CHAPTER 2 THEORIES AND LITERATURE REVIEW

Theories of pervaporation and vapor permeation are presented in this chapter providing the necessary understanding. In addition, research work related to permeation through inorganic membranes such as carbon and zeolite membranes are reviewed.

2.1 Membranes Process

The principle of membrane process is shown in Figure 2.1. Feed, a mixture of two or more components is separated by means of one or more species move through membrane better than another species. The movement of any species across the membrane is caused by one or more driving forces. These driving forces arise from a gradient of chemical potential or electrical potential. A gradient in chemical potential may be due to a concentration gradient or pressure gradient or both (Winston, 1992) [12]. Feed mixture that does not pass through the membrane is called retentate, and that passes through the membrane is called permeate. Although the feed, retentate and permeate are usually liquid or gas, the membrane may be nonporous polymeric film, porous polymer, ceramic, liquid, etc. The membrane must not dissolve and disintegrate. The important factor that indicates the ability of separation is the flow rate of substances that pass through membrane or permeate flux.

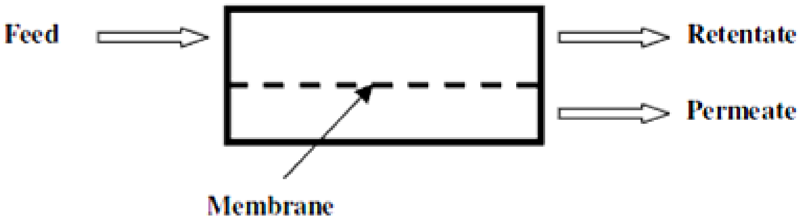

Figure 2.1 Principle of membranes process [13]

2.2 Pervaporation Process, PV

Pervaporation process is the separation of two or more components pass through the membrane at different diffusion rates [12]. Concentration and vapor pressure gradients are used to allow one component preferentially permeates across the membrane. Component that passes through membrane will be vapor. Vapor sample can be trapped in the permeate side (Figure 2.2) by decreasing temperature of substance, and then it will condense and becomes liquid at room temperature. Two types of membranes are used in pervaporation: hydrophilic membranes removing water from organic solutions, and hydrophobic membranes recovering organics substances from solutions. Applications of pervaporation are dehydration of alcohol solution, removal of organics from water, continuous water removal from condensation reactions such as esterifications, separation heat sensitive products, etc. The schematic diagram of the pervaporation process is shown in Figure 2.2.

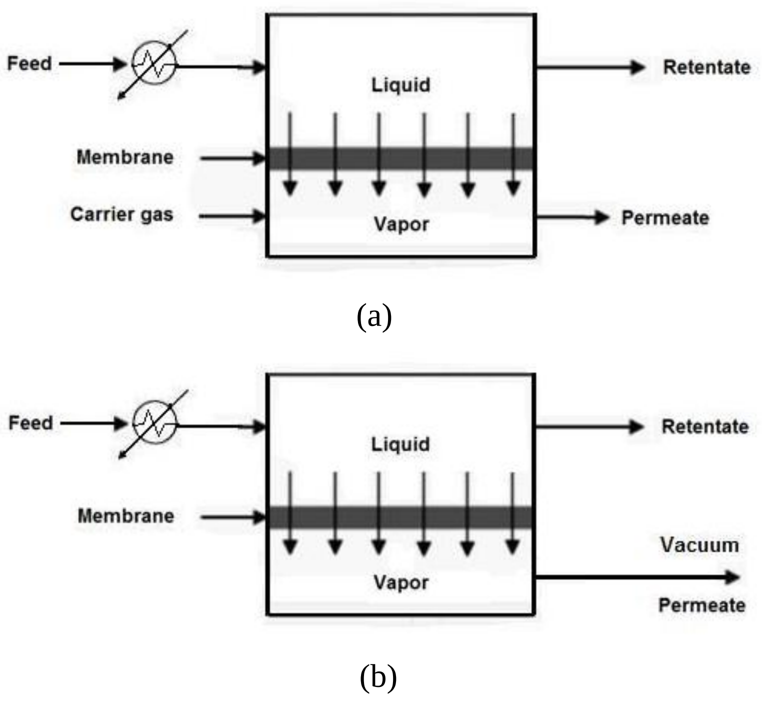

Figure 2.2 Schematic diagram of pervaporation processes [13]
(a) Carrier gas on permeate side and
(b) Vacuum on permeate side

2.3 Vapor Permeation, VP

In principle, vapor permeation is similar to membrane pervaporation. The feed stream is a mixture of vapors. As in pervaporation, the permeate partial pressure is maintained by use of an inert sweep gas or a vacuum [12]. Because the requirements for the membranes are similar to those in pervaporation, membranes currently being employed in vapor permeation are generally the same as those used in pervaporation. Applications of vapor permeation are removal of organics from air streams, dehydration of various organics, pollution treatment, etc. The schematic diagram of the vapor permeation process is shown in Figure 2.3.

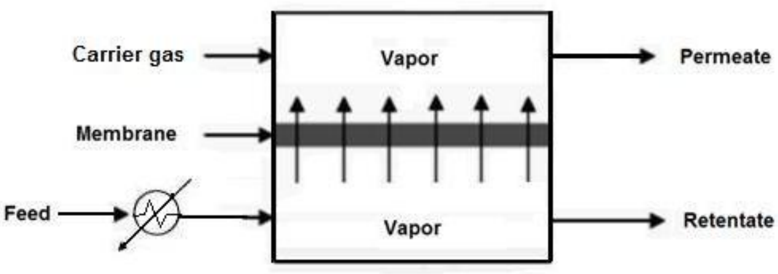

Figure 2.3 Schematic diagram of vapor permeation [13]

2.4 Membrane Performance Evaluation

The membrane performance can be evaluated in the terms of two parameters. They are permeated flux and permeability. The definitions of these parameters are given below.

2.4.1 The permeate flux (*J*)

Permeate flux (J) (mol/ m^2.h) is defined as

$$J = \frac{n}{At} \tag{2.1}$$

where n is the mol of permeate
A is the effective membrane area
t is the time of the experiment

2.4.2 The permeability (*P*) for PV

Permeability of component i (P_i) (mol.m/ m^2.h.kPa) is defined as

$$P_i = \frac{J_i \ l}{(x_i^F \gamma_i P_i^{sat} - \ y_i^P P^P)} \tag{2.2}$$

where	J_i	is the permeate flux of component *i*
	l	is the membrane thickness
	x_i^F	is the mole fraction of component *i* in feed
	γ_i	is the activity coefficient of component *i* in feed
	P_i^{sat}	is the vapor pressure of component *i* in feed
	y_i^P	is the mole fraction of component *i* in permeate
	P^P	is the permeate total pressure

2.4.3 The permeability (*P*) for VP

Permeability of component i (P_i) (mol.m/m^2.h.kPa) is defined as

$$P_i = \frac{J_i \ l}{(P_i^F - P_i^P)} \tag{2.3}$$

where	J_i	is the permeate flux of component *i*
	l	is the membrane thickness
	$P_i^{\ F}$	is the partial pressure of component *i* in feed
	$P_i^{\ P}$	is the partial pressure of component *i* in permeate

The activity coefficients of each compound in the mixture are determined with the Non-Random Two Liquid model (NRTL). The pure component vapor pressures are calculated with the Antoine-equation.

2.5 Mechanism of Mass Transfer through the Membrane

The separation mechanism in surface flow membrane is shown in Figure 2.4. The mechanism of mass transfer through the membrane consists of 3 steps [13] as follows:

2.5.1 Adsorption on the membrane surface

The adsorption step on the membrane surface is dependent on the membrane surface chemistry.

2.5.1.1 Hydrophilic membrane
Adsorption of compounds on the membrane can be Dipole – dipole interaction or hydrogen bonding between membrane and compounds. Compound that can hydrogen bonding with the hydrophilic membrane and/ or molecules with higher dipole moment will be adsorption on the membrane are better.

2.5.1.2 Hydrophobic membrane
Adsorption of compounds on the membrane was determined by intermolecular between non-polar forces. (dispersion or non-polar forces such as van der Waal force)

2.5.2 Diffusion through the membrane

Diffusion of compounds through the membrane depends on size and shape of molecules. Mostly, smaller substances can be diffusion faster.

2.5.3 Desorption on the permeate

Desorption or evaporation on the permeate side of the membrane in the vapor phase.

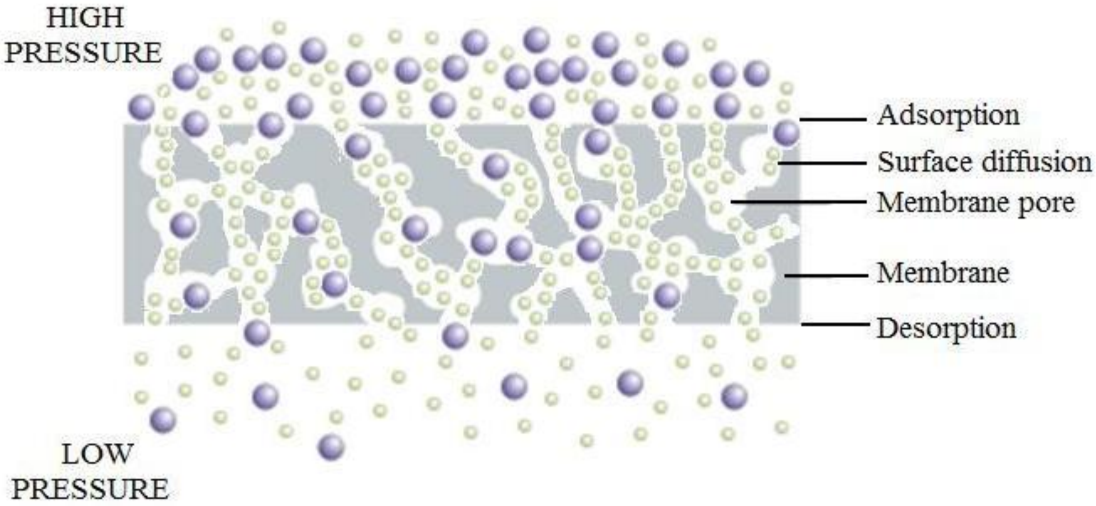

Figure 2.4 The separation mechanism in carbon membrane

The mechanism of mass transfer through inorganic membranes follows the adsorption-diffusion model. Adsorption on the membrane surface depend on molecules adsorb onto membrane surface because of intermolecular attractive forces between the adsorbent and adsorbate. The adsorption and diffusion depend on properties of penetrants and nature of the membrane [5, 14]. Previous research reported that the surface chemistry of carbon membrane possessed hydrophilic character. Jones and Koros [15] found that the micropores of carbon membranes would gradually plugged with water at room temperature, resulting in the decrease of the non-polar gases permeabities. The reason was the surface of membrane carbonized at relatively low temperature was affected by oxygen remaining in the inert purge gas during pyrolysis [16]. The surface was partially covered with oxygen-containing functional groups, thus making membrane be hydrophilic [17].

For alcohol vapor adsorption on inorganic membranes such as silicalite-1, A-type and mordenite zeolites, coverage near saturation are typically reached at pressures well below the saturated vapor pressures, p^{sat}. Saturation coverage, which is the maximum number of molecules adsorbed into the pore volume, is not expected to depend on temperature if the membrane structure, and thus the total pore volume, does not change with temperature. Instead, saturation coverage is only expected to depend on molecular size. For feed mixtures, the total coverage at the feed side is high, but the species competitively adsorb. The coverage decreases through the membrane and is low on the permeate side during steady-state permeation [14].

The amount of molecule coverage is related to heats of adsorption. All other properties being equal, heats of adsorption are higher for molecules with larger dipole moments [14]. Furthermore, dispersion forces increase with size or molecular weight of a molecule, but decrease as the amount of branching increases because branching decreases the contact surface area. For this reason, heats of adsorption increase with increasing molecular weight if the molecules are otherwise similar.

Chana P. [10] studied separation of methanol/water and propanol/water by pervaporation using carbon molecular sieve membranes. Varaporn K. [11] studied the synthesis of carbon molecular sieve membranes for ethanol dehydration. They found these membranes could be used to separate such mixtures. Using the membrane synthesized, experiments with a single-component feed demonstrated that the molecular diameter of the penetrating species played an important role in the permeation through the membrane. A comparison between water/alcohol selectivity of bi-component was higher than that of single-component feeds, indicating that the separation mechanism involved more than molecular sieving alone. It was possible that pore blocking by water had a considerable impact on the separation mechanism. Therefore, it is interesting to explore the factors that may affect the permeation of molecules through carbon membrane. As mentioned earlier that the permeation mechanism involved adsorption-diffusion, which was dependence on dipole moment and size parameters. In this work, the factors that were studied included feed composition, size parameters and dipole moment. The properties of organic compounds used in this work are shown in table 2.1.

Table 2.1 Properties of organic compounds. [14, 18]

Organic Compounds	Molecular Structure	Molecular diameter (Å)	Dipole moment (Debye)	P^{sat} (kPa)
Methanol	CH_3OH	3.80	1.70	68.34
Ethanol	C_2H_5OH	4.30	1.69	37.42
Acetone	C_3H_6O	4.69	2.98	97.25
Isopropanol	C_3H_8O	4.70	1.58	30.68

2.6 The effects of Operating Parameters [13]

2.6.1 The effect of feed concentration

The feed concentration affect permeate flux. If concentration increases, adsorption onto the membrane surface tends to increase, leading to a higher flux.

2.6.2 The effect of operating temperature

The operating temperature affects mass transfer through membrane. Because of this effect is the increase in mass transfer coefficient with increase temperature. In addition, increase solubility in the membrane and the polymer chains can move more. These have affected the diffusion through the membrane. Thus permeate flux increase with increase operating temperature but separation factor decreasing.

2.6.3 The effect of operating pressure

The most important effect of operating pressure is the increase in permeate flux associated with decreasing permeate pressure. The reason for this effect is that the decreasing permeate pressure increases the driving force for mass transfer. The separation factor may increase or decrease upon the increase in the permeate pressure, depending on the volatility of component. In most cases, the separation factor decreases with an increase in permeate pressure.

2.7 Kapton® Polyimide

Polyimide is a polymer that can be used at temperatures higher than 300 °C. Polyimide is not melted at high temperature, but it will change shape and degrade before the melting point. Polyimide is therefore a good precursor for the preparation of carbon membranes [20]. General properties of polyimide are hardness, high melting point and high glass transition temperature. It is also a polymer with high stability. In general, polyimide is synthesized from dianhydride and amine. A popular commercial polyimide is Kapton® polyimide. Structural formula of polyimide and Kapton® polyimide is shown in Figure 2.5.

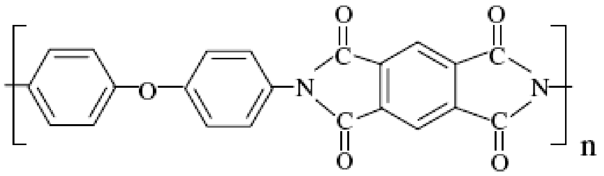

Figure 2.5 Structural formula of Kapton® polyimide [5]

2.8 Pyrolysis Process

Pyrolysis process (sometimes called carbonization) is preparation of carbon membranes by heating the carbon precursor under vacuum or inert atmosphere for a long time [4, 5 and 7]. This process produces a porous carbon fiber that results in products with microporosity. The microporosity is a property of the carbon molecular sieve. The porosity of carbon membrane relates to the separation ability. Normally, the pores sizes of carbon membranes are non-homogeneous. In general, a carbon membrane consists of small pores, varying in size, shape and continuity of pores (degree of connectivity). This depends on the nature of precursor and condition of pyrolysis process. Factors affecting the pores size in the pyrolysis process are temperature, heating rate, heating time, atmosphere in a pyrolysis, inert gas used, gas flow rate and operating process pressure. Structure and pyrolysis process of Kapton® polyimide is shown in figure 2.6.

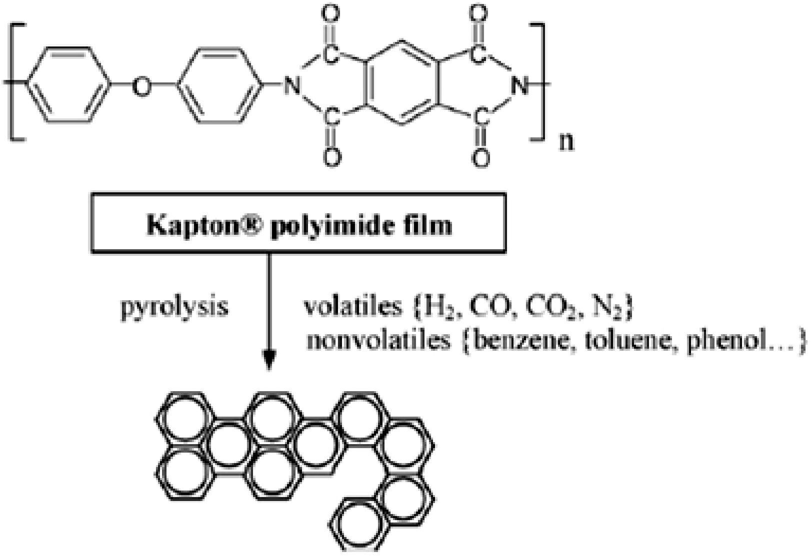

Figure 2.6 Structure and pyrolysis process of Kapton® polyimide [7]

2.9 Literature Review

Sommer and Melin [1] evaluated performance of microporous inorganic membranes in the dehydration of industrial solvents. The five commercial tubular inorganic membranes were used for 30 dehydration applications. These separations include alcohols, glycols, carboxylic acids, esters, etc. They found that the membranes showed different selectivity and flux because of their difference in structure and adsorption characteristics. They reported that the dominant separation mechanisms were selective sorption onto the membrane and shape selectivity. The mixture selectivity deviated considerably from the ideal selectivity for all zeolite membranes. This feature is common for microporous membrane in which molecules are significantly interfered by other components present in the pores. In mixtures the mass transfer through the membrane is determined by pronounced coupling effects. In general, water may block the pores of the hydrophilic membranes preventing the permeation of non-polar organics by preferential adsorption. On the other hand, alcohol molecules can also be dragged across the membrane with permeating water. Fluxes of alcohols obtained from single-component permeation were higher than those observed from experiments using the alcohol-water mixtures as feeds. In comparison with fluxes observed from one component permeation experiment, the fluxes of the bigger and more hydrophobic IPA and *n*-butanol obtained from mixture feeds were smaller, accounting for the preferential adsorption of water and a blocking of pores. In addition, each type of alcohols has different in more or less pronounced dragging effect.

Hatori et al. [4] used molecular sieve carbon membranes with nanopore channels for gas separation properties. They reported the control of micropore size distribution in molecular sieve carbon membranes prepared from polyimide. The pore size tends to be smaller at higher temperatures of heat-treatment. The pore size distribution of the molecular sieve carbon membranes was estimated by adsorption of gas molecules at ambient temperatures. The gases used in the study having different minimum dimension were CO_2 (0.30 nm), ethane (0.40 nm), butane (0.43 nm), and isobutane (0.55 nm). The molecular sieve carbon membranes from polyimide were investigated for hydrogen separation properties in pore channels with the diameter comparable to CO_2 or less. They found that the H_2/CO selectivity on permeation was quite high because of the accurate control of the membrane pore channels in sub-nanometer scale. Adsorption and diffusion properties of hydrogen in the very narrow nano-channels were measured by the permeability through the membranes. They reported that the experimental agreement supported the surface diffusion mechanism, adsorption and diffusion in very narrow pore channels even at ambient temperatures.

Suda and Haraya [5] studied the effects of the carbonization temperature of the carbon molecular sieve (CMS) membranes prepared from Kapton® polyimide. The carbonization under several conditions was carried out to observe the effects of heating rate and the atmosphere of the carbonization. Carbonized under vacuum, membranes exhibited the decrease in gas permeability because of the decreasing membrane pore sizes. The change in the heating rate affected the permeation properties to a lesser extent. However, the pyrolysis atmosphere (vacuum or inert pyrolysis) did not appreciably influence the properties within the experimental conditions studied. They found that the increase in carbonization temperature contributed to the decreasing with both of pore size and the limiting pore volume. The gas permeation rate was reduced with the decrease in the heating rate and changing the atmosphere of carbonization from vacuum to argon flow. For almost all the membranes, the permeabilities of the selected gases measured at 373 K and 308 K that were shown in order H_2 > He > CO_2 > O_2 > N_2, which was not exactly with the order of kinetic diameters of gas. The anomalous behavior that H_2, with a larger kinetic diameter, permeated faster than the smaller He was explained to originate in the larger sorptivity of H_2 than that of He. They observed that the sorption-diffusion theory of polymer membrane was acceptably applied to the gas permeation in CMS membranes in an analogous way. The permeation process of gas molecules through a membrane under a pressure difference was explained to consist of three steps: (I) sorption of gas molecules at the membrane surface of a higher pressure side, (II) diffusion of the sorbed gas molecules through the membrane under a pressure gradient, and (III) desorption of gas molecules at the membrane surface of a lower pressure side.

Aik Chong Lua and Jincai Su [6, 7] studied Influence of carbonisation parameters on the transport properties of carbon membranes by statistical analysis. The commercial membrane Kapton® 100 HN polyimide was used in the studied. The effects of the carbonisation atmosphere (Vacuum and inert gas i.e. argon, helium, nitrogen), the final temperature (873-1073 K), the heating rate (4.0 K/min and 0.5 K/min) and the thermal soak time (300 min 120 min) at the final temperature on the permeation rates of He, CO_2, O_2 and N_2 were examined. The results indicated that the carbonisation temperature has the strongest influence on transport properties through the carbon membranes. Both of the carbonisation atmosphere and the thermal soak time have limited effects on the pore sizes of the carbon membranes. However, the heating rate does not have any influence on the development of the membrane structure during the carbonisation process. Various carbonisation atmospheres have different effects on the structural characteristics and transport properties of the resulting carbon membranes. Under the same heating programme, the carbonization under helium would proceed at higher temperatures as compared to those for other atmospheres. Helium atmosphere resulted in the highest BET surface area, total pore volume and micropore volume which decreased when the carbonisation temperature was increased from 873 to 1073 K. Carbonisation under vacuum resulted in the lowest gas permeances.

Sommer and Melin [8] investigated the separation performance of two types of commercial, inorganic membranes. The inorganic membranes separation layers consisted of A-type zeolite and microporous silica. The influence of various operation parameters, such as concentration, temperature, pressure on flux and selectivity are presented and discussed for the dehydration of alcohols and other industrial relevant solvents by pervaporation or vapor permeation. The results indicated that the operating conditions have a large impact on the separation performance of membranes. The influence of the operation parameters on the separation characteristics was successfully described with a transport model, based on the standard solution–diffusion model. They found that the preferential adsorption of water and pore blocking by capillary condensation have a major impact on the separation mechanism in some case such as methanol, where molecular sieving effects are negligible. With a kinetic diameter of 0.36 nm the methanol molecules should be able to diffuse through the 0.41 nm pores of the NaA-zeolite. Nevertheless, with mixture selectivity of about 2000 the methanol content in the permeated is very small. The pure component adsorption selectivity would be only 4. This suggests that the adsorption of alcohol is almost completely inhibited by the presence of water, as this adsorbs strongly in the zeolite and non-zeolite pores of the A-type zeolite membrane and blocks the organic molecules from entering the pores. Vapor permeation, very good results for flux and selectivity can be realized, with the A-type zeolite and the amorphous silica membrane. When operating with a saturated vapor phase on the feed side the driving force is exactly the same as in pervaporation. Thus, fluxes and selectivity of the two modes are comparable. The saturation level of the feed vapor has an important impact on the performance of vapor permeation processes. The separation mechanism of the silica membrane is mainly based on a combination of adsorption and diffusion effects, while the zeolite molecular sieve allows a very sharp separation caused by size exclusion effects.

Okamoto et al. [9] studied the preparation zeolite NaA membrane by a gel with the composition Al_2O_3:SiO_2:Na_2O:H_2O=1:2:2:120 (in moles) and using one-time-only hydrothermal synthesis with a short reaction time of 3 h at 373 K a and porous α-alumina support tubes seeded with zeolite NaA crystals. The results showed that a dense intergrown zeolite crystal layer of about 30 μm in thickness was formed on the outer surface. The zeolite NaA membranes were highly permeable to water vapor but impermeable to every gas unless dried completely. The membranes indicated excellent water permselective performance in pervaporation (PV) and vapor permeation (VP) toward water/organic liquid mixtures. The gas permeance increased with an increase in temperature, and the membrane performance was much better for VP than for PV. For VP at 378 K and 10 wt % of feedwater, permeation flux Q values were 4.5, 3.5, and 7.8 kg/ (m^2 h) and separation factor α values were > 30000, 5700, and > 9000 for the water/ethanol, /methanol and /dioxane systems, respectively. They were proposed a mechanism of PV and VP based on the capillary condensation of water in the zeolitic and nonzeolitic pores and the blocking of other molecules from entering the pores. It is reasonable to consider that a similar mechanism is operative in the PV and VP of water/organic liquid mixtures through the zeolite NaA membranes. The zeolite NaA membranes were highly water-permeable since zeolite NaA is a strong water adsorbent because of its strong hydrophilicity. At 10 wt % of water content in feed the water content in permeate of every organic liquid was higher than

99.9 wt % except for methanol. They suggests that a small scatter in the composition analysis of the permeate leads to a large scatter in permeance. This should be taken into account in discussing some difference in such high values of permeance.

Varaporn [11] studied the synthesis of carbon molecular sieve membrane for ethanol dehydration by pervaporation. This research has been studied performance of membrane synthesized from polyimide. The membrane was prepared by carbonizing Kapton® polyimide at 600 °C. The conditions of carbonization are heating rate 3 °C/min under nitrogen atmosphere. The 95 wt % of ethanol solution was tested dehydration by pervaporation process. The permeate side of the membrane was swept by dry air at the flow rate of 50 ml/min. The results showed that ethanol flux is 1.2 x 10^{-3} kg/m^2.h and the membrane selectivity is 8606. While the single-component are ethanol 99.99 wt % and water has been tested. The results showed that pure ethanol and water fluxes are 0.48 and 0.82 kg/m^2h respectively. Which studied was found that the flux of single-component is higher than bi-component. This behavior may be caused by some mechanisms that occur in the compounds separation of carbon membrane.

Bowen et al. [14] reviewed fundamentals and applications of pervaporation through zeolite membranes. Zeolite membranes have uniform, molecular-sized pores, and they separate molecules based on differences in the molecules adsorption and diffusion properties. Zeolite membranes are thus well suited for separating liquid-phase mixtures by pervaporation. They have reviewed fundamental aspects of separations by pervaporation through zeolite membranes and examples of the selectivities and fluxes obtained are presented. Some aspects of these separations are similar to gas-phase separations using zeolite membranes, but feed-side coverages are close to saturation during pervaporation, making competitive adsorption and molecule–molecule interactions more important during multi-component diffusion. The effects of coverage, competitive adsorption, heats of adsorption, molecular sizes, temperature, membrane structure, non-zeolite pores, concentration polarization, and support resistance on transport and separations. They has determined about the adsorption in zeolites under pervaporation conditions. Adsorption in zeolites is physical adsorption, and is therefore a non-activated, exothermic process that is reversible. Molecules adsorb into zeolite pores because of intermolecular attractive forces between the adsorbent and adsorbate. All other properties being equal, heats of adsorption are higher for molecules with larger dipole moments. Furthermore, dispersion forces increase with size or molecular weight of a molecule, but decrease as the amount of branching increases because branching decreases the contact surface area. For this reason, heats of adsorption increase with increasing molecular weight if the molecules are otherwise similar. Zeolite membranes have additional advantages in separating mixtures with molecular size differences and/or adsorption differences, and high or low pH mixtures, many of which also form azeotropes. Separating mixtures by pervaporation through zeolite membranes depends strongly on competitive adsorption, and also on diffusion differences.

Bettens et al. [20] studied the transport of pure components in pervaporation through a microporous silica membrane. The pervaporation mechanism of pure components through a commercial microporous silica membrane was studied by performing experiments using water, methanol, ethanol, 2-propanol, and *n*-propanol at 40-80 °C temperature range. Experimental fluxes were correlated to feed temperature and viscosity. It was found that the transport mechanism follows the adsorption-diffusion model, which comprises both configurational (micropore) diffusion and surface diffusion. The contribution of convection was negligible. Size parameters such as molecular weight, kinetic diameter, and effective diameter are believed to have an influence on diffusion, yet there is no correlation with flux. This emphasizes the importance of the sorption step in the pervaporation process. The various models presented here are all based on a Fickian analysis of diffusion, and it is assumed that pure components are transported as gaseous species for which the ideal gas law applies. However, Fick's law as well as the ideal gas law may not be valid for multi-component mixtures where coupling effects can occur. The experiment was found a similar correlation between the dielectric constant and the flux. Furthermore, the flux increases in the same direction as the hydrophilicity of the pure components.

Dong et al. [21] studied gas permeation and pervaporation of water/alcohols through the microporous carbon membranes prepared from resorcinol/formaldehyde/quaternary ammonium compounds. They have studied on the formation mechanism for the carbon membranes in the presence of the TMAB and tetrapropylammonium bromide (TPAB). The pore size of the microporous carbon membranes was studied by single gas permeation tests. The carbon membranes were used for dehydration of water/ethanol (EtOH) and water/isopropanol (IPA) mixtures. The effects of the micropore size on the permeation flux and the selectivity to water were investigated. The results showed that pore sizes of the carbon membranes prepared using TMAB and TPAB were estimated to be about 0.4 and 0.5nm based on the molecular size of the gases (H_2, CH_4, CF_4 and i-C_4H_{10}) used in single gas permeations. The TMAB carbon membrane showed a high selectivity to water in the pervaporation of H_2O/EtOH and H_2O/IPA mixtures. The high selectivity to H_2O for the TMAB membrane can be explained by not only the hydrophilic nature of the pore surface but also the molecular sieving effect. The separation factor was decreased with increasing the pervaporation temperature, indicating that the apparent activation energy for the permeation of EtOH through the TMAB membranes is larger than that of H_2O. On the other hand, carbon membrane prepared using TPAB showed the flux of H_2O decreased at high temperature. The kinetic diameters of H_2O and EtOH molecules are about 0.30 and 0.43 nm, respectively. While the pore sizes of the TPAB membranes are estimated to be about 0.5 nm. Thus, EtOH molecules are easy to enter the pores of the TPAB membranes. It seems like that the permeation of EtOH at higher temperature partly blocked the permeation of H_2O molecules. The molecular sieving effect would be less dominant for the permeation of H_2O and EtOH through the 0.5 nm pores of the TPAB membrane.

Previous research has shown that the pore size of carbon membranes synthesized from commercially available Kapton® polyimide was found to be smaller than 1 nm [4, 5, 6 and 7]. The parameters effecting pore size of carbon membrane were the carbonization temperature and heating rate. Carbonization temperature should be in the range 500 - 900 °C, which resulted in the membrane with pore size between 0.30 to 0.55 nm and also low pore size distribution, providing good selectivity. Polyimide was widely used as a carbon membrane precursor, because it can be effectively used to separate gas with different molecular sizes.

In this thesis, pervaporation and vapor permeation of organic compounds having different dipole moment and molecular diameters through carbonized polyimide were studied. The main objective was to observe the relative significance of dipole moment, which affected the adsorption of organic compound on membrane surface and molecular diameter, which affected the diffusion of organic compound through membrane pores.