Recent Advances on Bioethanol Dehydration using Zeolite Membrane

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Abstract. Renewable energy has gained increasing attention throughout the world. Bioethanol has the potential to replace existing fossil fuel usage without much modification in existing facilities. Bioethanol which generally produced from fermentation route produces low ethanol concentration. However, fuel grade ethanol requires low water content to avoid engine stall. Dehydration process has been increasingly important in fuel grade ethanol production. Among all dehydration processes, pervaporation is considered as the most promising technology. Zeolite possesses high potential in pervaporation of bioethanol into fuel grade ethanol. Zeolite membrane can either remove organic (ethanol) from aqueous mixture or water from the mixture, depending on the framework used. Hydrophilic zeolite membrane, e.g. LTA, can easily remove water from the mixture leaving high ethanol concentration. On the other hand, hydrophobic zeolite membrane, e.g. silicate-1, can remove ethanol from aqueous solution. This review presents the concept of bioethanol dehydration using zeolite membrane. Special attention is given to the performance of selected pathway related to framework selection.

1. Introduction
Bioethanol is one of potential biofuel and has the potential to reduce pollution by replacing petroleum energy source [1]. Moreover, global environmental protection seen that industrial uses of fossil fuels released a large quantity of CO2 is released leading to increasing atmospheric temperature [2]. Bioethanol is commonly produced from fermentation route from sugar or starch containing raw materials such as molasses and cornstarch [3]. Fermentation route produces aqueous solution with low ethanol concentration. To obtain absolute ethanol from said solution, dehydration step is required commonly using azeotropic distillation due to the formation ethanol-water azeotrope. However, pervaporation is reported to require less energy than azeotropic distillation. Cardona Alzate and Sanchez Toro [4] reported that further energy saving could be obtained in bioethanol production plant by using pervaporation compared with using azeotropic distillation. Pervaporation only uses 1/5 energy that consumed by using azeotropic distillation. Kaminski et al. [5] compared the cost of ethanol dehydration using vapor permeation, pervaporation, distillation and adsorption. The total operating cost reported are US$ 15.75/tonnes, US$ 12.6-16.6/tonnes, US$ 31.95-45.65/tonnes and US$ 36.3/tonnes, respectively.

Membrane technology has shown its excellent performance in separation process [6-12]. Compared with other approach, membranes tend to have lower energy requirement and other operational cost. One type of membrane based separation is pervaporation. Pervaporation uses membrane as a selective layer between liquid phase feed and vapor phase permeate. Only desired
component can pass through membrane by vaporization. Vaporization of permeate is carried out using vacuum that kept on the permeate side while atmospheric or elevated pressure is used at feed side. Separation via pervaporation is not rely on vapor liquid equilibrium due to limiting transport resistance in the membrane [13, 14].

Zeolite has been used in various sectors such as gas/liquid separation [15-20], catalysis [21, 22], microelectronic, and corrosion resistant areas [23-26]. Zeolite owes uniform, well-defined pores in molecular size, high porosity, and excellent thermal and chemical stability. Zeolite is particularly promising in industrial scale with harsh condition.

There are some reviews in bioethanol purification using pervaporation [1, 5, 27, 28]. However, a brief explanation in zeolite membrane application and the progress in zeolite membrane performance are still needed. This paper will discuss general application of zeolite membrane for pervaporation in bioethanol production. Special attention will be given to progress on membrane flux and separation factor generated in order to compete with conventional distillation process.

2. Zeolite Membrane Concept in Bioethanol Production

Bioethanol is generally produced from fermentable raw materials containing sugar or starch, such as sugar cane molasses and cornstarch, cellulose, as well as industrial waste products [2, 29]. The production of bioethanol from fermentation route produces aqueous ethanol solutions. In order to obtain absolute ethanol from the aqueous ethanol solution, the dehydration process is carried out after fermentation process up to 99.5 wt% ethanol [30].

For the past few years, several researches are reported for the pervaporative dehydration of ethanol–water mixtures [31-35]. Kondo et al. [36] prepared NaA zeolite membrane on the surfaces of porous tubular supports composed of mullite, alumina and/or cristobalite using the hydrothermal synthesis. They obtained pervaporation fluxes and separation factor of 2.35 kg/m²·h and 5100 respectively for pervaporation of 95 wt.% ethanol–water mixtures at 95 °C.

High permeation flux while maintaining high separation factor is the major challenge of zeolite membrane. There have been various efforts towards increasing permeation flux. Generally, permeation flux has the correlation with mass transfer resistant of porous support and membrane layer. Reduction of membrane layer or support is one effective way. Another approach involves using more porous support since the separation factor is only affected by the membrane layer. However, the preparation using such high porosity support is more complicated since high porosity support poorly hold seed layer on it. Algieri et al. [37] conducted pervaporation experiments with thin MFI zeolite membranes synthesized by in situ nucleation and secondary growth at 70 °C and 9.4 wt.% ethanol–water mixtures. They obtained high fluxes (2.1 kg/m²·h) and low separation factor (EtOH/H₂O = 1.3). The fluxes and separation factor for NaA type zeolite membrane varies from 0.23 to 5.60 kg/m²·h and 3600 to 10,000 relatively. The fluxes and separation factor for these zeolite membranes are generally higher than the silicalite and mordenite type zeolite membranes. This is because the pore diameters are larger for these zeolite membranes, which means that they are less size selective for water and they are also less hydrophilic compared to NaA type zeolite membrane [38]. Li et al. [39] prepared NaA zeolite membrane using cheap coarse macroporous support to not only reduce mass transfer resistance but also reduce the price of zeolite membrane.

Utilization of zeolite membrane for ethanol recovery from fermentation broth has been proposed widely. Earlier scheme involve distillation of broth up to azetotropic limit continued with hydrophilic membrane pervaporation up to 99.5 wt% [40]. A further utilization of pervaporation module proposes direct pervaporation using hydrophobic membrane to deplete ethanol from fermentation broth [27]. However, a column is still needed when hydrophobic membrane cannot deliver high enough purity. Figure 1 depict proposed diagram of pervaporation using both hydrophilic and hydrophobic membrane. The dephlegmator in between modules is used to cool the mixture down (using coolant) and condense water from the mixture resulting in higher ethanol percentage on overhead product [28].
Figure 1. Proposed Scheme for Ethanol Recovery using Pervaporation adapted from [28]

3. Removal of Organic From Water

The first step after synthesizing ethanol via fermentation route is the recovering from fermentation broth. Fermentation broth may contain a lot of components depend on the condition of the reaction. Generally, the main component that hardly separated from ethanol is water since other components are larger in size than ethanol. Viable and dead whole cells, suspended solids, and other cell components have the potential to accumulate in membrane modules, blocking flow path hence reducing permeance [28]. Dissolved solids such as NaCl and Sugars such as glucose and xylose interact with water preventing it to pass through membrane. On the other hand, glycerol interacts with ethanol giving similar effect like sugar to water. However, dissolved solids may also precipitate when operating at higher temperature. pH may effect differently among zeolites used related to their stability but in general no direct effect caused by pH [28].

There have been a lot of researches that report pervaporative dehydration of ethanol-water mixtures [31-35]. Kondo et al. [36] fabricate LTA zeolite layer on porous tubular mullite, alumina and/or cristobalite via hydrothermal synthesis. The resulting membrane has flux and separation factor of 2.35 kg/m²h and 5100, respectively. Algieri et al. [37] was using MFI zeolite membrane prepared via in situ nucleation and secondary growth at 70 °C and 9.4 wt.% ethanol-water mixtures. High fluxes (2.1 kg/m²h) but low separation factor (EtOH/H₂O=1.3) was obtained. Several report on pervaporation of ethanol –water mixture using hydrophobic zeolite membrane is presented in Table 1.

| Zeolite Type | Support | Ethanol in Feed (wt.%) | T (K) | Membrane Performance | Ref |
|-------------|---------|-----------------------|-------|----------------------|-----|
| Silicate-1   | SS      | 5                     | 333   | 0.9                  | 106 | [41] |
| Silicate-1   | Al₂O₃   | 5                     | 333   | 1.8                  | 89  | [42] |
| B-ZSM-5     | Al₂O₃   | 5                     | 303   | 0.16                 | 31  | [43] |
| Ge-ZSM-5    | SS      | 5                     | 303   | 0.223                | 47  | [44] |
| ZSM-5       | α-Al₂O₃ | 5                     | 333   | 7.6                  | 51  | [45] |
| ZSM-5       | Al₂O₃   | 5                     | 333   | 9.8                  | 58  | [46] |
| B-ZSM-11    | Al₂O₃   | 5                     | 333   | 1.51                 | 35  | [47] |
| ZSM-5       | α-Al₂O₃ | 5                     | 333   | 2.9                  | 50  | [48] |
| ZSM-5       | α-Al₂O₃ | 10                    | 383   | 51.6                 | 5.2 | [49] |
Integration of membrane pervaporation with fermentation is also another approach to improve the performance of ethanol production [50]. In situ continuous ethanol extraction will boost fermentation efficiency since ethanol of about 10 wt% inhibits further fermentation [45]. Ikegami et al. [51] employed silicate membranes for pervaporation of fermentation broth to obtain ethanol. The result showed an increase in average glucose consumption rate of about ~20% compared with conventional batch reactor. The study also suggests addition of sugars will enhance ethanol selectivity through silicate membrane [52]. However, the selectivity of ethanol is still very low (~5). Nomura et al. [53] studied continuous pervaporation from fermentation broth using silicate membrane. The result shows good performance in terms of flux (0.1 kg/m²h) and separation factor (up to 218) for pervaporation of fermentation broth and ethanol concentration of 98.2% in the permeate side. This result is higher compared with using only water/ethanol mixture.

In general, MFI membrane possesses the highest potential in extraction of ethanol from fermentation broth. MFI has 0.5 nm pore size which is higher than ethanol and water but smaller than most fermentation broth component [54]. Therefore, MFI selectivity towards ethanol is mainly due to surface properties not molecular sieving. MFI not only has the resistance to withstand fermentation broth but also shows higher performance when fermentation broth feed is used [53]. Hydrophobic zeolite membrane can be used as simple as detached pervaporation module filtering batch fermentation products or attached to the bioreactor and enable continuous production of ethanol. However, there still are more room to the development of hydrophobic zeolite membrane in terms of increasing performance and reducing cost [55].

4. Removal of Water from Organic
Removal of water from organic is used as the downstream process of ethanol purification to produce fuel grade ethanol. This method is preferably placed in downstream because of low water content in the feed stream (~10%) thus reducing the membrane load. Moreover, high hydrophilicity zeolite membrane tends to have high Al content making it more prone to dealumination from acidic environment. Meanwhile, fermentation may be carried out in acidic condition and/or produce organic acid as a byproduct [56].

| Zeolite Type | Support | Water in feed (wt.%) | T (K) | Membrane Performance | Ref |
|-------------|---------|----------------------|------|----------------------|-----|
| NaA         | TiO₂ Tube | 10                   | 323  | 0.8-1.00             | 850 | [57] |
| NaA         | α-Al₂O₃ tube | 5                   | 318  | 0.23                 | 830 | [58] |
| NaA         | α-Al₂O₃ tube | 9.2                 | 366  | 2.5                  | 130 | [59] |
| NaA         | α-Al₂O₃ tube | 10                  | 348  | 5.6                  | >5000 | [60] |
| NaA         | α-Al₂O₃ tube | 10                  | 323  | 0.5                  | 16000 | [34] |
| NaA         | α-Al₂O₃ tube | 10                  | 398  | 3.8                  | 3600 | [61] |
| NaA         | α-Al₂O₃ tube | 10                  | 353  | 0.54                 | >10000 | [62] |
| Silica      | γ-Al₂O₃ disc | 10                  | 353  | 1                    | 800  | [63] |
| Mordenite   | α-Al₂O₃ tube | 10                  | 423  | 0.16                 | 139  | [64] |
| Mordenite   | α-Al₂O₃ tube | 15                  | 363  | 0.06                 | 60   | [65] |
| NaA         | α-Al₂O₃ tube | 10                  | 348  | 8.38                 | >10000 | [66] |
| NaA         | α-Al₂O₃ tube | 10                  | 348  | 11.1                 | >10000 | [67] |

Several studies for the pervaporative dehydration of alcohol from aqueous mixtures using hydrophilic zeolite membrane are presented in Table 2. The fluxes and separation factor for NaA type zeolite membrane varies from 0.23 to 5.60 kg/m²h and 3600 to 10,000 relatively. The fluxes and separation factor for these zeolite membranes are generally higher than the silicalite and mordenite type zeolite membranes. This is because the pore diameters are larger for these zeolite membranes,
which means that they are less size selective for water and they are also less hydrophilic compared to NaA type zeolite membrane [38].

The first commercialization of hydrophilic zeolite membrane for ethanol/water separation is using LTA membrane by Mitsui Engineering & Shipbuilding Co. in 1999 [68]. The first large scale pervaporation plant using zeolite NaA membrane is designed to dehydrate various solvents such as ethanol, IPA, and methanol. The plant is a major breakthrough in the development of zeolite membrane. It proves the reliability of LTA zeolite membrane on large scale operation. The highest reported water flux is 16 kg water/m²h in the pervaporation of water/i-propanol mixtures at 120 °C (Caro dkk. 2000). The plant uses 16 modules; each consists of 125 pieces of tubular type NaA zeolite membrane. The plant adopts two vacuum systems for more effective dehydration. Firstly, the feed is dehydrated up to 1.5 wt. % water at 15 mmHg permeate pressure. Then, a final dehydrated product of 0.5 wt. % water is obtained at 8 mmHg permeates pressure [68].

5. Summary and Future Outlook

General aspects of zeolite membrane aided organic acid esterification have been reviewed. Zeolite membrane can be used to completely separate ethanol from fermentation broth. A lot of works have shown the effectiveness of zeolite based membrane in pervaporation to substitute conventional processes. While downstream hydrophilic zeolite membrane process has had its place in industrial scale, hydrophobic zeolite membrane still requires further work to perfect its performance. However, current performance of zeolite membrane is already sufficient for early industrial development of full membrane ethanol purification from fermentation broth.

In the future, this technology needs some improvement in the subject of membrane (materials, methods, and reproducibility), and cost optimization (mainly for industrial implementation). Economical study of zeolite membrane pervaporation for ethanol recovery should be done to review the effectiveness of current zeolite membrane and set a quantitative target for several aspects. The numbers of researches that study various aspects of this technology suggest that it is ready for further industrial implementation.

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