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Microfiltration Performance of α-Alumina Membrane for Removal of Glycerol from Biodiesel

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Abstract. In biodiesel industries, the removal of glycerol from biodiesel is very important in the downstream process of the biodiesel production since the presence of glycerol in biodiesel causes diesel engine problems. Glycerol is commonly separated from biodiesel by extraction method using water, however, this method results in a vast amount of wastewater and requires a high energy consumption. In this work, a ceramic microfiltration membrane made of α-alumina was applied to remove glycerol from biodiesel. The microfiltration experiment was carried out using biodiesel containing various glycerol concentrations as the feed. For all investigated glycerol concentrations from 1000 ppm until 10,000 ppm in the feed, the membrane showed an excellent separation performance with rejection values of 91 to 99%. The profile of the permeate flux against the permeation time showed a flux decline because of the fouling phenomenon during the crossflow microfiltration experiment, and stable permeate fluxes were obtained after 2 h of permeation time. The result of this work showed that the separation process using the microfiltration membrane is a promising method to purify biodiesel instead of the conventional water washing method.

Introduction

In recent years, the demand of fossil fuels productions has increased because of the rapid growing of the global energy consumption. However, the combustion of fossil fuels contributed to around 70% of the total global greenhouse gas emission causing climate change and global warming [1]. Moreover, since fossil fuels are not renewable, the depletion of fossil fuels leads to the global energy crisis [2]. To mitigate the depletion of fossil fuels and its impact on the gas emission, substituting fossil fuels with renewable energy sources have become a prominent solution. One of the renewable fuels is biodiesel that can be used to replace the petroleum diesel or can be blended with the petroleum diesel to reduce the consumption of fossil fuel [3]. Biodiesel is very popular in many countries and usually produced through a transesterification reaction of vegetable oils with alcohol with the addition of catalyst [4]. There are international standards that must be fulfilled by biodiesel manufacturers. One of them is the content of glycerol which is the by-product of the reaction. The maximum limit of free glycerol content in biodiesel product is 0.02 wt% as regulated by the international standards such as EN 14214 and ASTM D6751. Problems in diesel engines such as injector fouling, and hazardous emission might occur due to a high amount of glycerol in biodiesel [5]. In most biodiesel plants, extraction using water (water washing) is commonly used to remove glycerol in biodiesel. The method is applied by adding water to the crude biodiesel to extract all impurities in biodiesel including glycerol [6]. However, this conventional method utilizes a high amount of water (3-10 L water per L biodiesel) that consequently resulting in wastewater and consumes a lot of energy for heating during the washing process [7-10].

On the other hand, membrane separation technology has been known as an effective separation technique because of the high selectivity of the membranes and the low energy consumption. It has been widely applied for separation and purification processes in various industries such as chemical, pharmaceutical, food and beverage industries, as well as water treatment and wastewater treatment processes [11]. Several studies reported the effectiveness of membranes such as microfiltration and ultrafiltration membranes for the biodiesel purification as an alternative method to replace the conventional washing method using water [12-16]. Porous polymer membranes can be used for biodiesel purification, but polymer membranes are usually of low chemical and thermal resistance. The use of ceramic membranes for biodiesel purification is desired since ceramic membranes exhibit a high chemical and thermal resistance [17-18]. Studies on the purification of crude biodiesel using ceramic microfiltration membranes were conducted by some researchers who reported that the membranes exhibited high rejection of glycerol with rejection values up ranging from 80 to 99%, however, the effect of glycerol concentration in the feed solution on the separation performance was not studied yet [13, 14, 15]. It is known that the glycerol concentration in the crude biodiesel ranges from 0.1 to 1 wt% [7] and the glycerol concentration in the feed may affect the separation performance of the membrane. Moreover, there were no reports on the analysis of the membrane microstructure that is crucial to explain the separation mechanism. In this study, a ceramic microfiltration membrane made of α-alumina was used to remove glycerol from biodiesel through a microfiltration process. The objectives of this research are to study the influence of the glycerol concentration in the feed solution on the microfiltration performance of the membrane and to understand the separation mechanism by studying the membrane microstructure.

Experimental

Microfiltration Experiment. The α-alumina ceramic membrane was a tubular membrane with an outer and inner diameter of 10 mm and 7 mm, respectively. The length of the membrane was 100 mm. The membrane was supplied by Nanjing Tangent Fluid Technology Co. Ltd., China. For the microfiltration experiment, the membrane was installed in a home-made microfiltration experimental set-up consisting of a beaker for the feed solution, a Masterflex pump, a control valve, and a pressure gauge installed at the retentate side. After installation, the effective membrane area of the membrane was 1.54 x 10^{-3} m^2. To study the permeation of biodiesel, first the microfiltration experiment was carried out using pure biodiesel as the feed. Then, the feed solution was changed with biodiesel containing glycerol and water with the weight ratio of glycerol and water of 1:2. The glycerol concentration in the feed was varied at 1000, 5000 and 10,000 ppm. The microfiltration was performed at an ambient temperature, while a trans-membrane pressure of 0.5 kg/cm^2 was applied and kept constant throughout the experiment. After attaining the steady state condition, the microfiltration experiment for each of the feed solutions was conducted for 120 minutes, and the permeate was collected every 10 min. Then, the permeate flux J was calculated with Equation (1) as follows:

$$J = \frac{V_P}{A\,\Delta t} \tag{1}$$

where V_P, A and Δt are the volume of the collected permeate, the effective membrane area, and the time interval, respectively.

Analysis of Glycerol Concentration. For the analysis of glycerol concentration in biodiesel, an analysis method proposed by Bondioli et al. was used [19]. Using this method, it was possible to measure the glycerol concentration in biodiesel using a UV-Vis spectrophotometer. The preliminary step of analysis included the preparation of working reagents and a calibration curve. Using the calibration curve, the glycerol concentration in the permeate samples could be determined. Then, the rejection value of the membrane towards glycerol was calculated using Equation (2):

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \tag{2}$$

where R, C_p and C_F are the rejection, the glycerol concentration in the permeate, and the glycerol concentration in the feed, respectively.

Flux Decline and Flux Recovery Ratio. The permeate flux decline through the membrane was measured by comparing the permeate flux of the feed solution biodiesel-glycerol mixture with the pure biodiesel permeate flux. The ratio of the flux reduction R_t was determined with Equation (3) [20]:

$$R_t = \left(1 - \frac{J_P}{J_1}\right) \times 100\% \quad (3)$$

Here, J_1 is the initial permeate flux using pure biodiesel as the feed and J_P is the permeate flux that was measured using biodiesel containing glycerol as the feed. After the membrane was used for the microfiltration of biodiesel containing glycerol, the membrane was cleaned using pure biodiesel that was circulated using a pump through the membrane for 60 min. Further, to study the effect of membrane cleaning on the flux recovery, the flux recovery ratio *FRR* was calculated using the equation below [20]:

$$FRR = \left(\frac{J_2}{J_1}\right) \times 100\% \quad (4)$$

where J_2 is the permeate flux of pure biodiesel after cleaning the membrane.

Microstructure Analysis. The analysis of the membrane microstructure was done to study the correlation of the membrane pore characteristics to the microfiltration performance. The analysis was conducted by using Scanning Electron Microscopy (SEM, Jeol JIB-4610F) and Brunauer-Emmett-Teller (BET) analytical instrument (BET Quantachrome Nova 4200e). The SEM analysis was conducted to study the visual microscopic image of the surface as well as the cross-section of the membrane, while the BET analysis was performed to study the surface area, the pore volume, the porosity, and the average pore size .

Results and Discussion

The result of the microfiltration experiment using pure biodiesel as the feed is shown in Figure 1. In the beginning, the alumina membrane showed unstable pure biodiesel permeate fluxes, then stable permeate fluxes were obtained after 60 min of the permeation time, indicating that a steady state condition was achieved with an average permeate flux of 245 L/(m^2h). Then, the feed was changed with biodiesel containing various concentrations of glycerol. The range of glycerol concentration in the feed was chosen between 1000 ppm and 10,000 ppm because this concentration range represents the glycerol concentration of crude biodiesel in most biodiesel industries before the wet washing method [7]. Figure 2 shows the permeate flux profiles within 120 min of the permeation time for various feed concentrations of 1000, 5000 and 10,000 ppm glycerol. For all feed concentrations, it was observed that the permeate flux decreased in the beginning of the permeation time, indicating that membrane fouling occurred. The membrane fouling is a very common phenomenon that occurs in separation processes using membranes and caused by the concentration polarization on the membrane surface and inside the membrane pores [21-23]. In the beginning of the experiment (at 10 min), the initial permeate fluxes were 247, 121, and 104 L/(m^2h) for the feed concentrations of 1000, 5000, and 10,000 ppm, respectively. However, after 60 min the permeate fluxes showed similar values for all feed concentrations due to the fouling phenomena. The permeate flux decline due to the membrane fouling is commonly expressed by the flux decline ratio R_t that can be calculated using Equation (3). Table 1 depicts the flux decline ratio R_t as a function of the glycerol concentration in the feed. The membrane showed a flux decline ratio of 58.5% for the feed concentration of 1000 ppm. The value of the flux decline ratio increased to 64.9% and 66.5% when the feed concentration was increased to 5000 and 10,000 ppm, respectively. The increase in the flux decline ratio with increasing feed concentration indicated that more glycerol molecules were deposited on the surface of the membrane or inside the pores, resulting in a higher resistance for the biodiesel to permeate through the membrane. The membrane was then washed using pure biodiesel and the permeate flux of the pure biodiesel was measured again to determine the flux recovery ratio using Equation (4). The result showed a flux recovery ratio of 55%, indicating that glycerol molecules remained as foulants in the pores of the membrane. The α-alumina membrane is categorized as a hydrophilic membrane since it is well known that hydroxyl groups are formed on the alumina surface. Glycerol molecules remained in the membrane pores because of the interaction between the glycerol molecules and the hydroxyl groups of the alumina membrane. Thus, for the future application of the membrane, it is necessary to use other cleaning methods such as physical or chemical cleaning to effectively remove the foulants [24, 25].

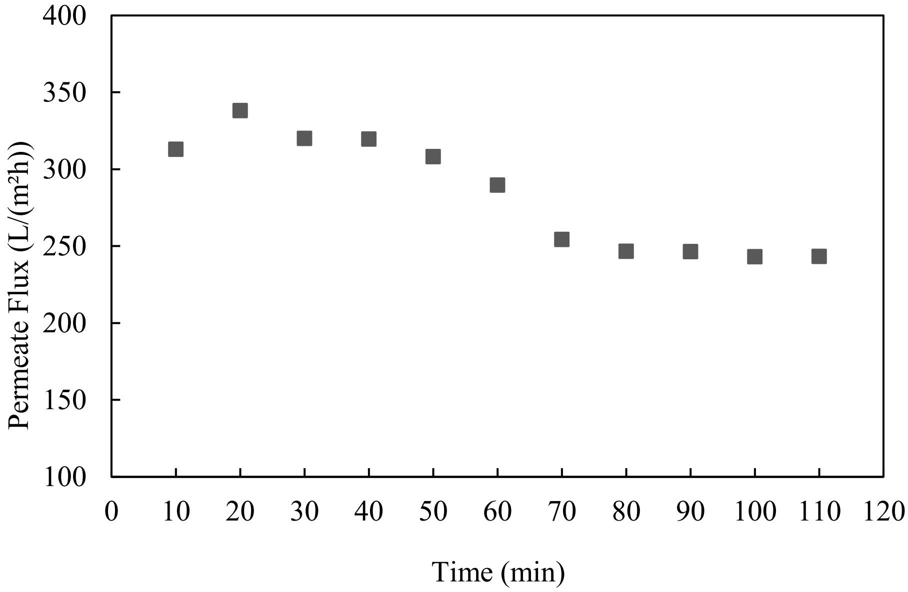

Figure 1. Permeate flux profile against permeation time using pure biodiesel as feed

Further, the glycerol concentrations in the collected permeate samples were analyzed using a UV-vis spectrophotometer and the rejection values were calculated. The results can be seen in Table 2. It was observed that the membrane exhibited very high rejection values for all feed concentrations. The rejection values of the membrane toward glycerol were 90.9%, 99.1%, and 99.3% for the feed concentrations of 1000, 5000, and 10,000 ppm, respectively. The increase in the rejection value with increasing feed concentration was also correlated with the membrane fouling and the flux decline ratio as described previously. It is interesting to note, that for all feed concentrations, the glycerol concentrations in the permeate samples were below 200 ppm (< 0.02 wt%), indicating the biodiesel purified with the alumina membrane fulfilled the international standards (e.g. EN 14214 and ASTM D6751) that limit the glycerol concentration in biodiesel product to be less than 0.2 wt%. Compared with other ceramic membranes as reported by other researchers, the α-alumina membrane used in this study exhibited higher permeate fluxes and comparable rejection values. Other study reported the performance of a ceramic microfiltration membrane for the biodiesel purification that showed steady state permeate fluxes ranging from 20 to 30 L/(m^2h) and a rejection value of about 80% for the glycerol concentration in the feed of 0.261 wt% [14]. Another ceramic membrane made of alumina and titania was reported to have steady state permeate fluxes ranging from 12 to 52 L/(m^2h) with a high rejection value of 99.6% for the glycerol concentration in the feed of 0.338 wt% [15].

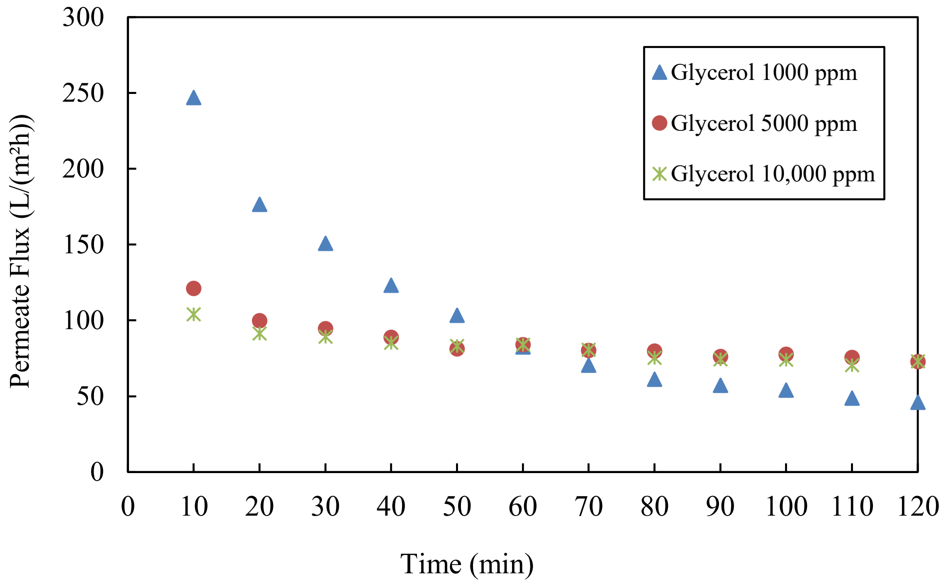

Figure 2. Permeate flux profiles against permeation time for various glycerol concentrations in feed

Table 1. Flux decline ratio of alumina membrane for various glycerol concentrations in feed

Glycerol Concentration in Feed C_F (ppm)	Initial Permeate Flux of Pure Biodiesel J_I [L/(m^{2}h)]	Average Permeate Flux using Biodiesel Containing Glycerol J_P [L/(m^{2}h)]	Flux Decline Ratio R_t (%)
1000	245.0	101.8	58.5
5000	245.0	86.1	64.9
10000	245.0	82.2	66.5

Table 2. Permeate concentration and rejection values for various glycerol concentrations in feed

Glycerol Concentration in Feed C_F (ppm)	Glycerol Concentration in Permeate C_P (ppm)	Rejection R (%)
1000	91.1	90.9
5000	44.3	99.1
10000	70.6	99.3

Further, the microstructure analysis was employed using the SEM method, which was done to be able to have the visualization of the surface and the cross section of the alumina membrane. The SEM analysis was conducted for the membrane cross section and the inner surface of the tubular membrane as the active layer. Figure 3 shows the SEM image of the cross section and the inner surface of the alumina membrane. It can be clearly seen that the membrane is an asymmetric membrane consisting of a supporting layer having large alumina particles and a thin active layer consisting of smaller alumina particles. The high permeate flux and the high selectivity in the separation of glycerol and biodiesel exhibited by this membrane was correlated with the asymmetric structure of the membrane that had a thin active layer with small pores, while the thick supporting layer consisted of larger pores. Further, the membrane was characterized for their microstructure by using a BET analytical instrumentation to study the surface area, the pore volume, the porosity, and the average pore size of the membrane. From the BET analysis, it was observed that the adsorption-desorption isotherm graph of the membrane showed the adsorption isotherm of type III based on the category by the International Union of Pure and Applied Chemistry (IUPAC), indicating a macroporous structure of the membrane with pore size of > 50 nm. The result of the BET analysis showed that the membrane had a surface area of 1.463 m^2/g, a pore volume of 0.11 cc/g, a porosity of 37.5%, and an average pore diameter of 0.29 μm. The separation mechanism in the microfiltration membrane is based on the difference between the pore size of the membrane and the particle size in the feed. In the case of biodiesel containing glycerol as the feed solution, biodiesel molecules passed through the membrane, while glycerol was rejected. According to the study conducted by Saleh et al., glycerol dispersed in biodiesel formed micelles with water and soap, and the size of the micelles are approximately 2-3 μm [14]. Thus, the glycerol micelles were rejected by the alumina membrane that had an average pore size of 0.29 μm.

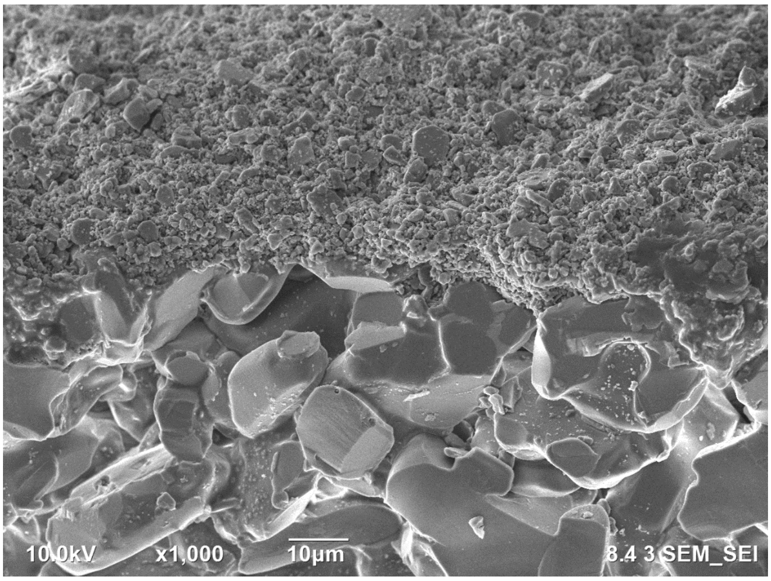

Figure 3. SEM image of the cross section and the surface of alumina membrane

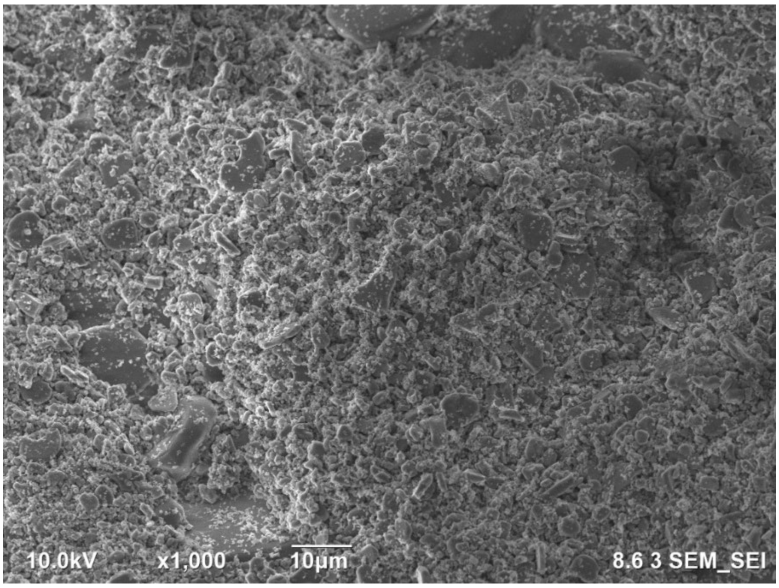

Figure 4. SEM image of the surface of alumina membrane

Conclusion

The results of the microfiltration experiments of biodiesel containing glycerol using the α-alumina microfiltration membrane showed that the membrane exhibited high permeate fluxes and high selectivity. The rejection values of the membrane toward glycerol were 90.9%, 99.1%, and 99.3% for the glycerol concentrations in the feed of 1000, 5000, and 10,000 ppm, respectively. The high permeate flux and rejection of the membrane was correlated with the microstructure of the membrane that consisted of a supporting layer with large pores and a thin active layer with smaller pores. For all investigated feed concentrations, the membrane exhibited glycerol concentrations in the permeates with values lower than 200 ppm (< 0.02 wt%), showing that the purified biodiesel met the international standards. The result of this work opens the possibility for the application of the ceramic microfiltration membrane for the downstream processing in biodiesel industries.

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