Separation of methyl ester from water in a wet neutralization process

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Abstract: The surfactant-water mixture generated from the industrial biodiesel (methyl ester) production washing process generates wastewater that is usually treated in a sludge pond by the addition of bacteria prior to being discharged into water courses. Nonetheless, the treatment is inadequate and it poses an ecological threat to the environment. Treatment of this mixture can take the form of conventional treatment methods for surfactant-water emulsions such as chemical, mechanical and thermal treatments. However, the disadvantages of such methods are low removal efficiency, operational difficulties and high operation cost. An ultra-filtration membrane can be used to separate water from the mixture, in spite of membrane fouling problems and a relatively low permeating flux. In this study, the membrane performances, inclusive of moisture contents in the recovered methyl ester, due to the types of membrane (hydrophobic or hydrophilic), cross-flow velocity and trans-membrane pressures are compared. The surfactant-water mixture used in this work was obtained from washing the palm-derived methyl ester (PME) with water during the product purifying processes from the biodiesel transesterification catalyzed with sodium hydroxide.

Keywords: Biodiesel-water separation, surfactant-water emulsion, hydrophilic, hydrophobic, micro-filtration membrane, ultra-filtration membrane, biodiesel oil, methyl ester

1. Introduction

Biodiesel is commercially produced by transesterification which entails the conversion of triglyceride (feedstock oil) to methyl esters (biodiesel) and glycerol (byproduct) in the presence of methanol and sodium hydroxide (NaOH) as catalyst. However, the problems of biodiesel in the downstream separation processes culminate when the free fatty acids (FFA) and water in this feedstock results in saponification and hence the production of soap in the presence of NaOH. The esters produced can also undergo saponification by hydrolysis in the alkaline conditions to form an alcohol and the salt of a carboxylic acid. The presence of FFAs can be a result of low quality feedstocks or oil contaminated by water condensation and exposure to air, resulting in oxidation, coupled with long storage time. A large amount of water is used to wash the impurities and soap in order to purify the methyl ester (biodiesel).

Wet washing of the produced biodiesel results in some emulsion consisting of dispersed soap particles formed from the neutralization reaction of the FFAs and sodium hydroxide as well as the soap from the saponification reaction at high resultant temperatures due to the leftover sodium hydroxide which acts to catalyze the reaction at a concentration of 0.5 mol/vol of catalyst to oil.

The objective of the membrane application is to reduce the quantity of water for washing the biodiesel as well as the oil content in the discharged water. Thus, it would improve product yield, reduce environmental impact and water consumption.

Conventional methods of biodiesel purification treatment utilize wet and dry washing. Wet washing is widely used to remove excess contaminants and leftover production chemical from biodiesel. This is done by spraying a fine water mist over the unrefined product, collectively removing the impurities as the water settles to the base of the wash container as effluent. This method is used because both glycerol and methanol are highly water-soluble. Residual sodium salts and soaps are water-soluble as well. However, the inclusion of additional water to the process offers many disadvantages, such as emulsions from high soap levels of high FFA feeds; poor separation and long separation time; loss of yield; effluent treatment translating into additional incurred disposal costs.

Dry washing involves an ion exchange resin or a silicone based adsorbent as Lastella et al. [1] used, such as magnesium silicate powder or Magnesol®, to neutralize impurities. This process eliminates the drying step, in spite of some yield losses, while reducing water usage and disposal costs. Nonetheless, the results gathered by Berrios et al. [2] showed that Magnesol and the ion exchange resins brought the glycerol levels down and reduced the soap content but not to the methanol and free glycerol levels required by EN 14214 Standard unlike wet washing. Soap removal was slightly influenced by the degree of agitation and can be completely removed by acidified water. However, none of the processes had any significant effect on acid value, glycerides or water content. Also, Karaosmanoglu et al. [3] came to a conclusion that the use of hot water washing at 50°C was an effective way to obtain a high purity (99%) and yield (86%) of the biodiesel product.

Membrane studies performed by He et al. [4], involved membrane extraction by slow dispersion through a hollow fiber membrane found that hydrophobic polysulfone hollow fiber membrane had the low refining losses and gave water content of about 0.042 wt % while the hydrophilic polyacrylonitrile membrane had refining losses of 10 wt % and a much higher water content of around 0.107 wt %.

2. Experimental

A surfactant-water mixture, having a volume ratio of 1:1, was prepared from unwashed palm-derived methyl ester (PME) produced from the biodiesel transesterification process with 0.5 mol/vol of sodium hydroxide as catalyst. Subsequently, the surfactant mixture results in an emulsion consisting of soap particles that are dispersed, trapping some methyl ester and causing the mixture to be more opaque.

The surfactant-water mixture was pumped across a flat membrane mounted on the test rig as shown in Figure 1. A finite cross-flow velocity was maintained on the membrane surface to prevent fouling. Two types of membrane were used - a flat micro-filtration mixed cellulose acetate polymeric membrane of 0.45 microns poresize from Advantec MFS, Inc. and a flat ultra-filtration PTFE polymeric membrane of 0.05 microns poresize from New Logic International Inc of part number #132157. The effective membrane area for both membranes was 3.38×10^{-6} m^2

and the membrane module used was from Tami Industries DISRAM 47mm membrane module.

The feed was pumped from a stainless steel recirculation tank to the membrane module. The recirculation tank was cooled by refrigeration in a water bath to maintain the mixture feed at constant temperature of 30°C. The methyl ester permeate which passes through the membrane is collected in a beaker as shown in Figure 1. The rejected fluid was treated as cross-flow which flowed along the membrane surface and back to the recirculation tank eventually. The transmembrane pressure (TMP) varied from 1.5 to 4.5 psi by means of a regulation valve. The value of TMP controlled the permeate oil volume flow rate (Q). The cross-flow velocity is calculated from the measured flow rate back to the recirculation tank. The experiments were conducted at 2 different flow rates of 670 ml/min and 800 ml/min, or approximately 1.3 m/min and 1.5 m/min of cross-flow velocities on the membrane surface.
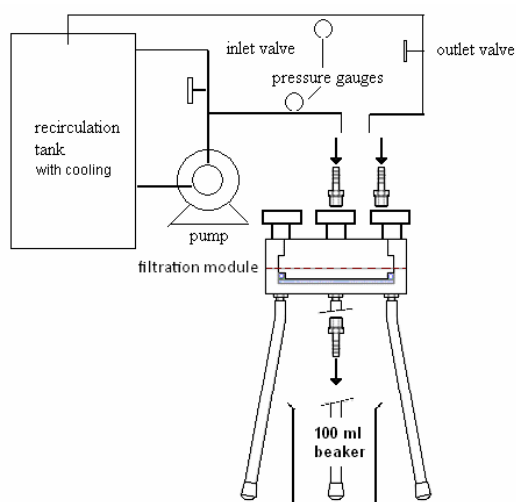

Figure 1. Experimental set-up schematic.

3. Results and discussion

3.1 Contact angle of fluids on membranes

The contact angle [6] of a drop of fluid on a flat surface, shown in Figure 2(a), is an indication of intermolecular forces between the fluid and surface material. If the contact angle of $\theta > 90°$, the surface is phobic to the fluid. If contact angle of $\theta < 90°$, it is philic to the fluid. In reference to Figure 3, the measured contact angle of distilled water on MCA membrane surface, $\theta = 70°$, while that on the PTFE membrane, $\theta = 100°$. These statistics showed that the PTFE membrane had better water rejection properties and was relatively more hydrophobic than the MCA membrane. On the other hand, the contact angle of the palm-derived unwashed methyl ester on the MCA membrane, $\theta = 27.64°$, while that on the PTFE membrane, $\theta = 27.07°$. The small difference indicated that both PTFE and the MCA membranes displayed good affinity for the methyl ester. Technically, the PTFE and MCA membrane are said to be methyl ester-philic.

Compared to the contact angle demonstrated by water ($\theta = 70° \sim 100°$) on the membranes and that of the methyl ester ($\theta = 27°$), the methyl ester exhibited better affinity to both the PTFE and MCA membranes.

Figure 2(b) shows a single fluid droplet on top of the membrane pores. On a philic membrane pore, the fluid drop was pulled into the pore passage by the surface tension. Little effort would thus be needed to push the fluid through the membrane pore. On the contrary, a fluid droplet on a phobic

membrane pore would be hindered from entering the pore passage by the surface tension. In this case, it would require a much greater force than a fluid droplet on philic pore, to force the fluid through the membrane pore.

The mechanism behind the methyl ester and water separation was believed to be attributed to the Gibbs-Marangoni effect [7]. Liquids with a high surface tension, such as water in the oil-water emulsion, pulled the surrounding liquids of the same type more strongly than liquids with a lower surface tension, such as methyl ester. This creates a surface tension gradient that causes the liquid to flow away from regions of low surface tension to regions of higher surface tension. As soon as the methyl ester comes into contact with the membrane surface, the methyl ester spreads and wetted the surface rapidly due to the better affinity property to the membrane surface. The rapid wetting of the membrane by the methyl ester forms a layer that repels water and the soap particles. The applied pressure then forces the methyl ester to permeate through the membrane pores while the supply of emulsion flow replenishes the methyl ester on the membrane surface. The soap micelles are expected to collide, deform and be repelled on the membrane surface.
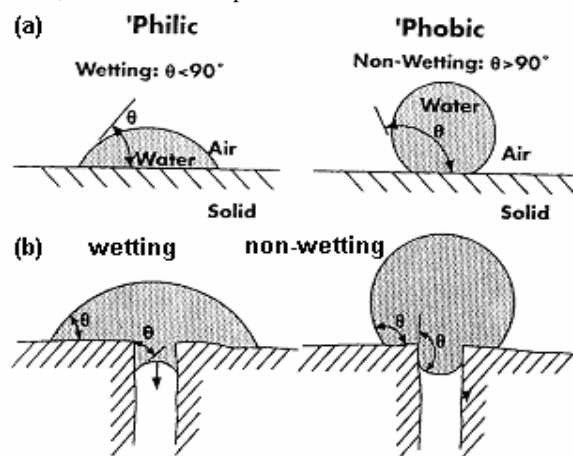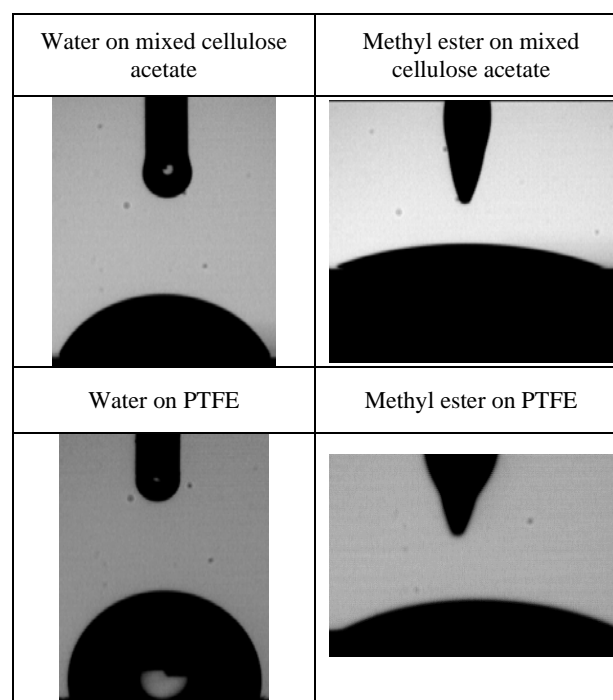

Figure 2. The water contact angle [3].

Figure 3. Contact angles [3] of water and methyl ester on the MCA and PTFE membranes.

3.2 Moisture and pH on oil permeate

The industrial standards required purified biodiesel to be < 0.05% of moisture by weight in order to satisfy EN14214 and ASTM6751 specifications. Table 1 shows that, given sufficient time to settle, the water and soapy later can be settled out of the permeate oil. This phenomenon can be attributed to the solubility of water in hydrocarbons, hydrophobic–hydrophilic forces in emulsions and interaction between membranes and emulsion [8].

Figure 4 indicates that when increasing the TMP, the moisture content mostly decreases in the case of the PTFE membrane while the moisture content remains more or less the same for a fixed flow rate for the MCA membrane. The effects of TMP on the moisture values were more significant for the PTFE membrane. At a low TMP of 0.75 psi and a single lower cross-flow velocity of 670 ml/min, a much higher moisture value was recorded for the MCA membrane, suggesting that a higher cross-flow value was effective in reducing the moisture content. However, a higher flux consistent with lower moisture values associated with higher TMP has a corresponding higher pH as can be seen from Figure 6. More soap particles pass through with poorer separation and hence a higher pH. The PTFE membrane had better ability in surfactant rejection as compared to the MCA membrane generally due to its smaller pore size and was less sensitivity to changes in cross flow velocity as Figure 4 depicts in the vertical drop portion at 0.75 TMP for the MCA. The first point of the PTFE curves was one conducted in a lower flow rate as well.

Figure 5 shows that a higher TMP corresponds to an increase in the methyl ester flux and subsequently, more hard soap passing through - higher pH. The PTFE membrane had better ability in the surfactant rejection compared to the MCA membrane generally due to its smaller pore size.

Table 1. Moisture and pH upon gravity settling

	Moisture (%)	pH
Retentate top layer after 1 day of gravity settling	1.104	6.5
Retentate top layer after 3 days of gravity settling	0.25	6.2
Retentate lower layer, primary emulsion which does not settle	too much for Karl Fischer settings	12.1

3.3 Membrane performance at low TMP

For low TMP of 1.5 psi on MCA, the repeated experiments showed that the reproducibility of the results was limited due to the sensitivity of membrane to different batches of methyl ester used. The poor reproducibility of the results were possibly due to the differences in the amount of sodium hydroxide from the feed methyl ester, therefore, better comparison could be achieved by using the same batch of unwashed methyl esters with the same pH. Nevertheless, it can be seen in Figure 6 that the permeate volumes were lower than that of using pure methyl ester. However the disparity in permeate volume between the pure methyl ester flow and the emulsified feed, 93 ml in 3 hours and 75 ml in 3 hours, respectively. This portrays the difficulty of separation with membrane application of the mixture.

As for the PTFE membrane, the cumulative permeate volume of the emulsified feed was generally lower than those using the MCA membrane. However, the membrane was less sensitive to the batches of methyl ester, as shown in Figure 7. This was probably due to the membrane characteristics - smaller pore size and strong water rejection. The great disparity in permeate volume between the pure methyl ester flow and the emulsified feed, 819 ml in 3 hours and 17 ml in 3 hours, respectively. The high pure methyl ester filtration quantity with low moisture content indicated that the PTFE membrane was extremely hydrophobic but methyl ester-philic. Comparing the

permeate volume of the two batches of feed after 4 hours of tests, the results from Experiment 1 had a sudden increase in permeate volume. This could be the result of the ageing of the mixture – likely the coalescence of oil drops in the emulsion at lower flow rates formed oil droplets of larger size.
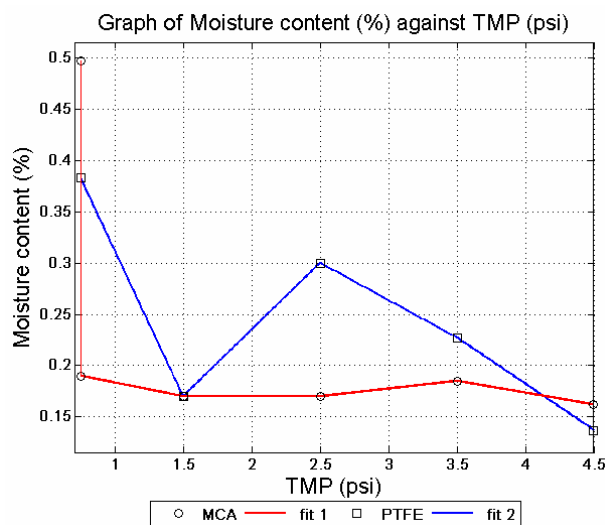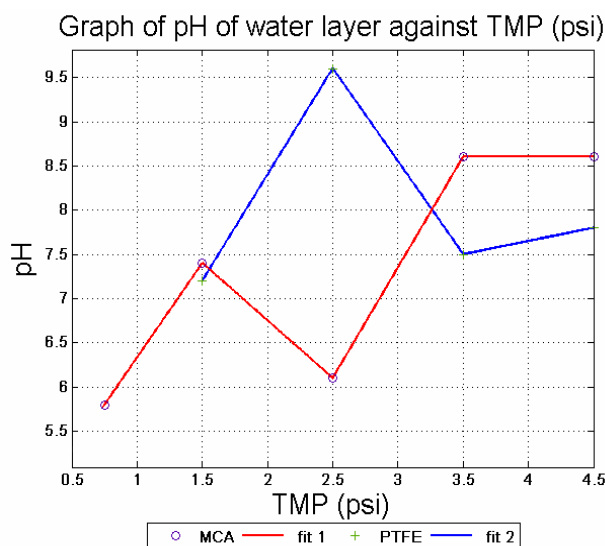

Figure 4. Graph of moisture against TMP.

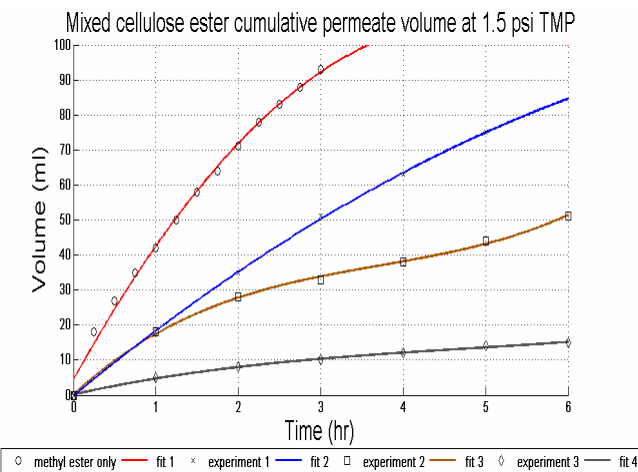**Figure 5.** Graph of water layer pH against TMP.

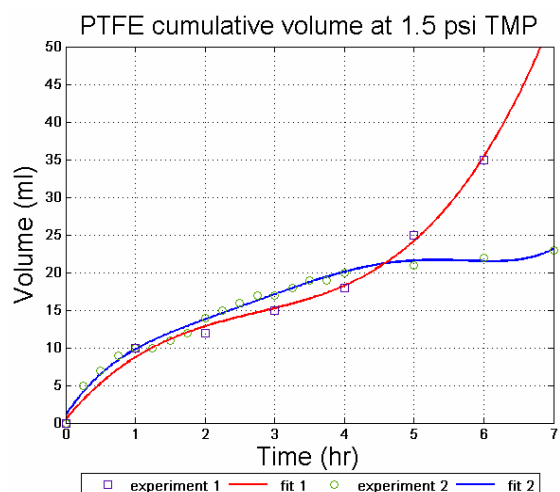**Figure 6.** Cumulative permeate volume for MCA membrane at 0.75 TMP.

Figure 7. Cumulative volume comparison of PTFE at 0.75 TMP.

3.4 Membrane performance at high TMP

The results of cumulative permeate volume conducted under different TMP using the PTFE membrane is shown in Figure 8. Generally, the permeate volume dropped due to the TMP increase. The low TMP promoted less backflow resistance (stronger cross flow velocity) and methyl ester was a more readily available in wetting the membrane surface. These effects promoted faster permeate rate.

However, when the TMP was raised from 3.5 to 4.5 psi, the said trend was reverted. The TMP to 4.5 psi likely attained the water intrusion pressure - pressure high enough such that the water and surfactant is forced through the membrane instead of only the methyl ester at lower TMP. Both the moisture content and pH value of the premeate methyl ester increased.

At low TMP of 1.5 psi, the permeate volume was twice the quantity from TMP of 2.5 psi. Raising TMP from 2.5 to 4.5 psi, the changes in the permeate volume was small in comparison with that from 1.5 to 2.5 psi. It implied that the TMP should be kept low for this application.

The results of permeate volume at various TMP using the MCA membrane are shown in Figure 9. The similar trend as the PTFE membrane was observed - reduction in permeate volume while raising TMP. However, the water intrusion pressure was 3.5 psi, lower than that of the PTFE membrane which was 4.5 psi. The permeate quality in term of moisture content and pH value dropped when TMP excceded the water instruction pressure.

It was interesting to note that the MCA membrane allowed lower quantity (56 ml in 4 hours) of methyl ester to pass through the membrane at TMP of 1.5 psi as compared with that (115 ml in 4 hours) of the PTFE though the former membrane pore size (0.45 µm) was 9 times larger than that (0.05 µm) of the PTFE membrane. These findings concurred with the fact that the hydrophilic membrane helped the water flux through the membrane while the olephilic membrane promoted greater flux for the oil–methyl ester.

4. Conclusion

In conclusion, a smaller pore membrane tended to have a higher water intrusion pressure than a large-pore membrane and thus a higher resistance to applied trans-membrane pressure.

It was discovered that the PTFE membrane with pore size 9 times smaller than that of the MCA membrane could have a higher methyl ester flux larger than that of the MCA membranes at low TMP. This showed how an olephilic membrane (or hydrophobic) could promote methyl ester permeate in the process of oil/water separation.

Based on permeate flux, the PTFE membrane operated better at low TMP. It was also better than the MCA membrane in view of the permeate flux and the likely soap and water contents of the permeate.
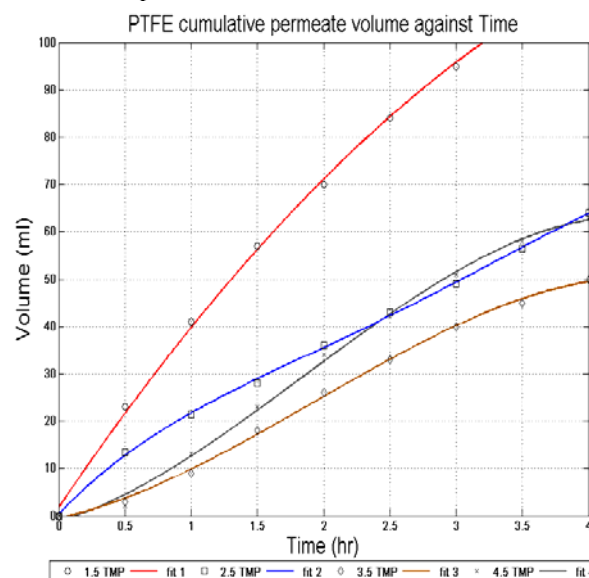

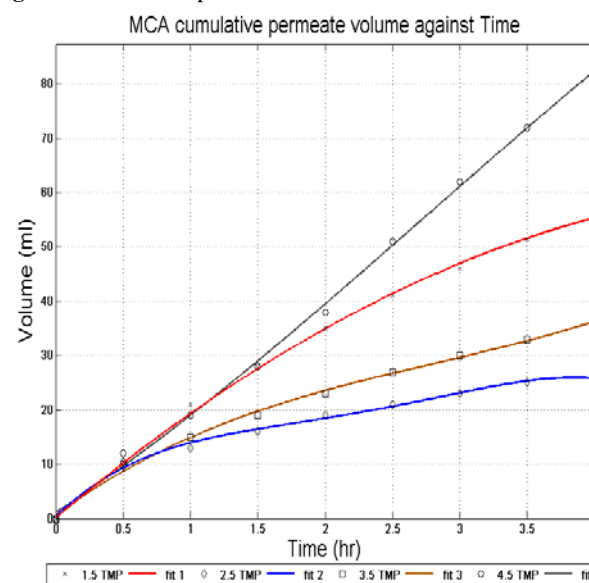**Figure 8.** Cumulative permeate volume at different TMP for PTFE.

Figure 9. Cumulative permeate volume at different TMP for MCA.

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