CHAPTER III

LITERATURE REVIEWS

3.1 Purification process of Ethanol/Water mixture for SOFC system

The distillation column was incorporated into the SOFC system designed by Jamsak et al. (2007) to purify ethanol from dilute bioethanol solution in order to obtain an appropriate composition for SOFC fuel feed. The bioethanol feed at 5mol% was introduced to the distillation column before feeding into a reformer and SOFC stack, respectively. The later two units were assumed to operate under isothermal condition. In this work, the ethanol concentration of 25 mol% was considered as a suitable concentration for ethanol steam reforming reaction producing high hydrogen rich gases. Thermodynamic assessment of the system was investigated, especially focusing on distillation energy consumption. The simulations were conducted under self-sustained energy operation condition (Q_{net}=0) to perform overall electrical efficiency and other essential results. Adjusting SOFC system configurations such as operating voltage and fuel utilization could obtain no external energy demand for the operating condition. For a distillation column, the ethanol recovery at 80% could offer an optimal electrical efficiency under Q_{net}=0. Nonetheless, the designed SOFC system at that condition gained somewhat low performance (0.32 W/cm^2, 173.07 kW, overall electrical efficiency is 33.3% at U_f = 80%, R_{EtOH} = 80% and C_{EtOH} = 41%) owing to high reboiler heat duty consumption. Furthermore, a large amount of heat in a condenser was not recovered. Therefore, it was necessary to have some methods to improve the performance of SOFC-Distillation system.

Afterwards, Jamsak et al. (2009) studied the use of a heat exchanger network for improving the performance of SOFC system integrated with the distillation column. The system utilized exothermic heat from a condenser and hot water from the bottom line of distillation column including cathode recirculation from the cathode outlet stream to supply the energy demanding units. The MER (maximum energy recovery) network was designed to avoid the pinch problem related to the air inlet temperature. The results were found that by eliminating the high temperature distillate heat exchanger, the total cost index could be reduced. The performance obtained from this modified SOFC system gave the overall electrical efficiency of 40.8%, 54.3% Combined Heat and Power (CHP) efficiency, respectively, as well as 0.221 W/cm^2 for power density.

After discovering the faults when using a distillation column, a low-energy pervaporation was proposed instead of the previous purification unit for bioethanol-fuelled SOFC system to improve the performance as investigated by Choedkiatsakul et al. (2011). This study presented significantly an improvement of SOFC system performance by comparing with two different purification units. At the based case (Q_{net}=0, R_{EtOH} = 80%, Operating voltage = 0.7V, T_{SOFC} = 1073 K), the results showed that the overall electrical efficiency obtained from using the pervaporation offered 42% compared to 34% of distillation column integrated with the system. However, the results indicated that the ethanol separation factor at high values were required when a pervaporation was operated at high ethanol recovery to achieve its high performance. Therefore, it should be concerned on the availability of the pervaporation membrane materials in a later study.

3.2 Pervaporation for Ethanol/Water separation

Among the various separation technologies, membrane-based pervaporation is an interesting alternative because of its high separation efficiency with low energy consumption. Kumar et al. (2010) showed the energy requirements of purification processes i.e. Distillation processes (Azeotropic, Low pressure, Extractive distillation), Solvent extraction and pervaporation for producing anhydrous ethanol. It was found that pervaporation was regarded as being the lowest energy consumption unit compared to the other processes. Pervaporation membrane materials consist of hydrophobic and hydrophilic types. Normally, the component which has smallest amount in the mixture should be permeated across the membrane due to energy saving. Thus, a selection of an appropriate membrane type depends on the property of that component between polar and non-polar. For improving pervaporation membranes, the critical issues to be concerned are: membrane productivity, membrane selectivity and membrane stability (Feng and Huang, 1997). Former research mostly studied the development of membrane materials for dehydration of ethanol/water system more than ethanol removal from aqueous solution. Due to the growing of research interest in application of biotechnology i.e. removal of ethanol from fermentation broths, developing of membrane materials for dilute ethanol removal has increased gradually. Generally, hydrophobic membranes for ethanol removal are constructed with silicone rubber or polydimethylsiloxane (PDMS). There are several research which study the modified PDMS membrane performance with different nanocomposites. Huang et al. (2009) developed pervaporation membrane for ethanol removal by incorporating polyphosphazene nanotube (PZSNTs) into polydimethylsiloxane (PDMS) to form nanocomposite membranes. SEM showed that PZSNTs were well dispersed in PDMS. The results exhibited higher separation factor than PDMS membranes. From these experiments, as PZSNT content increased from 0% to 10%, the permeation flux and separation factor increased. After this range, both parameters were kept rather unchanged. A decrease of PZSNT diameter leads to an increase in both permeation flux and separation factor. In this study, it was found that by using PZSNT which was adjusted to longest and smallest diameter of nanotube (50 μm and 40 nm) loading at 6 wt% on PDMS could give the maximum separation factor value of 10 compared to 5 (10 wt% ethanol feed at 313 K) from PDMS alone.

High-silica ZSM-5 zeolites (HiSiZ) were filled into PDMS polymers to form mixed matrix membranes by Vane et al. (2008). Several parameters including siloxane chain length, crosslinking agent concentration, density of reactive groups, catalyst level, zeolite type and loading, solvent type, mixing method, and size of a porous support membrane (UF and MF) were studied to assess the effect on pervaporation performance. According to this study, there were three parameters having a significant membrane performance: uniform zeolite particle dispersion, high zeolite loading, zeolite particle size (particularly as it is related to particle agglomeration). It was indicated that the membranes prepared with PDMS system based on DMS-V41/HMS-064 with hydride to vinyl equivalent ratio of 1.34 in case of varying zeolite loadings ranging from 0 to 65wt% had an interesting result. Ethanol-water separation factor increased steadily with zeolite loading from 8.7 at 0wt% to 43.1 at 65 wt% zeolite (5wt% ethanol feed, 323 K, permeate pressure 400-500 Pa).

Lin et al. (2003) investigated the preparation of silicalite membrane which involved in membrane separation properties. Silicalite membrane was synthesized by *in situ* crystallization to obtain highly selective silicalite membrane on porous tubular supports. The properties of membrane separation were varied by changing the preparation conditions: seeding, support types, silica sources and temperature. The results reported that the silicalite membranes gave a higher separation selectivity using colloidal silica. The highest ethanol separation factor from this experiment was 106 and flux of 0.9 kg/m^{2}h for 5 wt% ethanol feed at 333 K.

Claes et al. (2010) successfully applied Silica-filled poly(1-trimethylsilyl-1-propyne) (PTMSP) layers on the top of ultrafiltration support membranes and used in the pervaporation of ethanol/water mixtures. From the experiments, Reduction of the thickness of the separating PTMSP top layer and addition of hydrophobic silica particles resulted in a clear flux increase as compared to dense PTMSP membranes. The values of ethanol/water separation factors up to 12 were obtained and fluxes up to 3.5 kg/m^{2}h for 10 wt% ethanol at 323 K. In addition, the supported PTMSP-silica nanohybrid membranes prepared in this work performed even better than the best commercially available organophilic pervaporation membranes in terms of ethanol selectivity and flux. Characteristics of a polyvinylidene fluoride (PVDF) and a polyacrylonitrile (PAN) support membrane disclosed a more open structure for PVDF membrane and showed more hydrophobic surface. From the study, it was suggested that by using a PVDF support, the permeate fluxes can be increased by 30% compared to the PAN supported membranes. Because of their promising flux-selectivity combination, the prepared composite of PTMSP-silica membranes exhibited a great potential in the removal of alcohols from aqueous mixtures and give a new perspective on the removal of alcohols from aqueous streams, and could serve as an alternative for the commercial organic pervaporation membranes.

Pervaporation for product recovery from biomass fermentation processes was reviewed by Vane (2005). The literature stated that the separation factors of PDMS, PTMSP, composite membranes and zeolite are in the range of 4.4-10.8, 9-26, 7-59, 12-106, respectively. However, some research reported that the ethanol/water separation factors could exceed these ranges. For example, Nomura et al. (2002) used silicate zeolite membrane for ethanol removal from the fermentation broth of 20wt% ethanol. The obtained ethanol concentration was 98.2 wt% at the permeate side. The separation factor of ethanol over water is equal to 218 at 303 K. This high ethanol selectivity was due to the salt effect in fermentation broth. Separation technologies for biorefinery were reviewed by Huang et al. (2008). In the section of hydrophobic membrane for ethanol removal, they concluded that the ethanol/water separation factors are ranked in the following order: PDMS< PTMSP < composite membranes < zeolite membranes. Although zeolite membranes are more expensive than polymer membranes, it has higher separation factors and flux than others.

3.3 Vapor permeation for Ethanol/Water separation

Apart from the use of pervaporation in Ethanol/Water separation, membrane separation techniques also have vapor permeation which is another proficient separation unit to separate Ethanol/Water mixture. Since the transferring mechanism of component vapor in this unit has no phase change across the membrane, it can reduce the effect of concentration polarization occurring on the feed boundary layer and no temperature drop happened along the membrane (Ito, 1997). In addition, it can prolong the membrane life time as a result of low degree of membrane swelling.

Hayashi et al. (2000) proposed a vapor permeation that was incorporated into ethanol concentration process, obtaining dilute ethanol from the biomass alcoholic fermentation broth to further purify ethanol solutions sequenced from adsorption-desorption process and ethanol stripping column, respectively. Asymmetric polyimide membranes were used for vapor permeation to concentrate ethanol solutions from 30 to 99.6 wt% with ethanol recovery more than 98%. The optimum operating factors, operating conditions and the required membrane area were determined based on the numerical model. The simulation results indicated that the two-stage vapor permeation system could offer a desired concentrated ethanol with high ethanol recovery. Although the system required larger membrane area, the membrane area increased only about 10% compared to that of the single-stage system.

Ethanol dehydration using hybrid distillation-membrane process was investigated by Huang et al. (2010). A simple stripper column was used to purify dilute ethanol from 5 wt% to 50 wt% at the overhead column. Then, the obtained ethanol solutions was further purified with two cascade vapor permeation units achieving ethanol concentration at 90 wt% and 99.7 wt%, respectively. As the membrane in this process should be stable in ethanol/water mixture under the operating temperatures up to 403 K, this work then investigated the development of perfluoro polymer membranes to serve its conditions. Hydrophobic perfluoro polymers were considered because of their chemical and thermal stability which can be used at high temperature, especially up to 403 K. However, the water permeances of this membrane were quite low, compared with the cross-linked hydrophilic membranes. Thus, multilayer composite membranes combined with hydrophobic perfluoro and hydrophilic membrane were proposed. These membranes have a good thermal stability as well as high water permeances and good selectivity.