



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

REFERENCES

2.1 Bioethanol (Gasohol)

Biomass is one of renewable energy that can be produced from either agricultural feedstocks or industrial waste with a very low cost. It can be made from very common crops such as sugar cane, potato, manioc and corn.

Bioethanol has been proposed as an alternative to fossil fuels due to increasing oil prices and growing environmental concerns in recent years. It not only decreases the fuel cost but also increases the efficiency of engine. Biomass for bioethanol production has derived from different sources and the production concepts for bioethanol also depend on feedstocks (Fig 2.1) (Lipnizki *et al.*, 2010). Most ethanol production facilities are located in major corn producing areas, where the feedstock is readily available (Jonathan *et al.*, 2004).

Gasohol is a mixture of gasoline and ethanol. It has higher octane number or antiknock properties than gasoline. Additionally, it burns more slowly, coolly and completely, resulting in reduced emissions of some pollutants. However, it also vaporizes more readily, potentially aggravating ozone pollution in warm weather. Ethanol-based gasohol with higher concentration of ethanol can damage rubber seals and diaphragm (Paixao *et al.*, 2007)

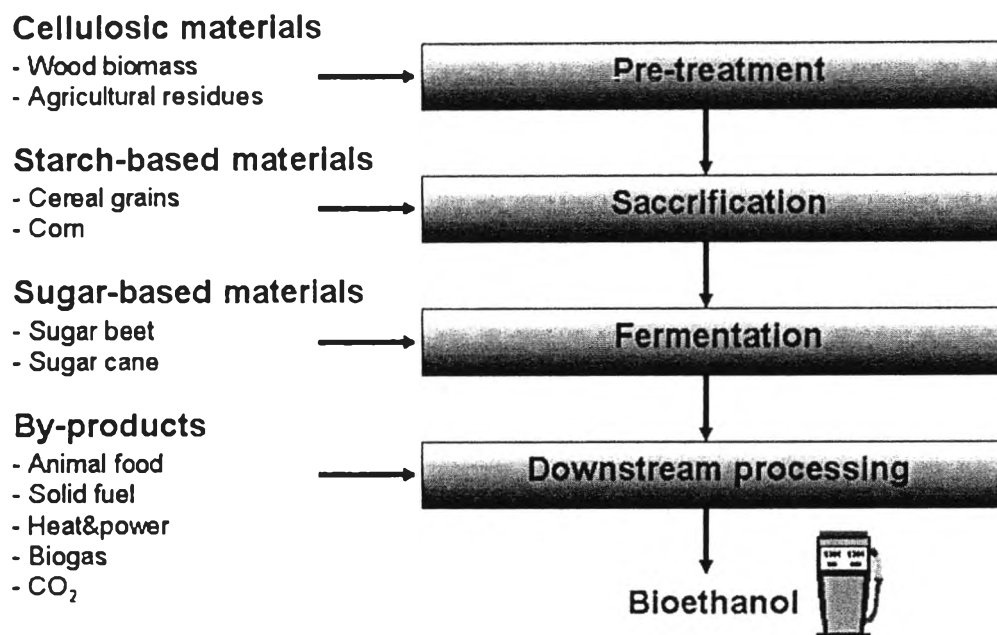


Figure 2.1 The production concepts for bioethanol from different feedstock. (Lipnizki *et al.*, 2010).

2.1.1 Types of Bioethanol

2.1.1.1 *E10*

E10 is a fuel mixture of 10% ethanol and 90% gasoline that can be used in the internal combustion engines of most modern automobiles and light-duty vehicles without need for any modification on the engine or fuel system. E10 blends are typically rated as 2 to 3 octane number higher than regular gasoline and are compatible with all new US automobiles.

2.1.1.2 *E15*

E15 is a fuel mixture of 15% ethanol and 85% gasoline that is the highest ratio of ethanol to gasoline that is possible to be used in vehicles recommended by auto manufacture.

2.1.1.3 *E20 and E25*

E20 is a fuel mixture of 20% ethanol and 80% gasoline while E25 is a fuel mixture of 25% ethanol and 75% gasoline. These blend have been widely used in Brazil

2.1.1.4 E70 and E75

E70 is a fuel mixture of 70% ethanol and 30% gasoline while E75 is a fuel mixture of 75% ethanol and 25% gasoline. These blends are the winter blends that have been used in the United States and Sweden. The seasonal reduction of the ethanol content to a winter blend is to avoid cold starting problem at low temperature.

2.1.1.5 E85

E85 is a fuel mixture of 85% ethanol and 15% gasoline that is generally the highest ethanol fuel mixture found in the United States and several European countries, particularly in Sweden. This mixture has an octane number of about 105, which is lower than pure ethanol but higher than normal gasoline that has an octane number of about 87

2.1.1.6 E95

E95 is a fuel mixture of 95% ethanol and 5% ignition improver that is used in some diesel engines where high compression is used to ignite the fuel, as opposed to the operation of gasoline engines where spark plugs are used. Because of the high ignition temperature of pure ethanol, the addition of ignition improver is necessary for successful diesel engine operation.

2.1.1.7 E100

E100 is pure ethanol fuel. This has been widely use in Brazil. The ethanol used in Brazil is the azeotrope and contain 4% of water.

At the moment, E10 is the most popular type of bioethanol use in Thailand. E20 just has been introduced to the market and the government is trying to promote it by reducing the tax of the car that can use this type of fuel.

The separation of ethanol from dilute aqueous solutions by distillation is unattractive since it requires high energy consumption and an auxiliary agent for purification due to the close boiling point ethanol and water that can form an azeotropic mixture. Other techniques including liquid–liquid extraction, carbon absorption, and air stripping require high operating costs and, have some limitations in some cases, which making these techniques unattractive for industrial applications. Therefore, more efficient ethanol/water separation techniques are preferred in order to reduce the gasohol production cost (Pakkethati *et al.*, 2011).

Pervaporation (PV) is a method for the separation of liquid mixtures by partial vaporization through a non-porous or porous membrane. Polybenzoxazine (PBZ), a newly developed addition cured phenolic system derived from a reaction between various aromatic/aliphatic amines, mono/diphenols, and formaldehyde, is very attractive for use as a pervaporation membrane due to polybenzoxazine provides excellent characteristics such as high heat resistance, flame resistance, good chemical resistance and electrical properties, low absorption of water, low shrinkage upon polymerization, no need of catalyst for polymerization, no by product or volatile generation and excellent molecular design flexibility (Ishida *et al.*, 1996).

2.2 Benzoxazine

Polybenzoxazine is a newly developed type of addition cured phenolic resin that can overcome the short-comings of traditional phenolic resins. Benzoxazine monomers can be derived from the reaction between various aromatic/aliphatic amines, mono/diphenols, and formaldehyde. Then the monomers are polymerized through ring opening of cyclic monomers by heat treatment process without catalyst and without generating any by-product (Fig 2.2). Since the benzoxazine monomers can be synthesized by using a wide variation of raw materials, they offer great molecular design flexibility depending on derived applications. Polybenzoxazines provide good characteristics found in the traditional phenolic resins such as flame retardance and heat resistance. They also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption and good dielectric properties. Thus, polybenzoxazines are an attractive materials for wide applications including a matrix of polymer composites or materials used in electronic packaging (Pakkethati *et al.*, 2011). Nevertheless, polybenzoxazines have some short-comings such as the cured materials are brittle and a relatively high temperature is needed for the ring-opening polymerization and processing into thin films is due to their brittleness (Takeichi *et al.*, 2005).

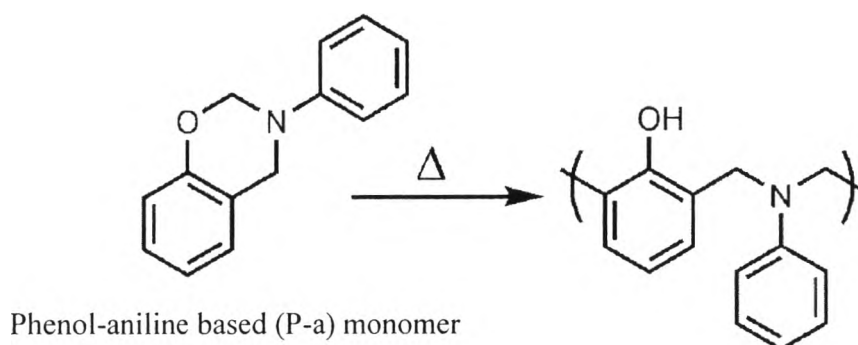


Figure 2.2 Curing reaction of benzoxazine monomer to polybenzoxazine.

Benzoxazines were first synthesized by Cope and Holy in 1940s (Sun *et al.*, 2008), after that the researchers have paid attention in these materials due to their lot of attractive properties such as near-zero volumetric change upon curing, low water absorption, some type of polybenzoxazines have glass transition temperature much higher than curing temperature, high char yield, no strong acid catalysts required for curing, and release of no toxic by-product during curing. The molecular structures of polybenzoxazines have high design flexibility, which allows the properties of the cured materials to be used in a wide range of applications (Men *et al.*, 2007 and Ghosh *et al.*, 2007).

Generally, polybenzoxazine precursors are derive from formaldehyde, mono/diphenols and various type of amine/diamine. One approach to synthesize polybenzoxazine is by using monofunctional amine, phenol, and formaldehyde as reactants yielding low molecular weight monomer prior to polymerization. However, polybenzoxazines obtained via this approach usually suffer from brittleness (Pakkethati *et al.*, 2011). The toughness of polybenzoxazine can improve by the addition of a flexible part into the molecular structure or incorporating a flexible difunctional amine as the central core, for example, switched multifunctionality of the benzoxazines to the amine portion so, the limitations of the bisphenolic linkage can be eliminated. The properties of polybenzoxazines that obtained such as room temperature modulus, glass transition temperature, crosslink density, thermal degradation temperature, and char yield exhibit strong dependence on the amine chain length (Allen and Ishida, 2005).

Another approach is preparation of polybenzoxazine from high molecular weight oligomers from diamine, bisphenol-A, and formaldehyde. The brittleness of these materials has been greatly improved when compared with cured films from the typical low molecular weight monomers. This provides polybenzoxazine to be an excellent candidate for flexible membrane applications (Pakkethati *et al.*, 2011). Tensile measurement of the polybenzoxazine films prepared from aromatic diamine exhibited the highest strength and modulus while polybenzoxazine from longer aliphatic diamine exhibited better elongation at break. Moreover, the glass transition temperature of polybenzoxazines derived from high molecular weight precursors was as high as 238-260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability (Takeichi *et al.*, 2005).

In 1965, Burke *et al.* synthesized Mannich condensation via a solvent process. Firstly, amine was added to formaldehyde at low temperature (10°C) to form an N,N-dihydroxymethylamine derivative product which then reacted with the active hydrogen of the hydroxyl group and ortho-position of the phenol at the higher temperature to form the oxazine ring as shown in Fig 2.3.

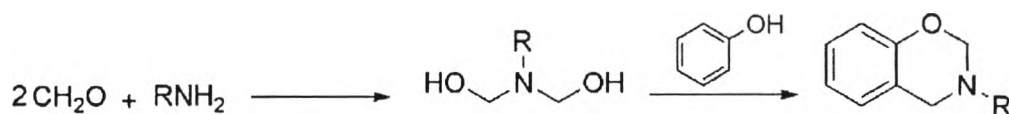


Figure 2.3 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

This synthesis had slow reaction rate, large amount of solvent required and, in some cases, the poor solubility of the precursors was the major disadvantages associated with the solvent synthesis process. The use of an organic solvent also increased the cost of the product and cause environmental problems. Additionally, the solvent residues in the precursors also lead to problems during processing of the benzoxazine resins. To overcome these shortcomings Ishida *et al.* developed a solventless in the melt state method to synthesize the benzoxazine monomers. The main advantages of the solventless method were improvement of reaction times and formation of fewer intermediates and by-products as contaminants (Liu, 1995 and Ishida and Heights, 1996). Various types of benzoxazine monomers can be

synthesized using derivative phenols and amines (aliphatic or aromatic) with different substitution as starting materials in the presence of formaldehydes, by employing solution or solventless methods.

2.3 Cardanol

Cardanol is a decarboxylated derivatives obtained by thermal decomposition of anacardic acids, the main component of cashew nutshell liquid (CNSL). CNSL is a blend of naturally occurring phenol-based monomer and is traditionally obtained as by product during the process of removing the cashew kernel from the nut. The production of CNSL is nearly 25% of the total nut weight. Natural (i.e. cold, solvent extracted) CNSL contains approximately 70% anacardic acid, 18% cardol, and 5% cardanol, with the remainder being made up of other phenols and less polar substances. Anacardic acid, cardanol and cardol consist of mixtures of components having various degrees of unsaturation in the alkyl side-chain. Cardanol obtained from that process includes more than one compound because the composition of the side chain varies in its degree of unsaturation. The major component is tri-unsaturated cardanol (41%) and the remaining cardanol is 34% mono-unsaturated, 22% bi-unsaturated, and 2% saturated. The structure of tri-unsaturated cardanol is shown in Fig 2.4.

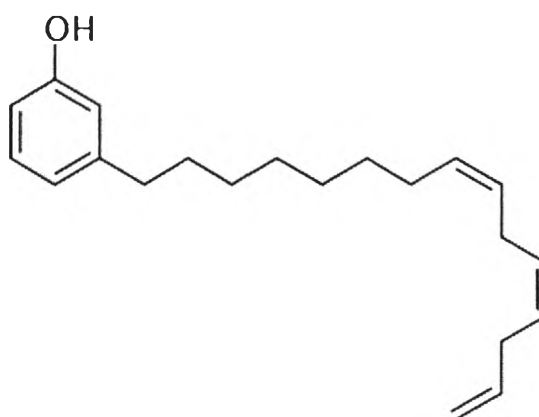


Figure 2.4 Structure of Tri-unsaturated cardanol.

The main producers of cashew nut are in Asia, Africa, and South America. Generally, cardanol can be used in many applications such as friction linings, paints and varnishes, laminating resins, rubber compounding resin, urethane-based polymer, surfactant, epoxy resin, modifier agent of phenol-formaldehyde resin for plywood production, reactant of wood composite production, and intermediate compound in chemical industries.

2.4 Cardanol-based benzoxazine

Novel cardanol based benzoxazine monomer that has an oxazine rings in its structure is attractive since cardanol can be derived from cashew nut shell.

Cardanol based benzoxazine was synthesized by the condensation reaction of various type of amine/diamine and formaldehyde with cardanol. The liquid cardanol based benzoxazine monomer, could be used for making bio-based composites as it can be used alone or as a diluent with other benzoxazine resins. Synthesis of cardanol based benzoxazine monomer and its conversion to polybenzoxazine was shown in Fig 2.5. (Rao and Palanisamy, 2011)

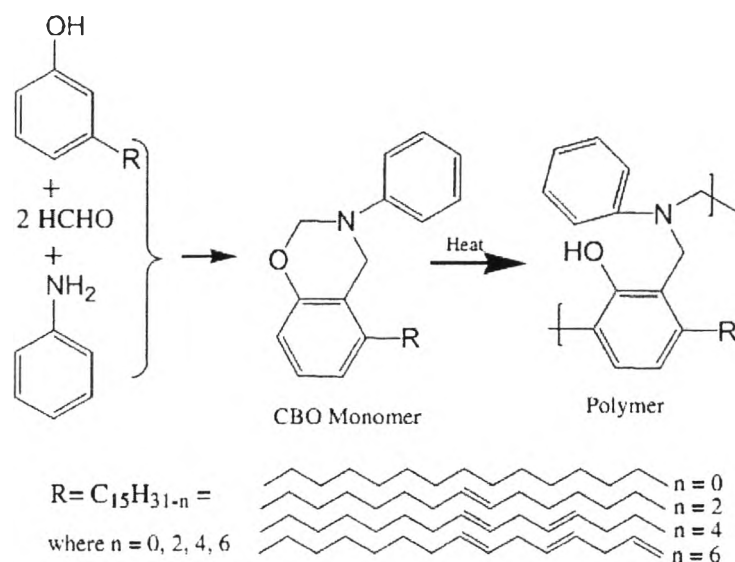


Figure 2.5 Synthesis of cardanol based benzoxazine monomer and its conversion to polybenzoxazine.

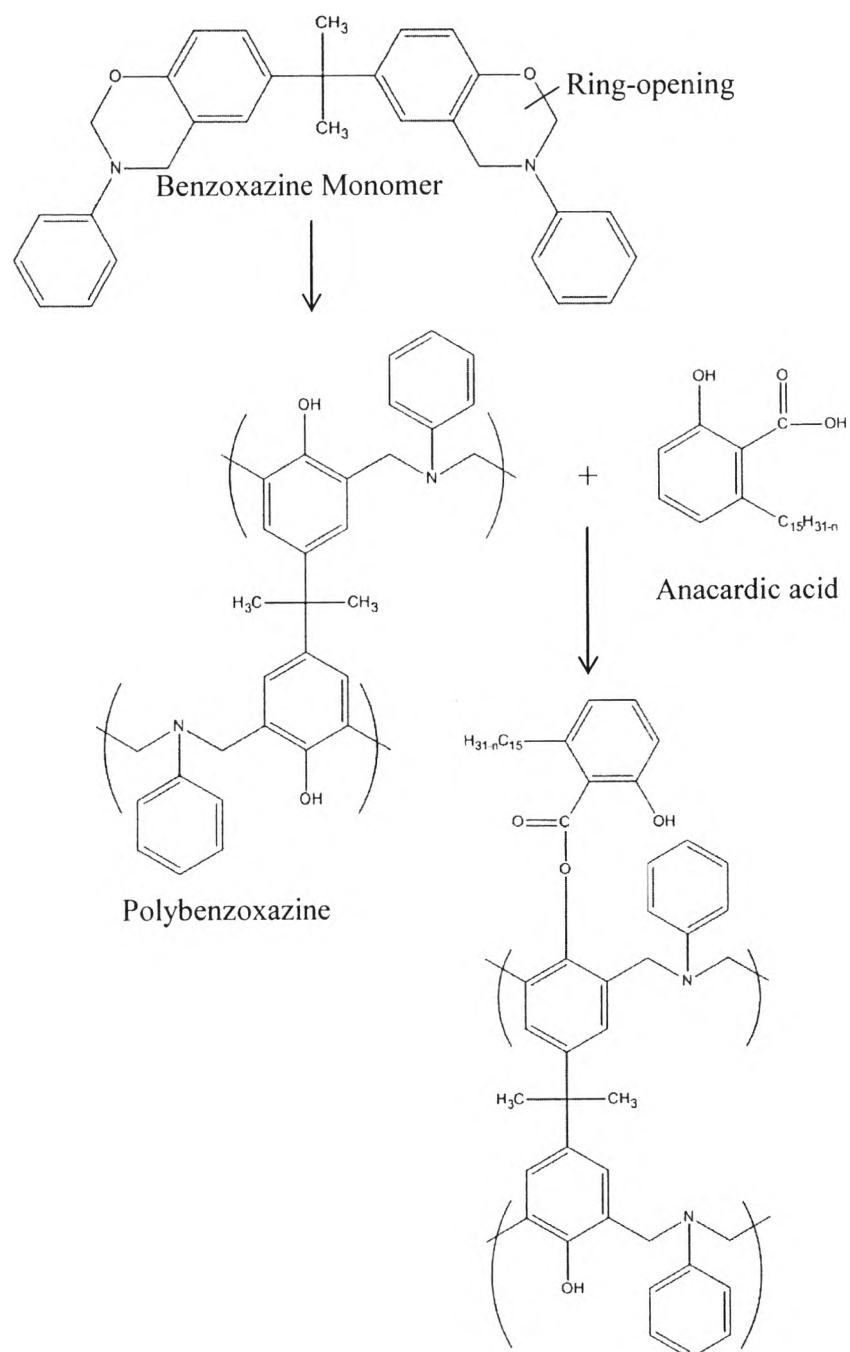


Figure 2.7 A possible reaction between BA-a and CNSL.

2.5 NaA Zeolite Membrane

Zeolites have a rigid, 3-dimensional crystalline structure consisting of a network of interconnected tunnels and cages. Zeolite structure has the uniform pore and channel sizes, allowing the crystal to act as a molecular sieve. There are nearly 50 different types of zeolites (clinoptilolite, chabazite, phillipsite, mordenite, etc.) with varying physical and chemical properties. Generally, zeolite A especially in form of NaA zeolite, an aluminosilicate containing aluminum and silica in the framework which presents a class of highly orders, porous and especially exhibiting uniform and small pore size of 4\AA (0.42 nm) was common used as the membrane for separation of mixture due to its hydrophilicity and making the electrostatic interaction between ionic sites of zeolite and the water molecule stronger (Kuanchertchoo N. *et.a.*, 2006). Because of zeolite adsorption, ion exchange and size selectivity properties, it could be used in many applications such as household product, aquaculture, agriculture, water treatment etc. Moreover, NaA zeolite has higher resistance to a variety of solvent and stability at elevated temperature (Sato *et al.*, 2008). All properties make zeolite different in behavior from polymeric membrane such as water is absorbed in to the pores of zeolite and, due to their opened structure, water molecules diffuse through the membrane rapidly. So, zeolite can be used to separate water from mixture (Ngamlertassamee P. 2010).

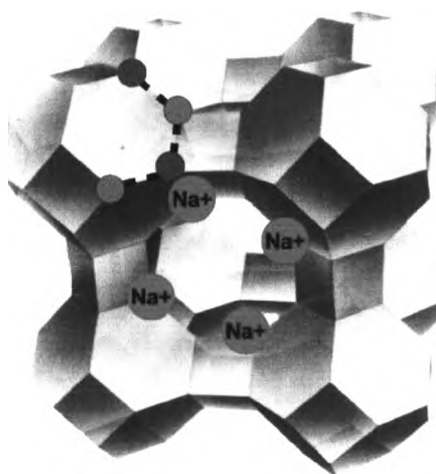


Figure 2.8 Structure of NaA zeolite. (www.safesalt.com.au/zeoliteresearch.html)

In terms of membranes, many researchers have been improve pervaporative membranes for water-alcohol separation including of (1) introducing a hydrophilic polymer on the hydro phobic substrate, (2) incorporating functional groups into a membrane in order to improve the interaction with the permeants. (3) blending a polymer between high flux and one with high selectivity, and (4) adding zeolite to the membrane. It was found that the permeation properties of the membranes obtained by the last methods more effective to enhance the selectivity than the others due to the basic transport mechanism to transport through the polymeric membranes are (1) penetrants sorption, (2) thermal motion of polymeric chains and diffusion jumps of dissolved penetrants, they cannot be changed via the first three methods. Therefore, zeolite-incorporated membranes may offer an alternative to give a high selectivity due to the effects of molecular sieving action, selective adsorption and different in diffusion rates (Guan H.M. *et al.*, 2006)

In 2002, Gallego-Lizon *et al.* studied the performance of the commercially polymeric membranes, microporous silica membranes and NaA zeolite membranes for binary mixture of *t*-butanol and water separation via pervaporation at 60 °C with 10 wt% water in feed. The results showed, when using microporous silica, larger flux were obtained (3.5 kg/m²h), followed by zeolite (1.5 kg/m²h) and finally by polymeric membrane (0.5 kg/m²h). For highest selectivity were obtained using zeolite membranes (16,000), followed by polymeric membranes (3,615), and finally by the microporous silica membranes (144)

In 2006, Kuanchertchoo *et al.* investigated the effect of synthesis parameters on zeolite membranes formation and performance by microwave technique. They found that, synthesis parameters such as seed amount, seeding time and synthesis time, affected the film thickness after synthesis and the separation performance. The higher film thickness, the lower the flux obtained. The higher temperature also caused the impurity phase on the membrane during synthesis, resulting in low separation factor. In the same year, Ahn *et al.* investigated the different of permeation flux and separation factor between hydrophilic zeolite NaA and NaY membrane to separate the water-ethanol mixtures via pervaporation. The results show that, the separation factor and the flux of the NaA zeolite membrane of

10,000 and 500 kg/m²h, respectively, while, the separation factor and the flux of the NaY membrane are 100-200 and 1.5 kg/m²h, respectively.

In 2011, Wee Shin Ling *et al.* studied the synthesis, characterization and pervaporation properties of microwave synthesized zeolite A membrane and they found that the separation performance for the membrane synthesized with seeding was observed to be much better than those synthesized without seeding under the same operating conditions.

2.6 Pervaporation of Ethanol-Water

Pervaporation (PV) is a method for the separation of liquid mixtures by partial vaporization through a non-porous or porous membrane. It is especially attractive alternative separation technique when compared to conventional techniques for the separation of azeotropic, close-boiling, isomeric and heat sensitive liquid mixtures which cannot separate by common distillation processes. Due to the lower temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant boiling azeotropes (Khayet *et al.*, 2008). This technique utilizes the concept of partial vaporization of liquid through a membrane that derived from the two steps of the process. Firstly, the permeation through the membrane and then its evaporation into the vapor phase (Pakkethati *et al.*, 2011). Pervaporation involves the separation of two or more components across a membrane by different rates of diffusion through a membrane and an evaporative phase change comparable to a simple flash step. A concentrate and vapor pressure gradient are used to allow one component to permeate across the membrane. A vacuum applied to the permeate side is coupled with the immediate condensation of the permeated vapors. This continues receiving an increase attention due to it has higher separation efficiency and potential savings in capital and energy consumption. Furthermore, Pervaporation technique is using polymer membranes, so it has good design flexibility to improve the membrane selectivity and permeability. Dehydration of alcohols and other organic solvents is a well-known example of pervaporation process (Guan *et al.*, 2006).

For removal of volatile organic compounds, other separation techniques such as distillation, liquid-liquid extraction, carbon absorption and air stripping are not relevant due to the limitations of feed conditions, large amount of byproducts or high cost of product treatments while pervaporation is not limited by these factors (Ahn *et al.*, 2005). Presently, industrial applications of pervaporation techniques are grouped into two categories, one is dehydration of alcohol and other organic solvents using hydrophilic or charged polymeric membranes and the other is the removal of small quantities of volatile organic compound from water using hydrophobic membranes (Zhang *et al.*, 1992). Pervaporation can be used for breaking azeotropes of mixtures, dehydration of solvents and other volatile organics, organic/organic separations such as ethanol or methanol removal, and wastewater purification.

The steps that pervaporation included are the sorption of the permeate at the interface of the feed and the membrane, diffusion across the membrane due to concentration gradients that is the rate determining steps, and finally desorption into a vapor phase at the permeate side of the membrane. The first two steps are responsible for the permselectivity. Due to material passes through the membrane a swelling effect makes the membrane more permeable, but less selective, until a point of unacceptable selectivity is reached and the membrane must be regenerated. The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing a partial pressure gradient is to sweep an inert gas over the permeate side of the membrane. These methods are described as vacuum and sweep gas pervaporation respectively.

The typical pervaporation system is shown in Fig 2.9. The feed is allowed to flow only one side of the membrane and a fraction of the feed passes through the membrane and leaves in the vapor phase on the opposite side of the membrane. The permeate side of the membrane is kept under a vacuum or purged with a stream of inert carrier gas. Permeate is finally collected in the liquid state after condensation. The liquid product is rich in the more rapidly permeating component of feed mixture. The retentate is made up of the feed materials that cannot pass through the membrane.

For polymeric pervaporation membranes, extensive researches were performed to find an optimized membrane material having selective interaction with a specific component of feed mixture to maximize the separation factor, permeation flux and the membrane stability. Polymer membranes can demonstrate the selectivity based on the solubility and diffusion constant (Atra *et al.*, 1999). Hence, the type of the membrane is very important since the efficiency of pervaporation depends enormously on the membrane used. Any formation of the liquid permeate film in the pores would inhibit the driving force. For example the hydroxyl group is considered to interact with water through hydrogen bonding membrane containing such a hydroxyl group may be able to permeate water with high separation factor. A trade-off normally exists between the flux and the separation factor. Consequently, membranes are much developed to yield good permeation fluxes and high separation factors simultaneously (Wijmans, 2003).

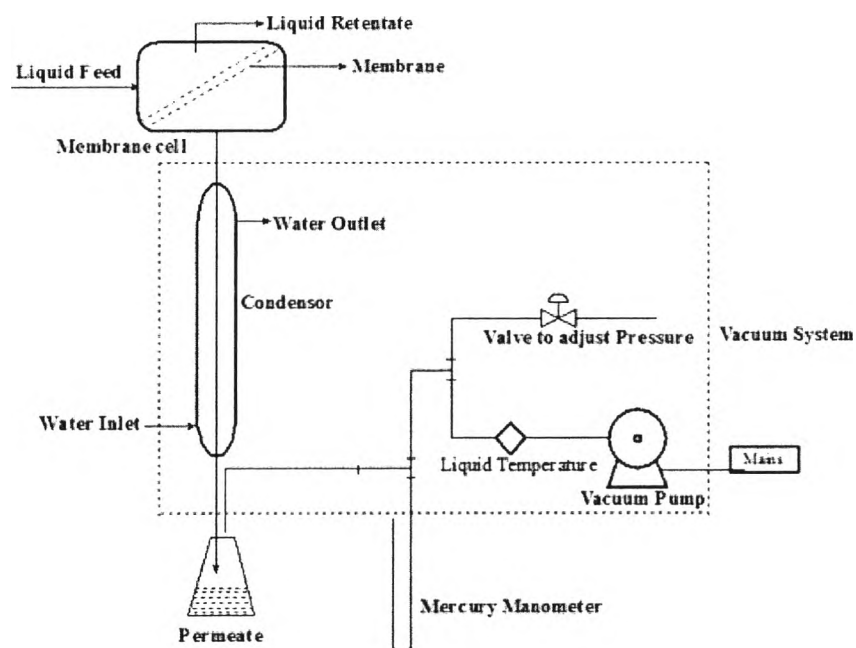


Figure 2.9 Simplified Pervaporation Process.

Nevertheless, the performances of the membranes are strongly depended on process conditions such as feed concentration and temperature (Verkerk *et al.*, 2001).

In general silicone containing polymers were found to exhibit good organophilicity. Silicone rubber base membranes, mainly polydimethylsiloxane, were investigated for separation of organic aqueous mixtures such as alcohols, ketones, phenols and chlorohydrocarbones. Permeation of molecule through a dense non-porous polymer matrix is generally governed by the sorption and diffusion mechanism. Relative sorption of permeants in membrane depends on their relative solubility in the membrane. Extents of solubility or miscibility of component in or with polymeric membranes can be explained by the solubility parameter theory. Solubility parameter was defined by Hildebrand and Scott using “cohesive energy density” which is a measure of cohesive force that holds molecules together in liquid phase (Mandal and Pangarka, 2002).

Alcohol/water separation is a well-known example of pervaporation process in chemical industry. Separation of alcohol/water mixtures by pervaporation is important for obtaining liquid used as fuel from biomass sources. Many researchers reported pervaporation process principles and experimental results using different types of hydrophobic membranes. From the previous research, the results show both mixtures, increasing alcohol concentration increases permeation fluxes of both alcohols and water, however, water flux increases more significantly than alcohol flux resulting in a separation factor reduction. This can be due to the fact that increasing alcohol concentration increases membrane-free volume and simultaneously side chain mobility increases. Effect of temperature on pervaporation of methanol/water and ethanol/water mixture through PDMS membrane showed that total permeation flux of ethanol/water mixture was slightly higher than that of methanol/water mixture and the separation factor of ethanol was less than that of methanol because of their different molecular sizes and also solubility parameter (Tsai *et al.*, 2008).

Pakkethati and coworker synthesized polybenzoxazine from bisphenol-A, formaldehyde, and three different types of diamines: hexamethylene-diamine (hda), tetraethylenepentamine (tepa), and tetraethylenetriamine (teta) via a facile “quasi-solventless” method. To study the possibility of using polybenzoxazine membranes in a pervaporation system for ethanol-water separation, the sorption and swelling behaviors of these membranes were investigated. They found that, when

hda was used as a reactant, the resulting polybenzoxazine membranes showed the best service time and interestingly only water permeated the membranes under the studied operation conditions. The total permeation flux was found to be 1.52 kg/m²h and the separation factor was higher than 10,000. Additionally, an increased permeation flux was achieved by raising the temperature of the feed solution and decreasing the membrane thickness. The optimum conditions for this study were 70 °C for the feed mixtures when a membrane with 200 µm thickness was used (Pakkethati *et al.*, 2011).

Pervaporation Analysis

The permeation flux of water (kg/m²hr) and the separation factor of the ethanol/water mixture were determined by using the quantities of ethanol and water obtained from GC, as follows;

2.5.1 Permeation flux of water (J, kg/m²hr)

The J can be calculate from equation 2.1

$$J = M/At \quad (2.1)$$

Where M = Permeate weight
A = Effective membrane surface area (m²)
t = Pervaporation time (hr)

2.5.2 Seperation factor ($\alpha_{\text{water/ethanol}}$)

The $\alpha_{\text{water/ethanol}}$ was calculated from equation 2.2

$$\alpha_{\text{water/ethanol}} = (Y_{\text{water}}/Y_{\text{ethanol}})/(X_{\text{water}}/X_{\text{ethanol}}) \quad (2.2)$$

Where Y_{water} = the weight fraction of water in the permeate side
 Y_{ethanol} = the weight fraction of ethanol in the permeate side
 X_{water} = the weight fraction of water in the feed
 X_{ethanol} = the weight fraction of ethanol in the feed