CHAPTER II
THEORETICAL AND LITERATURE SURVEY

2.1 Introduction to Sodium A Zeolite (NaA) Powder and Membrane

Sodium A (NaA) zeolite or called zeolite A, an aluminosilicate framework, was synthesized from silica (silicon compound) and alumina (aluminum compound) under conventional heating. It has small pore size of 0.4 nm and uniform microporous structure. NaA zeolite membrane can be made by coating the NaA zeolite on the surface of support, such as alumina support. It has been used worldwide since it has good thermal stability, high mechanical strength, and high resistance to relatively extreme chemical environments (Bein *et al.*, 1996; Jansen *et al.*, 1998).

NaA zeolite (zeolite A) membrane was used as a membrane for water dehydration due to the pore size of the NaA zeolite close to the kinetic size of water molecule (around 0.32 nm) in comparison with alcohol, especially ethanol having its kinetic size around 0.446 nm. Moreover, NaA zeolite, unlike other zeolites, has hydrophilic property which absorbs the water molecules better than alcohols.

2.2 Pervaporation System

Pervaporation system is the technique for separating a liquid mixture (2 mixtures or more) by partially vaporizing through membrane. The membrane acts as selective barrier between two phases, liquid phase feed and vapor phase permeate.

The performance of NaA zeolite membrane is evaluated in terms of total water flux ($kg/m^2/h$) and separation factor (dimension less)

Total water flux (J) is expressed as:

$$J = W/[A*t] \qquad (I)$$

where W is the water permeate (kg), A is the membrane area (m^2), and t is the time (h). In this work, the total water flux was determined when the time was varied in the recycle-continuous pervaporation testing. A high total water flux means that more water molecules pass through the membrane to the permeate side, indicative of good performance of the membrane.

Separation factor (α) is expressed as:

$$\alpha = [X_{H2O}/X_{EtOH}]_{perm} / [X_{H2O}/X_{EtOH}]_{reten} \qquad \text{(II)}$$

where X_{EtOH} and X_{H2O} are the molar fractions of ethanol and water, respectively. The subscripts of "perm" and "reten" represent permeate and retentate sides, respectively. A high α indicates good separation of water from the water–ethanol mixture, implying that a very small amount or none of the ethanol passed through the membrane to the permeate side.

2.3 Literature Review

NaA zeolite membrane can be synthesized via conventional heating or autoclave techniques, using silica and alumina as silicon and aluminum sources. Kita *et al.* (1995) synthesized NaA zeolite on the cylindrical alumina support and showed a total water flux of 1.10–2.15 kg/m^2/h with a separation factor of higher than 10,000 at 323–348 K. Huang *et al.* (2007) reported the preparation of NaA zeolite membrane using vacuum seeding (seeding technique) or secondary growth to improve the orientation of the zeolite membrane on the support and the conventional heating technique. They produced a total water flux of 1.67 kg/m^2/h with a separation factor higher than 10,000 for the water-ethanol separation at 343K.

Microwave technique, providing homogeneous heating, is used to reduce synthesis time for synthesizing NaA zeolite membrane (Mirskii *et al.*, 1970). Li *et al.* (2006) synthesized a NaA zeolite membrane on a tubular alumina support using the microwave synthesis technique without seeding, and studied the pervaporation of water-ethanol. They obtained a total water flux of around 0.51–0.64 kg/m^2/h with a separation factor of higher than 10,000 at 338–343 K. Kuanchertchoo *et al.* (2006, 2007) synthesized the tubular NaA zeolite membranes by the microwave technique and showed higher the total water flux of 0.5–1.5 kg/m^2/h with moderate performance in the separation factor of 6,532 at 343K.

Electrophoresis is also an effective technique for an oriented and continuous layer of zeolite seed on the support to act as nuclei for the crystal growth step, thus, highly oriented NaA zeolite membranes were prepared on α-Al_2O_3 support, as reported by Huang *et al.* (2000), who also showed moderate performance in the separation of a water-isopropanol mixture with a separation factor of 3281 at 343K, while the total water flux was 1.24 $kg/m^2/h$.

There are many parameters that affect the efficiency of NaA zeolite membranes. Ahn *et al.* (2006) showed that the total water flux increased with the system temperature. Bhattacharya *et al.* (1997) showed that the total water flux of system increased with the feed flow rate. Xu *et al.* (2004) showed that the well inter-grown zeolite membrane provided a good performance of membrane in pervaporation system, and the thickness of membrane always affected to the performance of NaA zeolite membrane.

The stability of the NaA zeolite membranes is the most important factor in the pervaporation of water-ethanol mixture to produce high purity of ethanol (higher than 99.5% by volume). Ahn *et al.* (2006) showed the stability of NaA zeolite membrane used in pervaporation system for water-ethanol separation as a function of time, and found a good stability within 1 week in terms of the total water flux ($kg/m^2/h$) and the separation factor (dimensionless).

In term of techno-economic analysis of the NaA zeolite membrane in comparison with different processes used to produce high purity alcohol, Van Hoof *et al.* (2004) used the Aspen Plus version 11.1 and PV to design calculation program (RWTH Aachen) to obtain the economic data on the distillation and pervaporation processes, respectively. They compared between azeotropic distillation and hybrid systems of distillation-pervaporation, and distillation-pervaporation-distillation of polymer and ceramic membranes. Theresults showed that the hybrid system of the distillation-pervaporation with ceramic membranes provided a decrease of the total costs and energy with no need to use entrainers in the system, resulting in the environmentally friendly process.