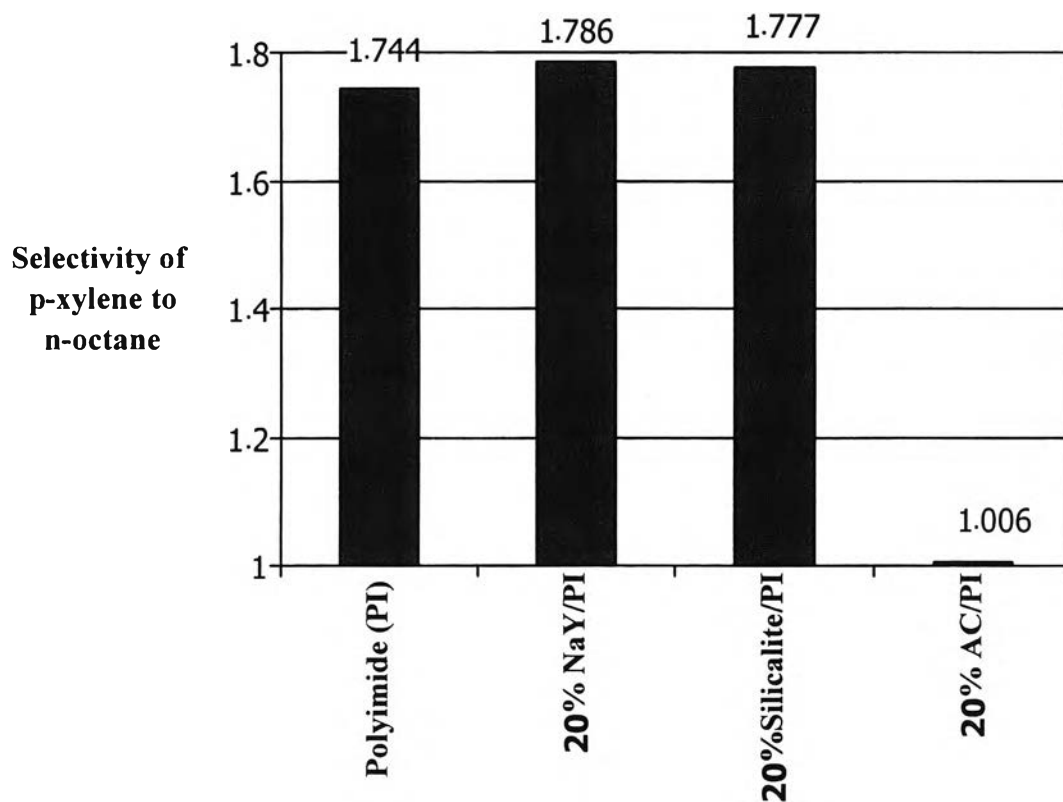


Figure 4.8 Selectivity of p-xylene with respect to n-octane from the pervaporation unit using polyimide membrane and MMM from pervaporation unit. Feed composition of octane: octene: PX = 1:1:1 (wt. ratio)