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# Pervaporative concentration of ethanol–water mixtures using heterogeneous polydimethylsiloxane (PDMS) mixed matrix membranes

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ABSTRACT

The PDMS mixed matrix membranes containing 10-μm sized zeolite were prepared, characterized, and tested on the pervaporation (PV) performance for ethanol–water solutions. We found that the membrane with the zeolite mixed after the PDMS cross-linker addition (“post-addition”) was more effective at removing ethanol from the aqueous mixtures than the pristine PDMS and the PDMS–zeolite membrane made with the zeolite addition prior to the PDMS cross-linker addition. The ethanol solubility and diffusivity increased as the zeolite loading increased, and this increase contributed to a greater ethanol flux for the 30% zeolite-containing PDMS than the pristine PDMS for the same ethanol solution. The conventional flux and separation factor data were converted to permeability and selectivity values for a comparison with the data in the literature on the PV for a 10% ethanol solution. The post-addition PDMS–zeolite membrane that was prepared in the present work exhibited the highest ethanol permeability and the third greatest selectivity among the PDMS membranes, the PDMS copolymer membranes, and the PDMS-based mixed matrix membranes reported in the literature.

## 1. Introduction

The world has relied on petroleum as an important and indispensable energy source for decades. Because of the increasing price of crude oil and the generation of greenhouse gases, the need for alternative energy sources is so urgent that the search for these sources has become a priority in many developed and developing countries. Bioethanol has been shown to be effective as a potential fuel. Not only can bioethanol be derived from food crops [1], but this fuel can be produced from non-food ingredients, such as cellulose, the waste from cereal production, and urban waste [2]. Bioethanol is generated by microorganisms that help to ferment the biomass of carbohydrate into ethanol ($C_2H_5OH$).

Bioethanol has been used as an alternative fuel for gasoline and can be used in existing car engines. In the United States, for example, a mixture of 85% bioethanol and 15% gasoline (E85) is used as an alternative fuel for cars. One of the advantages of using bioethanol fuel is that it has a higher octane value than gasoline, indicating that this type of fuel is cleaner and leads to a lower amount of carbon dioxide emissions [3]. The ethanol concentration in the fermentation broth is usually less than 15% [4] and further concentrating treatment is needed to increase this content. For practical use, a water content of 1.26 wt% or less is desirable in fuel-grade ethanol [5]. In addition, other organic components are present in the fermentation broth: methanol, propanol, and acetaldehyde, among others. The most commonly used methods for the dehydration of alcohol are distillation, extraction, molecular sieves adsorption, and pervaporation [4,6]. During this process, it is critical to minimize the amount of energy consumption, and pervaporation (PV) is considered to be a potential technology that will facilitate the production of higher bioethanol concentrated alcohol with lower production costs than the conventional methods. For example, Sommer has shown that alcohol dehydration costs € 84 per ton using traditional processes (i.e., extraction and distillation processes), whereas the production cost using the PV process is € 54 per ton. The PV process can result in an 85% reduction in energy use and a 40% decrease in the production cost for the alcohol fuel manufacturing [7].

Several researchers used hydrophilic polyurethane (PU) [8–11], polyvinyl alcohol [12], hydroxyl sodalite [13], Nafion [14], alginate [15] or alginate/chitosan [16] to remove water from ethanol mixtures. This process is a useful practice for ethanol dehydration, as in mixtures predominated by ethanol. For dilute ethanol–water solutions, it is desirable to develop ethanol-selective membranes because it is more efficient to remove the minor component, ethanol, from the aqueous solutions. Many hydrophobic polymers and inorganic membranes have been tested for removing ethanol from these aqueous solutions [17–20]. Polydimethylsiloxane (PDMS) membranes [21], membranes constructed from its

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copolymer or PDMS-based mixed matrix membranes [4,22–25], and composites on porous supports [26–28] have become the most popular materials for this type of application.

The addition of zeolite into PDMS membranes has been shown to enhance the separation factor of a 5% ethanol solution [4,29–37]. Vane et al. [4] published a literature survey on the dependence of the separation factors on the zeolite content of PDMS–zeolite mixed matrix membranes for the pervaporative separation of this 5% ethanol aqueous solution. They also reported that the separation factor and normalized ethanol flux increased from 8 and $8.23 \times 10^{-11}\,\mathrm{kg\,m^{-1}s^{-1}}$, respectively, for the pristine PDMS membrane to 28 and $13.30 \times 10^{-11}\,\mathrm{kg\,m^{-1}s^{-1}}$, respectively, for the membrane containing 50 wt% zeolite. Recently, Baker et al. [38] proposed that the permeability is a better measure to account for the intrinsic membrane characteristics of permeant transport because it is less dependent on the operating conditions (temperature, membrane thickness, and permeant vapor pressure, among others) than other measures. These authors calculated the ethanol and water permeabilities and selectivities of 2–13% ethanol–water solutions at 75 °C using a PDMS membrane and a PDMS–zeolite (60%) mixed matrix membrane. They reported that PDMS is water-selective (selectivity of 0.6) and that PDMS- zeolite is ethanol-selective (selectivity of 1.9) for the ethanol-to-water permeability ratio of these mixtures.

PDMS is usually cured using a cross-linker to obtain films with a sufficient amount of mechanical strength. We have found that the cross-linking of PDMS renders a more complicated mixed matrix membrane; the unreacted short-chain cross-linker is embedded in a cross-linked three-dimensional polymer network [39]. The objective of the present research is to investigate the PV performance for ethanol solutions using PDMS mixed matrix membranes that contain zeolite. The ten percent (10% by weight) ethanol aqueous solution was selected because this concentration represents a typical ethanol concentration that results from the process of biomass fermentation [23]. The zeolite used in the present study was 10 μm in size with inter-connected pores of 5–6 Å. The zeolite was added to the polymer solution before or after the PDMS was mixed with the cross-linker. The membrane characteristics and their effects on the sorption, diffusion, and PV behaviors were measured.

## 2. Materials and methods

### 2.1. Membrane preparation

Dense PDMS membranes were prepared from two-component kits (Shin-Etsu Chemical Co. Ltd., Tokyo, Japan) using a procedure that was similar to that in our previous paper [39,40]. One component (KET-3001) was a pre-polymer that contained vinyl groups with a small amount of a Pt catalyst. The second component (CAT-3001, Shin-Etsu Polymer Co. Ltd., Tokyo, Japan) was a low molecular weight fraction that contained SiH functional groups as a cross-linker. The pre-polymer (10 g) was diluted with toluene solvent (15 g, Mallinckrodt Baker Inc., Phillipsburg, NJ, USA). Next, the cross-linker (1 g, 10% of the weight of pre-polymer) was added to the pre-polymer/toluene solution. This solution was degassed in an ultrasonic bath at 12 ± 1 °C for 30 min to avoid significant viscosity increase accompanied by instant cross-linking reaction, and the solution was poured onto a Teflon plate. An adjustable film applicator with a gap clearance of 400 μm was placed at one edge of the solution and was drawn slowly toward the other end to produce a polymer film with a uniform thickness. The film was dried and cured at 80 °C for 6 h prior to its use. A digital thickness gauge (model 345, Elcometer Instrument Ltd., Edge Lane, England) was used to measure the membrane thickness at 10 locations, and the average thickness was reported. The film thickness was 200 ± 20 μm. The polymer density of the pristine PDMS membrane was $1.083\,\mathrm{g\,cm^{-3}}$ [40].

Two types of zeolite/PDMS composite membranes were prepared. The zeolite (TZP-9023) was purchased from Tricate Zeolites, Bitterfeld, Germany. It had a Si/Al ratio of 666, which was estimated from XPS measurement. The zeolite "pre-addition" PDMS membranes were composite membranes to which zeolite was added prior to the PDMS cross-linker addition. Ten grams of pre-polymer was mixed with 15 g of toluene, and a predetermined of zeolite was added to the pre-polymer solution and was stirred for 2 h. Next, 1 g of cross-linker (10% of the weight of the pre-polymer) was added to the toluene solution that contained pre-polymer and zeolite. This slurry was degassed, cast, dried, and cured, according to the procedure for PDMS preparation outlined in the previous paragraph. Alternatively, the zeolite "post-addition" PDMS membrane was prepared by diluting the pre-polymer (10 g) in toluene solvent (15 g). Next, 1 g of the cross-linker (10% of the pre-polymer weight) was added to the pre-polymer/toluene solution and was mixed for 30 min at room temperature. Following that 1.2–4.8 g of zeolite was added to the PDMS toluene solution (which was viscous but not completely cross-linked) and was continuously stirred for 2 h. The slurry was degassed, cast, dried, and cured, according to the procedure for PDMS preparation.

### 2.2. Zeolite and membrane characterization

The zeolite particle size and distribution was measured using a Mastersizer (model Mastersizer micro & Micro plus, Malvern, Worcestershire, UK). Approximately 0.01 g of the zeolite powder was dispersed in 8 mL de-ionized water with one drop of non-ionic surfactant (Igepal® CO-520, Rodia S.A., Paris, France). The suspension was ultra-sonicated for 30 min prior to the analysis. A scanning electron microscope (SEM, model S-3000N, Minami-ku, Kyoto, Japan) was used to evaluate the particle morphology of the zeolite and the surface and cross-sectional structure of the membranes. An X-ray diffractometer (XRD, model D5005 D, Berlin, Germany) was used to examine the crystalline diffraction characteristics of the zeolite, the PDMS, and the zeolite/PDMS composites. The X-ray radiation was generated using Cu Kα (wavelength 1.54056 Å) from an anode that operated at 40 kV and 40 mA. The scanning rate was one scan per second with a 0.02° increase in resolution. The XRD intensity was recorded between the angles of 10 and 50°. The chemical structure of the zeolite, the PDMS, and the zeolite/PDMS composites were determined using an attenuated total reflectance Fourier-transform infrared spectrometer (ATR-FTIR, model Horiba FT-730, Minami-ku, Kyoto, Japan). The FTIR spectra were recorded in the range of $4000–600\,\mathrm{cm^{-1}}$ for 32 scans. The membrane thermal stability was evaluated using a thermogravimetric analyzer (TGA 2050, TA Instrument, New Castle, DE, USA). The weight changes of the tested samples (10–15 mg) were recorded in a nitrogen atmosphere under a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ until 680 °C was reached.

### 2.3. Sorption of pure solvents in the membranes

The sorption levels of ethanol and water in the membranes were determined using the gravimetric method. The dried membranes were cut into 10 mm × 20 mm specimens, and the dried weight and thickness of the membranes were recorded. The dry films were immersed in pure ethanol or water at 25 °C. After each time interval, the membrane was removed and wiped with tissue paper to remove the remaining liquid on the surface of the film. Next, the membrane was weighed using a microbalance (Model BP211D, Sartorius, Goettingen, Germany). The equilibrium solvent uptake ($w_\infty$, in kg of solvent per kg of dry membrane) was measured until no significant weight increase was observed for the swollen membrane,