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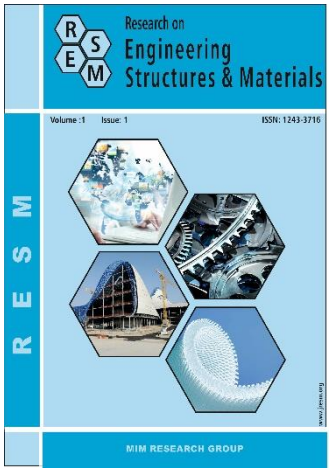

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Research Article

Fuel butanol dehydration by using a membrane based pervaporation method

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Abstract

The usage of bio-fuel for transportation fuel has become mandatory to reduce the greenhouse gas emissions and increase the fuel quality. It is well known that the bio-fuels such as bio-ethanol and bio-butanol are produced by the fermentation process and the final concentrations of these alcohols in fermentation broth are very low. Therefore, effective and selective separation processes are required to be used. Pervaporation is a cost effective and selective membrane process that separates azeotropic, close-boiling-point mixtures from each other. It is commercially used as a hybrid process with distillation in the fermentation plant. The performance of this method depends on the productivity, durability, stability, and selectivity of the membrane. Thus, academic studies related to the pervaporation membrane production are still in progress. The purpose of this study is dehydration of bio-butanol by using pervaporation. Montmorillonite clay incorporated carboxymethyl cellulose composite membrane has been prepared. Effects of temperature and butanol-water concentration on separation performance have been investigated.

1. Introduction

Bio-butanol is a second generation bio-fuel that can be produced by the fermentation of sugar containing biomass. It is also produced by modification of bio-based fuel or pyrolysis of bio-waste. The usage of butanol has some advantages compared to bio-ethanol and gasoline. Owing to the higher number of carbon, it has higher energy density [1-2]. The structure of butanol resembles gasoline in many aspects. Therefore, it can be blended with gasoline in a wide range of concentration. Although the energy density of butanol is lower than gasoline, compared to gasoline it reduces the carbon emissions approximately 85 percentage [3-5].

Clostridium type microorganism is used for the anaerobic fermentation of butanol production [6]. After the fermentation, dilute acetone-butanol-ethanol (ABE) mixture is produced. In this solution, the concentration of ABE is no more than 3 wt. % and the concentration of the broth changes according to the activity of microorganism, the acidic value of the fermentation, and type of the reactor. Owing to the very low concentration of butanol in broth (maximum amount is 20 gL^{-1}), many efforts are required to purify butanol from ABE solution [7-9]. If the bio-fuels blend with gasoline, it must be anhydrous. If the trace amount of water reacts with chemicals such as sulfur, a corrosive acid can be formed and the engine can be damaged. Therefore, water must be completely removed from the fuel. Due to the azeotropic nature of alcohol-water mixture at special operating conditions, dehydration by using distillation is applied up to a certain

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concentration. After that point, more complicated processes are required to purify butanol. There are many techniques such as azeotropic distillation, absorption, and extraction to separate butanol efficiently. However, many of these techniques are required additional solvent or adsorbents. Therefore, the total energy consumption and the cost of overall system increase. It is reported that the big portion of the total production cost is comprised of the purification cost. Recently, pervaporation (PV) has become an emerging technology to be used in bio-fuel production facility for purification of bio-fuels [9].

Pervaporation is a non-porous membrane separation process that is driven by chemical potential gradient. Due to the selective separation capability of the membrane used in PV, separation occurs according to the membrane-solvent interaction. Additionally, diffusivity, solubility and vapor pressures of the components play critical roles in PV. Hence, membrane selection is the key factor for system efficiency.

Indeed, there are two types of PV systems used in commercially biofuel facilities. Hydrophobic PV system is used for the direct separation of the butanol from the ABE solution. In this system, non-porous hydrophobic membranes such as poly(dimethyl siloxane) or natural rubber are used [10-12]. Hydrophilic PV dehydrates the fermentation broth by removing the water from the fermentation broth. Due to the small amount of butanol in bulk solution, hydrophobic PV seems more feasible. However, broth solution contains at least three types of organics. The polarities and kinetic diameters of these components are closer to each other. Thereby, butanol selectivity of the hydrophobic system is very low. In the case of the hydrophilic PV separation, water-selective membrane is preferred. In the literature, relatively superior flux and selectivity values have been observed and 99 percentage of water purity has been obtained accompanied with above 2000 selectivity [13]. However, hydrophilic membranes – polymeric ones- show high swelling tendency to water. Polymeric chain's structure of membrane change according to the operating conditions and this plasticization effect shortens the membrane lifetime. Additionally, separation performances of hydrophilic polymeric membranes are not stable under the harsh operating conditions [14]. In order to reinforce the strength of the polymeric membrane, inorganic fillers such as zeolite, clay can be incorporated into the matrix. These types of membranes are defined as mixed matrix membrane [15-17].

In this study, Sodium montmorillonite (Na^+MMT) loaded carboxylmethyl cellulose (CMC) mixed matrix membrane was prepared by solution casting method. In order to make a good adhesion between the clay and CMC, the membrane was prepared by using priming method. Inorganic-organic compatibility was determined by means of microscopic analysis. Based on the literature survey, butanol recovery from the fermentation broth by using a hydrophobic membrane and butanol dehydration by using a hydrophilic membrane have been studied in many times [17-22]. To the best our knowledge, this is the first study on use of Na+MMT loaded CMC membrane for the separation of butanol from the model butanol-water solution. In order to obtain the affinity of the membrane to the components, sorption experiments were performed. Effects of temperature and water concentration on separation performance were evaluated as function of flux and separation factor.

2. Material and Method

Na^+MMT and CMC were hydrophilic materials and it was important to keep them as a stable membrane in the aqueous solvent media. Therefore, a cross-linking procedure was

applied. For this purpose, glutaraldehyde, hydrochloric acid (HCl), acetone and water were used.

2.1 Material

Na^+MMT clay, CMC, butyl alcohol (n-butanol) were purchased from Aldrich chemicals, Turkey. Glutaraldehyde (GA), hydrochloric acid (HCl), acetone were supplied from Merck Chemicals in Turkey.

2.2 Membrane preparation

The composite membrane was prepared by using solution casting method. Wt. 1.5% CMC-water solution was prepared and stirred for 24 hours at room temperature. Separately, predetermined amount of clay was added to 5 ml water. A small amount of CMC-water solution was poured into clay-water solution and the clay particles were allowed to cover with CMC solution. This procedure was called as 'priming'. The primed solution was stirred for six hours. Polymer-clay mixture was poured into a poly (methyl methacrylate) plate and dried three days at room temperature. After the membrane had formed, it was taken to a cross-linking bath for five hours. The cross-linking bath was included glutaraldehyde and HCl. Finally, the cross-linked composite membrane was taken to a vacuum oven to vaporize remain acid.

2.3 Membrane characterization

The clay distribution and membrane structure were analyzed by using JEOL JSM-6335 F Field Emission Scanning Electron microscope. The samples were coated with gold before the analysis and broken into pieces with liquid nitrogen.

2.4. Swelling experiment

The degree of swelling test was done to determine the membrane affinity to water and butanol at 303 K. Membranes were immersed in pure water and butanol for ten hours separately. Swelling was calculated from the weight difference of the swollen (W_s) and dry (W_d) membranes as seen in Eq. 1;

$$DS(\%) = \frac{W_s - W_d}{W_d} * 100 \quad (1)$$

2.5 Pervaporation test

Pervaporation experiments were applied for butanol-water mixtures at different concentrations (7 wt. %, 10 wt. %, 15 wt. %, and 20 wt. % water in butanol), and temperatures (303 K, 313 K, 323 K, 333 K) for six hours. Experimental PV unit and membrane module was shown in Fig. 1. The downstream pressure was 30mbar and the upstream was kept at atmospheric pressure. The membrane cell capacity was 250 ml and the effective membrane area was 19.625 cm^2**.**

System performance was evaluated as function of flux and separation factor. Flux (J) ($kg/m^2.h$) was calculated from the measured weight of the permeate sample as shown in Eq. 2

$$J = \frac{W_p}{t.A} \quad (2)$$

Separation factor (α) was calculated from the data obtained from gas chromatography of the permeate concentration as shown in Eq. 3.

$$\alpha = \frac{Y_a / X_a}{Y_b / X_b} \tag{3}$$

W_p is the weight of permeate (kg), t is the time (h), A is the effective membrane area (m^2), Y_a and Y_b are the mass or volume fractions of a and b compounds in the permeate respectively. X_a and X_b are the mass or volume fractions of a and b compounds in the feed respectively.

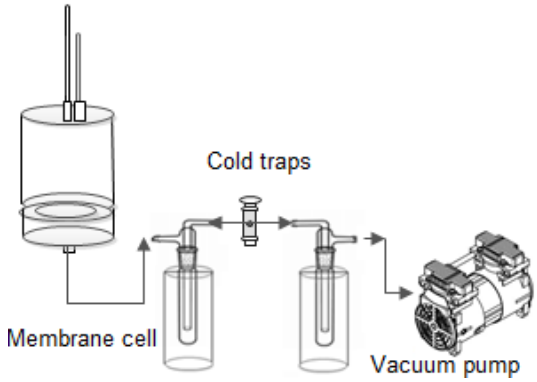


Fig. 1. Experimental pervaporation set-up

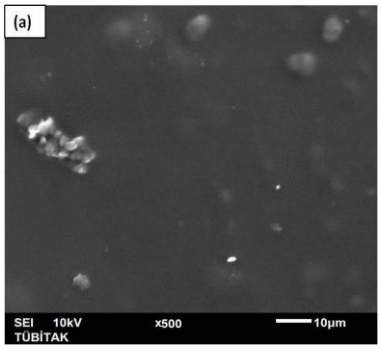
2.6 Analysis

Butanol-water concentrations in the permeate side were determined by using Agilent 7980 gas chromatography with FID detector. HP-FFAP polyethylene glycol capillary column was used.

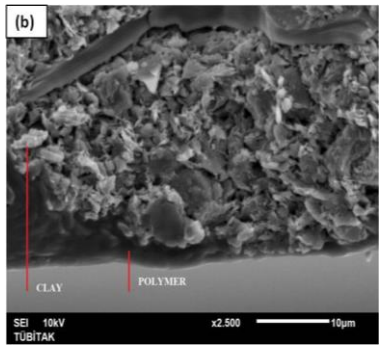
3. Results and Discussion

3.1 SEM Results of the composite membrane

Fig. 2 indicated the surface (Fig. 2a) and cross-sectional (Fig. 2b) views of the clay incorporated CMC membrane. There were no contact-free or adhesion defect regions between the interfaces of clay-polymer materials.



(a)



(b)

Fig. 2. Surface (a) and cross-sectional (b) SEM micrographs of clay loaded membrane

This was an important observation. In order to achieve a selective separation in pervaporative separation, the membrane should not include any interfacial voids. These voids could cause a reduction in water separation factor. SEM micrographs proved the successful membrane formation by using the priming method.

3.2. Swelling experiment

The swelling degree is a numerical value to obtain the membrane affinity to the selected component. When the membrane contacts with the affiliated solvent, water is absorbed by the membrane and the membrane swells. The swelling value should be within allowable limits. The degree of swelling is a desirable variation for a selective separation membrane. However, after a certain point, excess swelling degree can prevent the selective separation property of the membrane. Plots in Fig. 3 showed the time-dependent swelling behavior of the composite membrane within water and butanol at 303 K separately. As seen in Fig. 3 , composite membrane showed high affinity to water compared to butanol. This was an expected result owing to the hydrophilic and polar nature of CMC and clay.

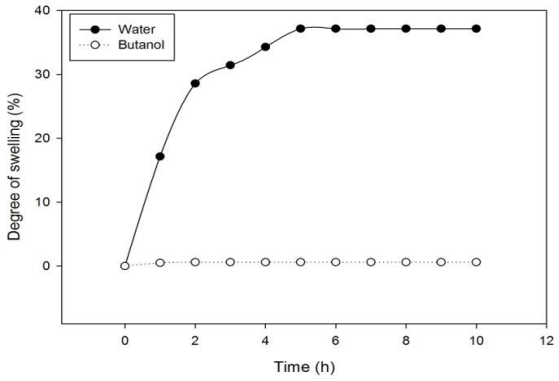


Fig. 3. Degree of swelling results of clay loaded membrane (303 K

3.3 Effect of temperature on separation performance

Flux and separation factor are two important factors to define the PV efficiency. Separation factor has significance to determine the selective separation capability of the membrane. In order to manufacture a commercial membrane, flux and separation factor should be a reasonable value. Indeed, flux is a quantity of the membrane productivity. It depends on temperature, feed composition, membrane material thickness, etc. The relationship between the flux and temperature can be evaluated in multiple ways. Firstly, temperature directly affects the mass transfer rate of the component. It changes the diffusion rate and solubility of the separated compound. When a polymeric membrane is used, temperature also affects the free volume of the membrane. Fig. 4 showed the temperature dependent separation performance of the composite membrane. The temperature was gradually increased from 303 K to 333 K when the water concentration was kept at 7 wt. %. As seen in Fig. 4, flux was enhanced by the temperature increment owing to the mentioned reasons.

However, these reasons affected the water separation factor negatively. Just an example, increasing void spaces caused an unselective separation through the membrane. When

the temperature increased from 303 K to 333 K, separation factor decreased from 429 to 152. At the low temperature (303 K), 99.2% water was obtained in the permeated mixture.

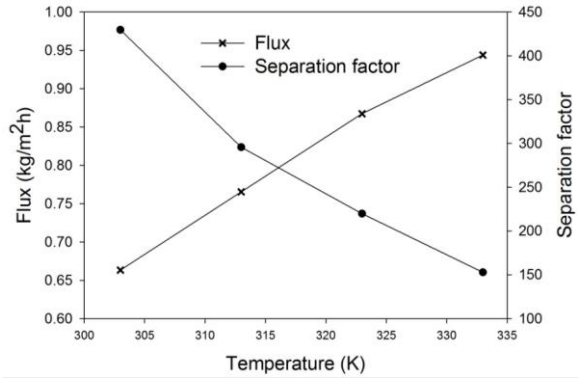


Fig. 4. Effects of temperature on separation performance (7 wt. %water)

3.4 Effect of feed concentration on separation performance

The changing feed concentration is another determinant factor to evaluate the pervaporation performance. Increasing concentration of the selected compound enhances the plasticization effect of the polymeric membrane. Therefore, flux enhances and separation factor decreases. In this study, both CMC and clays were hydrophilic and showed strong affinity to the water.

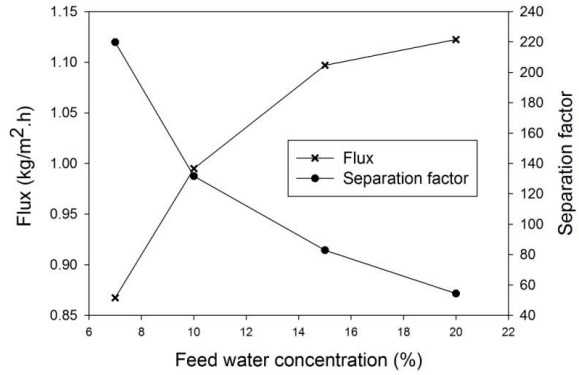


Fig. 5. Effects of feed water concentration on separation performance (323 K)

As could be observed from the Fig. 5, the feed water concentration directly affected the flux and separation factor. Owing to the hydrophilic character of the clay and CMC, membrane swelled with increasing water content in feed and flux increased as expected. However, the separation factor selectivity decreased from 221 to 54 caused by the drifting of the butanol with water.

3.5. Comparison with literature data

In the pervaporation studies, it is important to achieve a high separation factor associated with a desirable flux value. In order to evaluate the overall performance of the PV, pervaporation separation index (PSI)(Eq. 4) has been defined by the researchers.

$$PSI = J(\alpha - 1) \quad (4)$$

As it was mentioned before, Na+MMT loaded CMC membrane had very good flux and separation factor. Table 1 confirmed these results as shown below. Between the literature results, very good and admirable flux and separation factors were achieved by using the Na+MMT loaded CMC membrane in the pervaporation system.

Table 1. Comparison the results of present study

Membrane	Temp. (K)	Water in butanol (wt.%)	Total Flux (kg/m².h)	Separation Factor	PSI (kg/m².h)	Ref.
Pervap 2510 (Commercial)	333	7	0.8	190	152	[23]
Chitosan/HEC	313	10	0.18	728	131	[24]
Microporous silica	353	5	0.6	220	132	[25]
Na+MMT loaded CMC	323	7	0.87	221	191.4	This study

4. Conclusions

Fuel bio-butanol production has become an emerging technology for the future's energy demand. However, the selective separation of butanol from fermentation broth consumes a huge amount of energy. Pervaporation is a promising method to separate butanol selectively. In recent years, researchers have claimed that this method can save the energy for fuel production. The efficiency of the system is directly related to the membrane performance. For this reason, this study focused on an appropriate selective membrane production and high purity butanol-water separation. In this study, the selective separation capability of the model butanol-water solution by means of a non-porous Na+MMT clay loaded CMC membrane. At the low temperature (303 K), water was selectively removed from broth above 99 % purity with very reasonable flux value. When the temperature increased from 303 K to 333 K, flux increased, but separation factor decreased. Separation results proved the commercial availability of Na^+MMT loaded CMC membrane for butanol-water separation, especially at low fermentation temperature.

Acknowledgements

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References

[1] Yilmaz N, Francisco MV, Kyle B, Stephen MD, Antonio C. Effect of biodiesel–butanol fuel blends on emissions and performance characteristics of a diesel engine. Fuel. 2014; 135: 46-50. https://doi.org/10.1016/j.fuel.2014.06.022

[2] Doğan O. The influence of n-butanol/diesel fuel blends utilization on a small diesel engine performance and emissions. Fuel. 2011; 90: 2467–2472. https://doi.org/10.1016/j.fuel.2011.02.033

[3] Kaminski W, Tomczak E, Gorak A. Biobutanol - Production And Purification Methods. Ecological Chemistry And Engineering. 2011; 18: .31-37.

[4] Durre J P. Biobutanol: An attractive biofuel. Biotechnol. J. 2007; 2: 1525–1534. https://doi.org/10.1002/biot.200700168

[5] He H, Lui H, Ru Gan Y. Genetic Modification of Critical Enzymes and Involved Genes in Butanol Biosynthesis from Biomass. Biotechnology Advances. 2010; 28; 651-657. https://doi.org/10.1016/j.biotechadv.2010.05.015
[6] Pfromm PH, Boadu VA, Nelson R, Vadlani P. Bio-butanol vs. bio-ethanol: A technical and economic assessment for corn and switchgrass fermented by yeast or Clostridium acetobutylicum. Biomass and bioenergy. 2010; 34: 5 1 5 – 5 2 .
[7] Shi GM, Yang T, Chung TS. Polybenzimidazole(PBI) /zeoliticimidazol ate frameworks(ZIF-8) mixed matrix membranes for pervaporation dehydration of alcohols. Journal of Membrane Science. 2012; 415: 577–586. https://doi.org/10.1016/j.memsci.2012.05.052
[8] Lou X, Singh PM. Role of water, acetic acid and chloride on corrosion and pitting behaviour of carbon steel in fuel-grade ethanol. Corrosion Science. 2010; 52: 2303–2315. https://doi.org/10.1016/j.corsci.2010.03.034
[9] Vane LM. Separation technologies for the recovery and dehydration of alcohols from fermentation broths. Biofuel, Bioproduct and Biorefining. 2:553–588 (2008). https://doi.org/10.1002/bbb.108
[10] Gongping L, Wang W, Hao W, Xueliang D, Min J, Wanqin J. Pervaporation performance of PDMS/ceramic composite membrane in acetone butanol ethanol (ABE) fermentation–PV coupled process. Journal of Membrane Science. 2011; 373: 121–129.
[11] Li SY, Srivastava R, Parnas RS. Study of in situ 1-butanol pervaporation from A-B-E fermentation using a PDMS composite membrane: validity of solution-diffusion model for pervaporative A-B-E fermentation. Biotechnol Prog. 2011; 27: 111-120. https://doi.org/10.1002/btpr.535
[12] Li J, Chen X, Qi B, Luo J, Zhang Y, Su Y, Wan Y. Efficient production of acetone-butanol-ethanol (ABE) from cassava by a fermentation-pervaporation coupled process. Bioresour Technol. 2014; 169: 251-257.
[13] Kujawski W. Application of Pervaporation and Vapor Permeation in Environmental Protection. Polish Journal of Environmental Studies. 2000; 9: 13-26.
[14] Mathias U. Advanced functional polymer membranes. Polymer. 2006; 7: 2217–2262.
[15] Susheelkumar GA, Malladi S, Lata SM, Raju KVSN, Tejraj M A. Sodium montmorillonite clay loaded novel mixed matrix membranes of poly(vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane. Journal of Membrane Science. 2006; 285: 182–195.
[16] Shao P., R.Y.M. Huang. Polymeric membrane pervaporation. Journal of Membrane Science. 2007; 287: 162-179. https://doi.org/10.1016/j.memsci.2006.10.043
[17] Zhen H, Huai G, Wee l T, Xiang YQ, Santi K. Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly(vinyl alcohol) membranes: Effect of zeolites. Journal of Membrane Science. 2006; 276: 260–271. https://doi.org/10.1016/j.memsci.2005.09.056
[18] Li Y, Shen J, Guan K, Liu G, Zhou H, Jin W. PEBA/ceramic hollow fiber composite membrane for high-efficiency recovery of bio-butanol via pervaporation. Journal of Membrane Science. 2016; 510: 338–347. https://doi.org/10.1016/j.memsci.2016.03.013
[19] Shina C, Chena XC, Prausnitza JM, Balsara NP. Effect of Block Copolymer Morphology Controlled by Casting-Solvent Quality on Pervaporation of Butanol/Water Mixtures, Journal of Membrane Science. Article in Press, doi.org/10.1016/j.memsci.2016.09.054 https://doi.org/10.1016/j.memsci.2016.09.054

[20] Wang X, Chen J, Fang M, Wang T, Yu L, Li J. ZIF-7/PDMS mixed matrix membranes for pervaporation recovery of butanol from aqueous solution. Separation and Purification Technology. 2016; 163: 39–47. https://doi.org/10.1016/j.seppur.2016.02.040

[21] Rom A, Friedl A. Investigation of pervaporation performance of POMS membrane during separation of butanol from water and the effect of added acetone and ethanol. Separation and Purification Technology.2016; 170: 40–48. https://doi.org/10.1016/j.seppur.2016.06.030

[22] Jeea KY, Kim N, Lee YT. The effect of metal complex on pervaporation performance of composite membrane for separation of n-butanol/water mixture. Journal of Industrial and Engineering Chemistry. 2016; 44:155–163. https://doi.org/10.1016/j.jiec.2016.08.022

[23] Guo WF, Chung TS, Matsuura T. Pervaporation study on the dehydration of aqueous butanol solutions: a comparison of flux vs. permeance, separation factor vs. selectivity. Journal of Membrane Science. 2004;245:199–210.

[24]Sridhar S, Dhanuja G, Smitha B, Ramakrishna M. Dehydration of 2-Butanol by Pervaporation Through Blend Membranes of Chitosan and Hydroxy Ethyl Cellulose, Separation Science and Technology. 2005; 40: 2889–2908.

[25]Sekulic J, Elshof JE, Blank DHA. Separation mechanism in dehydration of water/organic binary liquids by pervaporation through microporous silica. Journal of Membrane Science. 2005; 254: 267–274. https://doi.org/10.1016/j.memsci.2005.01.013