Preparation of Mixed Matrix Polymeric Membrane for removing of contaminants in Crude Biodiesel

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Abstract
The adsorptive membrane had been prepared successfully by embedding purolite particles on polymer chitosan employing phase inversion method. The obtained membranes were characterized and used to purify crude biodiesel from acid, soap-level content and total glycerol. The result has shown that the adsorptive membranes have an open porous structure and the purolite particle surface is available for adsorption of contaminants in which the optimum compositions of the adsorptive membranes were 3% (g/v) of chitosan, 15% (v/v) of DMF and 60% of purolite particles. The porosity and the swelling degree of the membrane were 42.83% and 51.95% respectively. The membrane of clean water flux was 254.4 $Lm^{-2}h^{-1}$ at the transmembrane pressure of 1 bar.

The obtained membrane has shown a good performance on capturing some contaminants in crude biodiesel. The highest adsorption capacity of the membrane could be obtained at 60 minutes of its contact time and the acid value in biodiesel was reduced from 1.07 to below 0.19 mg/g, agreeing with a standard value. The highest soap adsorption value was up to 78.57%, which was obtained by using the adsorptive membrane. The total glycerol can be reduced to be above 63.93% after biodiesel sample treatment with the prepared membrane. Finally, it could be noticed that the membranes can be reused for multiple adsorptions with a high adsorption capacity.

Keywords: Biodiesel, contaminant, mixed matrix membrane, purification.

Introduction

In line with world population growth, fuel consumptions for ensuring human life are increasing as well. Unfortunately, the fossil fuel resources are decreasing significantly. Therefore, in order to provide alternative fuel resources, many scientific works have been proposed to explore and search an alternative, renewable fuels in replacing the fossil fuels. Relating to this issue, biodiesel is a viable option, which is more environmentally and biodegradable, as an alternative renewable energy resources[1].

Most of common method used to make biodiesel is transesterification reaction. Fat or oil reacts with alcohol (methanol or ethanol) to produce fatty acid ethyl esters (FAME), or biodiesel which has the molecule size and property similar to diesel fuel. Although the ester is the desired product of the reaction, there are also some contaminants produced in the end of transesterifications. They are free fatty acids, glycerol, water, soap and the rest of the catalyst[2]. The slightly smaller contaminants can harm the machine and the environment; therefore, the product of the esterification reaction must be purified before it can be used as biodiesel. Impure biodiesel will lead to the degradation of engine lubricants, corrosion of injector and blockage of the fuel injector due to high soap levels. The product of methyl ester from transesterification can be classified as biodiesel to meet the quality standards, including: ASTM D6751 (North America), EN14214 (Europe) or SNI-04-7182-2006 to be sold in Indonesia[3].

Recently, separation and purification of biodiesel are considered to be a high cost process. There are various types of contaminants which have to be removed from mixtures before biodiesel can be used in order to meet the desired quality of biodiesel. Considering the economical aspect, the ideal biodiesel purification process should optimize its yield and maintaining low production costs. Almost all large-scale process configurations of biodiesel purification are based on water washing and dry washing. However, these methods have severe, major drawbacks and limitations[4].

In order to have a simple and economical method in purifying biodiesel, the water washing method has been one of the popular methods applied in many biodiesel industries. However, the biodiesel purification using the water washing method is posing some weak points, such as: high energy consumption, long time requirement and significant waste production. Therefore, the application of the adsorbent or dry washing method could be an alternative method to improve the efficiency of the biodiesel refining process. Compared to water washing method, dry washing method has several advantages in reducing water usage during purification process, shortening the process for the purification of biodiesel (up to 30 minutes) and reducing the formation of liquid waste significantly.

On the other hand, the used adsorbent might be regenerated for further purification[5]. Ensuring adsorption process will be taking place optimally in early stage of experimental. It should confirm that the adsorbent material should have a large surface area and is able to bind impurities to be removed. However, the application of the adsorbent column method has a drawback, among other sensitive columns, namely fouling and plugging, high-pressure drop, low throughput, time consuming and bed compression[6].

Recently, the membrane filtration methods are being developed for biodiesel purification. Membrane filtration methods also have the disadvantage of poor ability to eliminate all impurities in biodiesel. The developed and used purification methods are unable to eliminate the entire biodiesel impurities[4,7]. Taking concern on economic aspects, the biodiesel purification method should be economical, fast, reliable and recycled-indispensable in the biodiesel industry[8,9].

Therefore, to improve the quality of biodiesel, a more effective purification method in covering the weaknesses of previous purification methods is needed. A mixed method between adsorbent and membrane filtration methods is considered to be employed. The combination of these two methods would produce a reliable separation method because it can shorten the process of separation and purification, the maximum result in simpler, more economical and easier to scale up[6].

In this case, the membrane act as filter and absorbent at the same time, which means that this membrane is capable for filtering some impurities and simultaneously absorbing targeted compounds. Application of adsorptive membrane could be expected to be an alternative and efficient method which might be used for the purification of biodiesel from impurities. This membrane technology allows further development of biodiesel purification without washing with water[2,4,8].

Finally, in order to have an efficient and effective method in purifying the biodiesel, this work proposed preparation of polymer chitosan with an addition of cation exchange resin purolite by using a phase inversion method via evaporation process of the solvent. The produced membrane was characterized and applied in the biodiesel purification. This study provides an update on scientific information relating to a new separation method for biodiesel purification process.

Material and Methods

Materials: Chemical materials used in this study were chitosan, purolite, biodiesel, acetic acid glacial, dimethyl formamide, distilled water, sodium hydroxide, potassium hydroxide, ethanol, phenolphthalein indicator, bromophenol blue indicator, hydrochloric acid, acetone, chloroform, potassium iodide, sodium thiosulfate, hydrochloric acid, amilum, periodate acid and potassium dichromate.

Preparation and Characterization Adsorptive Chitosan Membrane: To obtain membranes with adsorptive properties, purolite ion exchange particles were added to a solution containing 3% (wt) of chitosan and 15% of dimithyl formamide in the solvent of acetic acid 1% (w/v), in which particles used were 60%. The solution is left and stirred for 24 hours until the entire purolite is mixed. The determination of the adsorbent amount mixed into the polymer (% loading) could be expressed using the following equation (1)[6]:

$$R_{loading} = \left[\frac{W_r}{W_{p+W_p}}\right] x\ 100 \quad (1)$$

where Wr refers to the amount of ion exchange resins (g) and Wp is the number of chitosan polymer in the casting solution (g). After the polymer solution is completely homogeneous, the solution is printed on a ceramic plate and the solvent is the object to evaporate until dry at room temperature for 24 hours. The membrane was washed with 1% NaOH, rinsed with water and then dried at room temperature. The obtained membranes were characterized and tested for adsorption capability.

Membrane Characterization

a. Scanning electron microscopy (SEM): The membranes were characterized by Scanning Electron Microscopy (SEM) with several times enlargement in Quaternary Geology Laboratory (PPGL), Bandung. The cross section was scanned as well as the top and bottom surfaces of the membrane.

b. Membrane porosity and swelling degree: The membrane porosity was determined by the water uptake of a calibrated volume of membrane. Average values were obtained from three different samples. The membrane porosity, ε and swelling degree, sd, were determined from the swelling experiments. The wet and dry membranes were weighed each three times. A micrometer of Mitutoyo was used to measure the thickness of the membrane. Porosity was calculated by equation (2)[6]:

$$\varepsilon(\%) = \frac{V_{membrane,wet} - V_{membrane,dry}}{V_{membrane,wet}} x100 \quad (2)$$

The swelling degree was determined by the volume of water compared to the volume of the dry membrane as in equation (3):

$$\varepsilon(\%) = \frac{V_{membrane,wet} - V_{membrane,dry}}{V_{membrane,dry}} x100 \quad (3)$$

where V_{dry} and V_{wet} are the volume of the dry membrane and the volume of the swollen membrane after 24-hour immersing in a water bath at room temperature respectively. Before weighing, the attached water was removed by dry padding the membrane with filter paper.

Biodiesel purification experiments

Contact time adsorption capacity Determination: The contacting time and adsorption capacities of the prepared mixed matrix membranes have been determined by batch experiments. The number of membrane materials with confirmed weight is introduced to biodiesel. The mixture remained under constant shaking in a sealed container in several room temperatures which are 10, 20, 30, 60 and 120 minutes. The concentration of the sample was determined before and after treatment. The adsorbed contaminant amount, q_{eq} [mg/g membrane], at equilibrium is calculated by equation (4):

$$q_{eq} = \frac{(C_0 - C_{eq})V}{W_{membrane}} \quad (4)$$

where C_0 is the initial contaminant concentration [mg/ml], C_{eq} is the contaminant concentration at equilibrium [mg/ml], V is the volume of the solution [ml] and $W_{membrane}$ is the weight of the dry membrane [g].

Regeneration and reuse of membrane: After the adsorption process, the mixed matrix membranes were regenerated by using methanol and ethanol. In practical application, the membrane was inserted into each Erlenmeyer flask containing ethanol and methanol. The mixture remained under constant shaking in a sealed container at room temperature for 1 hour. Then it was rinsed with distilled water and dried in an oven. Furthermore, the regenerated membrane was re-tested for its ability to purify crude biodiesel.

Analysis of biodiesel: Samples of purified and unpurified biodiesel were analyzed by inspecting its acid number, soap and glycerol total. The acid number analysis was performed according to AOCS Cd 3-63 (FBI-A01-03). The soap was determined with the method AOCS CC 17-19. The determination of total glycerol was performed according to AOCS Ca 14- (FBI-A02-03).

Results and Discussion

Membrane Preparation: Functional groups and adsorption properties of chitosan base membrane are made by incorporating the adsorbent into the polymer chitosan membrane. The purpose of the mixed matrix membrane is to create a membrane which has a high content of functional groups in order to have a maximum ability in adsorbing the target compound. However, the amount of adsorbent can be incorporated in the membrane influenced by the ratio of the number of adsorbent particles and the polymer is added in solution. The maximum loading of those particles that can be incorporated into a polymer membrane around 65% (wt), whereas more loading than 65% (wt) causes the casting solution very viscous and cannot be used in casting process of the membrane.

On the other side, a very high amount of the adsorbent may affect the mechanical strength and the morphology of the membrane. In this study, the chitosan concentration used was 3% (w/v) and the maximum loading of the adsorbent material was obtained at 60% (wt). The mixed matrix membranes were prepared containing purolite particles which possess sulfate functional groups (R-SO_3Na); a cation exchange resin which is confirmed by SEM-EDX results as shown in fig. 1(B) where the elemental composition of the purolite has been indicated. It could be described that in this study, purolit particles mixed into a solution of the polymer chitosan 3% (w/v) were dissolved in acetic acid 1% (v/v), added dimethyl formamide 15% (v/v) and then stirred for 24 hours at room temperature until the solution was homogeneous.

The morphology of the particles used in the membrane is shown in fig. 1. The SEM image shows that the particles of purolite have a porous structure. These particles exhibited the bigger particle size and the surface area of the adsorbent particles pulverized and sieved to a fraction with an average size of 100 mesh sieve. Images in cross sections and surface sections of prepared membranes are presented in fig. 2, in which the particles are dispersed well and held tightly together within the porous polymeric structure. Increasing particles amount in the polymer solution enhanced the viscosity of the solution and leads to the growth areas with less polymer and producing a membrane with a porous structure containing a small relative pore network.

The addition of the particles into the membrane will affect the porosity, the swelling degree and the thickness of the membrane. The characteristics of mixed matrix membranes obtained an increase in the swelling degree as a result of the ability of the particles to absorb water. Purolite mixed matrix membrane porosity increased to 42.83% and the swelling degree to 74.95%. Besides, the resulting membrane showed an increase in thickness as a result of the increased viscosity of the casting solution. The addition of dimethyl formamide as an additive can help the formation of porosity of the membrane. The obtained value of the clean water fluxes of the membrane was 254.4 L / m^2h at pressure of 1 bar.

Biodiesel Purification: Adsorption capability of the membrane was measured using bath system; the membrane is considered as an adsorbent material to remove same impurities contained in the biodiesel sample. It could be understood that biodiesel containing various impurities such as free fatty acids, soaps, glycerol and the remainder of the catalyst could be removed by employing the membrane adsorbent.

In evaluating the adsorption capacity of the membrane, the crude biodiesel was used as sample prepared from used cooking oil through transesterification reaction using alkaline catalyst (KOH). The quality of the initial crude biodiesel containing free fatty acids, soaps and glycerol are above the threshold allowed. Free fatty acid content is 1.07 mg KOH / g, 522.7 ppm soap levels and 0.6 total glycerol (% -wt). The threshold is used before applying a further purification process prior the biodiesel used as biofuel on the machine.

The contact time is required for adsorption of all impurities in biodiesel. Experimental results of studies showed that the optimum time for the optimum adsorption of free fatty acids, soaps and glycerol is different. In case of free fatty acids and soaps, they can be removed by 30 minutes of contacting time while glycerol has been adsorbed optimally at the contact time of 1 hour. The adsorption performance of the prepared membrane for free fatty acids and soap in biodiesel can be seen in fig. 3. As it can be seen that the concentration of the initial acid number is 1.07 mg/g in crude biodiesel and it was reduced to 0.19 mg/g after contacting with the membrane

adsorbent which is in line with the standards quality of biodiesel. Employing the mixed matrix membrane as adsorbent is significantly reducing free fatty acid from biodiesel where more than 84% of free fatty acid in biodiesel was removed successfully.

The optimum time for soap removal was obtained in 30 minutes in which the soap level in the initial biodiesel of 522.7 ppm was reduced to 120 ppm. The value is however still above levels of soap in ASTM standard, whereas the maximum value of the soap recommended by ASTM is 66 ppm. Fig. 4 shows how soap adsorption occurs significantly at the contact time of 30 minutes by removing 77.04% of soap. It can be noted that after running for 30 minutes in contacting between membrane adsorbent and biodiesel, the soap adsorption on membrane surface was saturated due to all adsorbent surface covered by adsorbed particles and the membrane was unable to bind all impurities which still existed in the biodiesel sample.

As mentioned previously, it could be assumed that various impurities in the biodiesel could be cleaned by adsorption process. The adsorptive membrane has an important role in absorbing total glycerol in biodiesel. Fig. 5 shows the result of total glycerol adsorption in the variation of the contact time. In this experiment, it is proven that the total glycerol in biodiesel was reduced from 0.61% to 0.23%-b in 60 minutes of adsorption time, which is equal to 62.29% of total glycerol adsorbed by the membrane in 60 minutes. The quality of produced biodiesel has matched with the standard of SNI 04-7182-2006 and in accordance with the standard FBI-A02-03 that is the quality standard of 0,24%-b.

It can also be informed that the ability of free particles of purolite to absorb the total glycerol was 72.13% at the optimum time, having been investigated. Moreover, the ability of chitosan membrane to adsorb glycerol total was 21.13% so that it could be assumed that the purolite particles possess high capacity to absorb the total glycerol compared to the pure membrane adsorbent. Combination of pure chitosan membrane with purolite particles can increase the membrane ability to absorb the total glycerol in biodiesel.

Regeneration and Reuse of the membrane: Regeneration process of the membrane was carried out to gain the state of the used membrane as its initial condition. The regeneration process was demonstrated by employing an organic solvent. The organic solvent used in this experiment was methanol (CH_3OH) and ethanol (CH_3CH_2OH) and it assumed that both of these two solvents are able to elucidate impurities having been adsorbed on the membrane surface.

In order to understand this possibility, fig. 5 shows the profile of the adsorption capacity for fatty acids by the adsorptive membrane after its regeneration. The value of the acid number decreased from 0.19 mg/g to 0.22 mg/g and 0.28 mg/g using methanol and ethanol respectively. Both solvents could not pull all the impurities existing on the membrane; however, regenerated membrane has enough capacity to adsorb impurities in biodiesel. The quality of the acid number in biodiesel after treated with regeneration membrane met the quality standard (0.8 mg/g).

Adsorptive membranes washed using methanol indicated a better ability to reduce soap levels compared to that of ethanol solvent. The different performance of the membrane adsorptive after treating with different solvent is due to the difference in polarity. Methanol is, however, more polar than ethanol so that the membrane capacity became higher when treated with methanol. On the other hand, it could be predicted that the free fatty acids and soaps existing polar side can interact better with methanol, otherwise the more polar compound is the better to be used as a solvent to wash any adsorbed components on the surface of adsorptive membrane materials. Considering the molecular size, the methanol size is also smaller than that of ethanol. Methanol can allegedly get into the pores of the membrane and bind the impurities attached to the membrane.

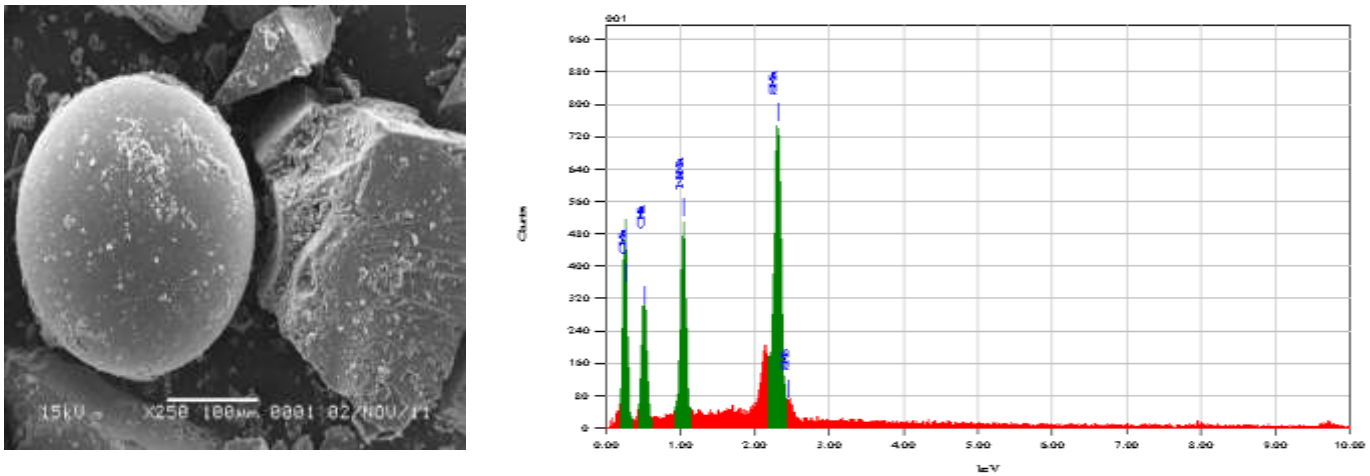

Figure 1: SEM micrograph of particle purolite by (A) SEM-EDX, magnification 250x (B) Purolite particles element composition.

Table 1
Element compositions of mixed matrix membrane incorporated with purolite particles

S. N.	Element	Mass%	Compound	Mass%
1	C	46,24	C	46,24
2	O	27,52		
3	Na	10,24	Na_2O	13,00
4	S	16,00	SO_3	39,96
	Total	100,00		100,00

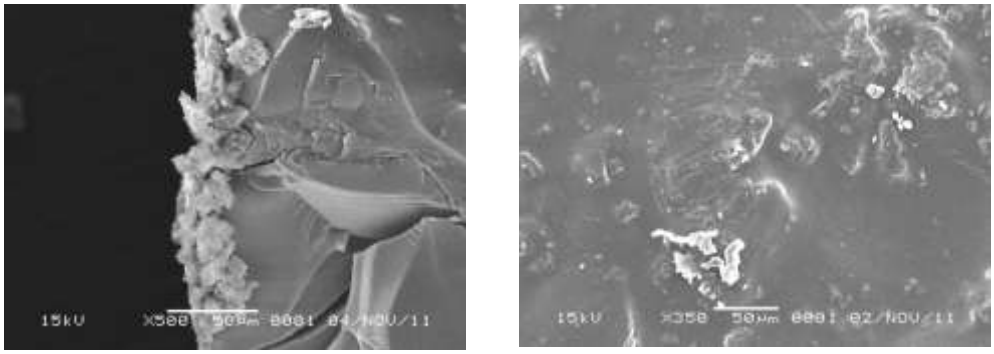

Figure 2: SEM micrograph of the membrane prepared out of a 3% chitosan, 15% dimethyl formamide, in 1% acetic acid solution containing 60% loading purolite. A). Cross section, magnification x500, the size bar indicates 50μm; B) Bottom surface, magnification x350, the size bar indicates 510 μm.

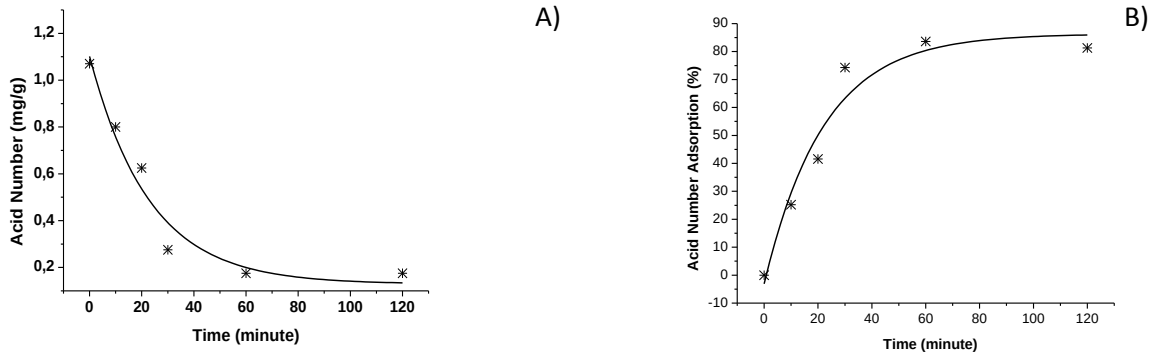

Figure 3: Free fatty acid adsoprtion in crude biodisel by purolite mixed matrix membrane. A) The content of acid numbers in biodiesel during the adsorption process by the mixed matrix membrane. B) The percentage of acid numbers in biodiesel which can be removed during the adsorption process by the mixed matrix membrane.

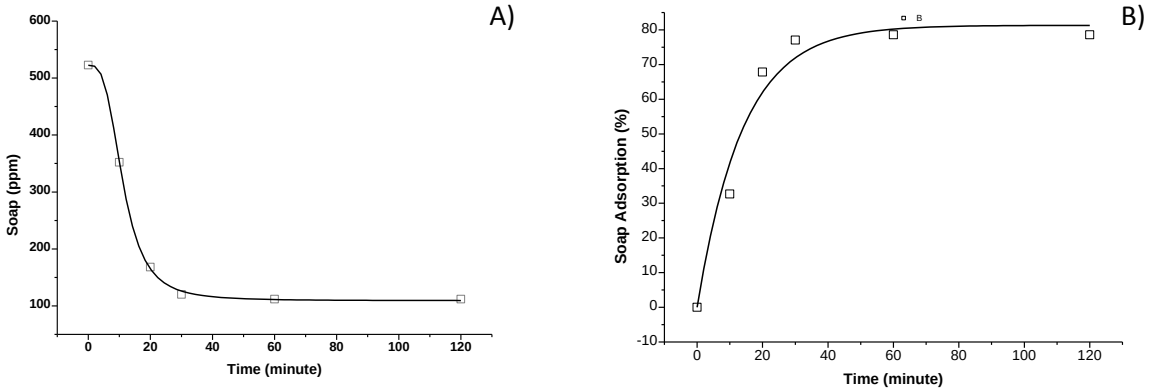

Figure 4: Soap adsorption in crude biodisel by purolite mixed matrix membrane. A) The content of soap number in biodiesel during the adsorption process by the mixed matrix membrane. B) The percentage of soap in biodiesel which can be eliminated during the adsorption process by the mixed matrix membrane

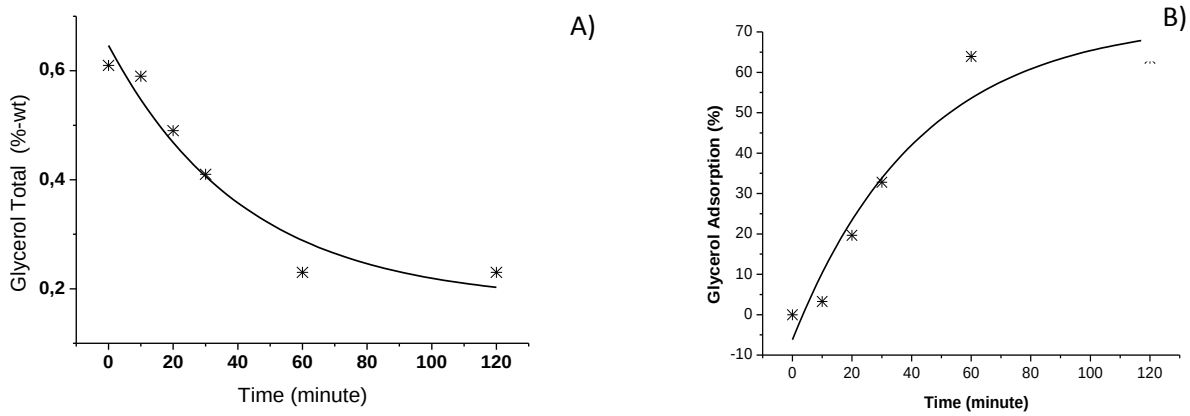

Figure 5: Glycerol adsoprtion in crude biodisel by purolite mixed matrix membrane. A) The content of total glycerol in biodiesel during the adsorption process by the mixed matrix membrane. B) The percentage of total glycerol in biodiesel which can be removed during the adsorption process by the mixed matrix membrane.

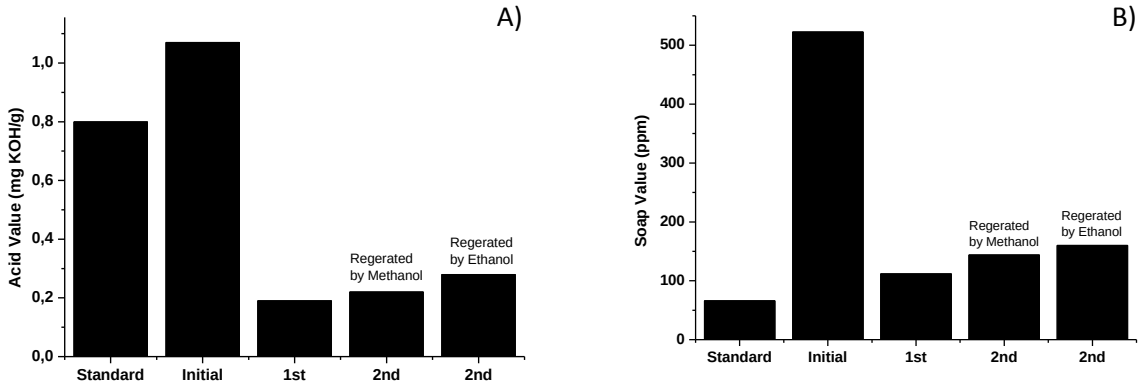

Figure 6: Use of Mixed matrix membrane repeatedly regenerated using methanol and ethanol to reduced (A) acid value and (B) soap numbers.

Conclusion

The adsorptive membrane has been contracted using the raw materials by integrating chitosan polymer with adsorbent. The adsoprtive membrane prepared with its optimum composition was 3% of chitosan, 15% of dimethyl formamide and 60% of particle purolite. The adsorptive membranes produced in this study have an open porous structure and exhibit the purolite particle surface which plays an important role for contaminated adsorption in biodiesel sample. Finally, the membrane showed a good performance to remove some contaminants in crude biodiesel, in which the high adsorption capacity was at 60 minutes of its contacting time. The acid value was reduced from 1.07 to below 0.19 mg/g, which is in line with the standard value.

The high soap of adsorption value of 78.57% was obtained by applying the adsorptive membrane as adsorbent and the total glycerol could be reduced above 63.93 %. In this study, we also observed that the prepared membranes could be reused for multiple applications with a high adsorption capacity.

Acknowledgement

We would like to acknowledge the Ministry of Education of the Republic of Indonesia for financial support on this research work under a Competitive Grant Research Program.

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