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Improved biobutanol recovery through mixed-matrix PVDF membrane with hydrophobic MAF-6 as filler

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In this study, enhancing the hydrophobicity of the membrane by using MAF-6 was considered an effective strategy to improve the performance of organophilic pervaporation (PV) membranes. This was achieved by incorporating superhydrophobic MAF-6 into polyvinylidene fluoride (PVDF) polymer to create mixed matrix membranes (MMMs). Various characterization techniques were employed to assess the morphologies of the MAF-6 nanocrystals and the membranes, including BET and SEM. The pervaporation experiments involving butanol/water mixtures demonstrated that the MMMs exhibited enhanced flux and separation factors compared to the PVDF pristine membrane. The optimal flux achieved was 1.35 g/m^2 h, with a separation factor of 16.7. This enhancement in performance was attributed to the hydrophilicity and high porosity of MAF-6, which effectively overcame the trade-off effect usually observed in such membranes.

Keywords: Biobutanol, MAF-6, membrane, PVDF, pervaporation

INTRODUCTION

The global transition toward renewable energy sources gained momentum in the late 1990s, driven by rising petroleum prices, increasing raw material costs, and depletion of fossil fuel reserves [1, 2]. Biofuels, including densified agricultural residues, ethanol, butanol, hydrogen, and biodiesel, are produced through biochemical or thermochemical conversion of various plant and organic wastes [3]. Among these, butanol—a flammable alcohol—emerges as a promising biofuel. It offers several benefits over bioethanol such as being non-hygroscopic, having a higher heating value, better compatibility with gasoline and diesel, and causing less corrosion and flammability concerns. Additionally, butanol is extensively used as an industrial solvent [2, 3]. The production of biofuels *via* acetone-butanol-ethanol (ABE) fermentation has a long history dating back to 1861 and has regained interest amid the ongoing search for alternative fuels, particularly after renewed focus on ABE fermentation for butanol production since the 1960s [4].

Conventional techniques for recovering butanol from fermentation broths include distillation, adsorption, extraction, and gas stripping, but each method faces certain limitations. Pervaporation, a membrane-based separation process, offers an alternative that can overcome some of these challenges. In pervaporation, the liquid feed contacts one side of the membrane, while the permeate is collected as vapor on the opposite side under vacuum. The membrane's selectivity depends on the relative solubility and diffusivity of the components within the membrane matrix. Therefore, developing membranes with a strong affinity for the target compound is essential for achieving efficient pervaporation performance [5].

Mixed matrix membranes (MMMs) are hybrid materials that effectively combine the flexibility and ease of processing of polymers with the selectivity and durability of inorganic fillers. This combination provides a promising approach for improving separation performance, especially in gas separation and pervaporation applications. MMMs consist of an organic polymer matrix embedded with dispersed inorganic fillers such as zeolites, metal–organic frameworks (MOFs), carbon nanotubes, silica, and graphene oxide. The aim is to leverage the mechanical flexibility and manufacturability of polymers alongside the high selectivity, thermal stability, and chemical resistance of inorganic fillers. The polymer component provides mechanical strength and ease of fabrication. Typical polymers used are polyvinylidene fluoride (PVDF), polysulfone (PSf), polyimide (PI), poly(ether-block-amide) (PEBAX), and polydimethylsiloxane (PDMS). In the present study, VDF was preferred as

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polymer matrix material and MAF-6 as inorganic additive [6-7].

PVDF is a high-performance membrane material, which has received extensive attention due to its excellent heat resistance, chemical resistance, and mechanical properties. PVDF is a well-known hydrophobic polymer that is used in the pervaporation process [8-10].

MAF-6 is a type of metal-organic framework (MOF) known for its remarkable hydrophobicity, which arises from the uniform distribution of ethyl groups on its pores and particle surfaces, as well as its RHO topology. It features a high surface area of 1622 m^2/g and a large pore aperture of 0.76 nm, exceeding the molecular kinetic diameter of 1-butanol (0.50 nm). This structural characteristic facilitates the efficient adsorption and diffusion of butanol molecules [11].

In this study, pervaporative recovery of biobutanol was investigated with mixed-matrix PVDF membrane with hydrophobic MAF-6 as filler. MAF-6 and mixed matrix membrane were characterized by BET and SEM, respectively. The effect of MAF-6 concentration and feed butanol concentration on the separation performance was investigated.

EXPERIMENTAL

Materıals

Ethanol, 1-butanol, methanol, n-hexane, 2-ethylimidazole, cyclohexane and 25% aqueous ammonia solution were sourced from Merck. Zinc hydroxide ($Zn(OH)_2$) was supplied by Thermo Scientific Chemicals. The polyvinylidene fluoride (PVDF) polymer was obtained from Solvay.

MAF-6 synthesıs and characterızatıon

$Zn(OH)_2$ was dissolved in aqueous ammonia solution (solution A). 2-Ethylimidazole was dissolved in a solution containing ethanol and cyclohexane (solution B). Both solutions were stirred separately at room temperature until dissolved. Solution A was slowly poured over solution B to bring the two solutions together. The resulting solution was collected by centrifugation. The remaining solid portion was dried in an oven at 80 °C for 12 h [11].

MAF-6 was characterized by scanning electron microscopy (SEM) and surface area analysis (Brunauer-Emmet-Teller (BET) method).

Mixed matrix membrane synthesis and characterization

5 wt. % PVDF was stirred in DMF until homogeneous. To the homogeneous solution obtained, 0.25 wt. %, 0.5 wt. %, 0.75 wt. % and 1 wt. % of the synthesized MAF-6 particles were added and mixed. The prepared MAF-6-doped PVDF membrane was poured onto a Teflon surface and allowed to dry at 120°C for 5 h. The dried membrane was carefully removed from the surface and made ready for use. The membrane was characterized by scanning electron microscopy (SEM).

Pervaporative recovery of biobutanol

The pervaporation recovery of biobutanol was carried out using a laboratory-scale pervaporation system. This setup consists of a membrane cell containing the membrane and feed mixture, a mechanical mixer to ensure uniform mixing, a vacuum pump to maintain low pressure on the permeate side, and cooling traps for collecting the permeated vapor. The membrane is positioned inside the membrane cell, and the feed mixture is pumped into the cell, with the mechanical mixer providing thorough homogenization. Using hydrophobic membranes, biobutanol from the mixture selectively permeates through the membrane during the process, while water remains in the feed as it cannot pass through. In pervaporation, one side of the membrane is in contact with the liquid feed, while the opposite side is under vacuum. Biobutanol passes through the membrane and evaporates under reduced pressure on the permeate side. The biobutanol vapor is then condensed back into liquid form in the cooling traps using liquid nitrogen. The separation performance of the membrane was assessed by determining flux and selectivity, calculated as described in Equations 1 and 2, respectively.

$$Flux = \frac{\text{Mass of permeate}}{\text{Effective Membrane Area}*\text{time}} \quad (1)$$

$$Selecitivity = \frac{\frac{Y_B}{Y_W}}{\frac{X_B}{X_W}} \quad (2)$$

Y is the percentage by weight in the permeate side and X is the percentage by weight in the feed side. Biobutanol concentration was determined by gas chromatography.

RESULTS AND DISCUSSION

MAF-6 characterization

The surface area of the synthesized MAF-6 was obtained as 795.936 m^2/g. Figure 1 shows the SEM image of MAF-6. It can be seen that all samples have uniform particle size distributions. The morphology of the crystals represents a rhombohedral dodecahedron structure.

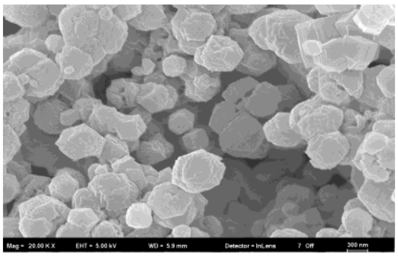

Figure 1. SEM image of MAF-6

Mixed matrix membrane characterization

Figure 2 shows the SEM image of the MAF-6 doped PVDF membrane.

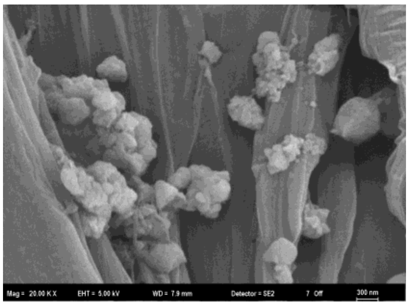

Figure 2. SEM image of MAF-6-doped PVDF membrane.

MAF-6 is observed to be dispersed in the membrane. It exhibits a structure compatible with PVDF. No gap formation is observed between the membrane and MAF-6.

PERVAPORATION RESULTS

Effect of MAF-6 concentratıon

Membranes containing three different MAF-6 loading concentrations (1%, 3% and 5%) were employed in the experimental study for the pervaporative recovery of biobutanol. The tests were performed at room temperature using butanol-water mixture with a butanol content of 10%. The influence of MAF-6 concentration on the membrane's separation performance is presented in Figure 3. It is observed that the flux value increases as the amount of MOF increases. The reason for this can be interpreted as acceleration of material transfer by increasing the surface area with the increase in the amount of metal organic framework. In addition, as the amount of MOF increases, the hydrophobic character of the membrane increases, absorbing more butanol and allowing its transport. Therefore, the flux value increases. It was also observed that the selectivity increased with increasing MOF amount. While the increase in MOF leads to an increase in hydrophobic region, it also adsorbs more butanol molecules, which leads to an increase in selectivity [12-15].

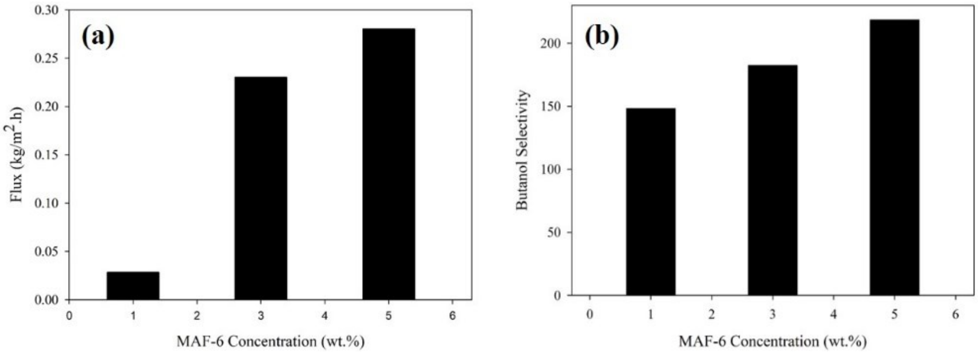

Figure 3. Effect of MAF-6 concentration on flux and selectivity

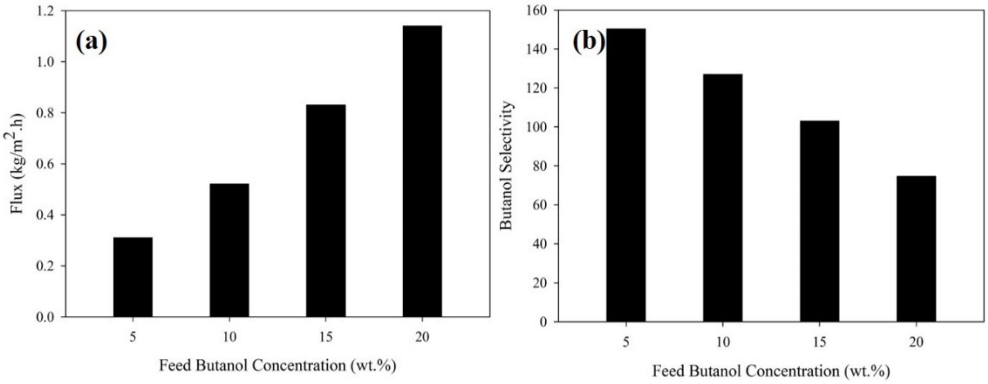

Figure 4. Effect of feed butanol concentration on flux and selectivity

Effect of feed butanol concentratıon

Figure 4 displays the results of the pervaporative recovery of biobutanol conducted at room temperature using a 5 wt.% MAF-6-doped mixed matrix membrane. The study examined the impact of varying feed butanol concentrations by testing butanol-water mixtures containing 5, 10, 15, and 20 wt% butanol.

As the concentration of butanol in the feed mixture rises, the overall permeation flux through the hydrophobic membrane increases due to a greater sorption of butanol into the membrane matrix. This sorption induces membrane swelling, which expands the free volume and enhances molecular mobility, thereby facilitating the diffusion of butanol. Because of the membrane's hydrophobic nature, butanol has much higher solubility and diffusivity than water, resulting in a significant increase in butanol flux. As a result, the membrane’s selectivity for butanol over water generally improves with increasing feed butanol concentration, especially at low to moderate levels [16-18].

CONCLUSION

This study systematically examined how MOF content and feed butanol concentration affect the performance of hydrophobic mixed matrix membranes. The findings showed that increasing the MOF loading in the membrane significantly boosted the total permeation flux. This enhancement is attributed to the larger surface area provided by the MOF particles, which accelerates mass transfer, and to the increased hydrophobicity of the membrane, which facilitates greater butanol sorption and transport. Additionally, membrane selectivity for butanol improved with higher MOF content, as the more hydrophobic and porous structure favored the adsorption and diffusion of butanol molecules over water. Similarly, raising the butanol concentration in the feed positively impacted membrane performance. Increased butanol levels promoted greater sorption into the hydrophobic membrane, causing swelling of the polymer matrix, expansion of free volume, and enhanced diffusivity. As a result, both butanol flux and butanol/water selectivity increased, especially at low to moderate butanol concentrations. These results suggest that optimizing MOF loading and feed composition can significantly improve membrane-based separation efficiency for butanol recovery. Optimum operating conditions were obtained by using a 5 wt. % MAF-loaded membrane at 20 wt. % feed butanol concentration. The flux and selectivity values obtained at optimum conditions are 1.14 kg/m^2.h and 74.6, respectively.

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