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PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

Abstract

Raw glycerin as a by-product of the transesterification process has low economic value and limited applications. Under this condition, purification of raw glycerin is required to increase the quality of glycerin. Membrane process using ultrafiltration membrane is an alternative to purify the glycerin. However, flux decline behaviour during the ultrafiltration process is a major limitation. In this research, flux decline, rejection, and blocking mechanism at various Trans Membrane Pressure, temperature, and pH were observed. Experimental runs was carried out at the variation of the transmembrane pressure/TMP (3,16 – 4,83 bar), temperature (51,63 – 68,36 ºC), and pH (6,32 – 9,67). The research showed that the flux decline was significant at all variation of the process parameter. This condition was caused by the presence of small size impurities such as Free Fatty Acid which can lead to clogging inside the membrane pore. Both TMP and temperature had no significant effect to flux decline. Rejection value was proportional to TMP and temperature while at pH variation the rejection was determined by the characteristic of impurities. Hermia's model was selected to analyze the blocking mechanism during filtration. It was confirmed that the mechanism was dominated by cake formation for all process parameters except for pH 7. At pH 7, the mechanism was controlled by intermediate blocking at an early stage and then followed by standard blocking. This research demonstrated that membrane separation via ultrafiltration process was capable of removing some impurities up to 68,33% for total impurities and up to 70,98% for the free fatty acid.

Keywords: Glycerin, Purification, Ultrafiltration, Fouling, Blocking Mechanism.

1. Introduction

Production of biodiesel generates crude glycerin as a by-product. It was reported that production of 10 kg biodiesel produced 1 kg of crude glycerin [1]. Crude glycerin from biodiesel production has low economic value since the glycerin product is mixed with impurities in its heavy phase. On the other hand, glycerin is raw material for many industries such as pharmacy, food, cosmetic, cigarette, automotive, textile or chemical industry. In addition, pure glycerin is potential for bio-lubricant, additive and an alternative fuel by adjusting the combustion cycle [2]. As a by-product, glycerin is found in its crude form (crude glycerin) which is contain many impurities and Matter Organic Non-Glycerol (MONG) at various concentration. Application of crude glycerin has many disadvantages, and high cost since it contains many contaminants such as water, inorganic salts and other organic materials (Free Fatty acid (FFA), Fatty Acid Methyl Ester (FAME/biodiesel), alcohol and tri-, di-,mono-glyceride) [3].

In general, crude glycerin is purified by distillation. However, the low vapour pressure of glycerin and its temperature sensitivity causes degradation or polymerization of glycerin, and hence vacuum distillation is applied more frequently than the normal distillation [4]. As a consequence, application of vacuum distillation is expensive due to the high energy requirement to create vacuum condition and evaporate glycerin [3,4]. Other purification processes such as adsorption, ion exchange, saponification, acidification, neutralization (pre-treatment), extraction and drying have been implemented to obtain high purity glycerin. Nevertheless, the usage of chemicals and energy requirement has a consequence of high cost.

Purification of glycerin by membrane technology has been developed and studied due to its ease of process and can minimize energy requirement by utilizing concentration difference, electron potential and hydroscopic pressure [4, 5]. One type of the membrane for purification or separation glycerin is Ultrafiltration (UF). Separation of glycerin from Fatty Acid Methyl Ester (FAME) by ultrafiltration and microfiltration ceramic membrane was studied [Saleh]. The research confirmed that the biodiesel met the ASTM Standard for glycerin content. a similar result was also found by Wang et al. [6]. Experiments focused on glycerin purification have been performed. Dhabbai et al. [3] investigated purification of crude glycerol using a sequential physicochemical treatment, membrane filtration, and activated charcoal adsorption. It was reported that result of maximum glycerol content was 97.5 wt% with acid value and free fatty acid (FFA) content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Other studies focused on the application of UF for glycerin model of glycerin separation. Amin et al. [7] evaluated UF fouling characteristic for filtration of mixture pure glycerin having 15% w/w and found that the flux decline involved cake layermodel as well as pore blocking model. In addition, separation of glycerin mixed with fatty acids (palmitic, stearic, and oleic acids) by Poyethersulphone (PES) ultrafiltration membrane was also studied [8]. It was reported that the PES membrane exhibited severe fouling for all types of fatty acids in solution with glycerol–water. Similar study by Amin et al. [9] investigated glycerin-rich fatty acid solutions confirming that the adition of fatty acid had an effect on significant flux decline. Mah et al [10, 11] studied on ultrafiltration of palm oil-oleic acid-glycerin mixture and evaluated the fouling mechanism, flux decline, fouling pattern and the UF performance.

2. Materials and Method

2.1. Materials

Raw glycerin supplied from Biodiesel Plant of PT SMART Tbk, Tarjun, Indonesia was used as a raw material. The raw glycerin composed of glycerin 38,53%, FFA 45,01% and MONG other than FFA of 16,47%. In this research, Polyethersulphone (PES) flat sheet UF membrane (Synder Filtration XV) having 1 kDa molecular weight cut-off was purchased from Sterlitech Corp, USA.

2.2. Ultrafiltration Membrane

Experimental runs were carried out by a laboratory-scale Ultrafiltration Cell equipped with compressor and instrumentation control as illustrated in Fig. 1.

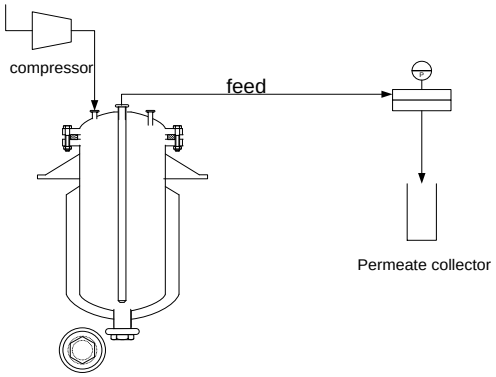

Fig 1. Schematic Illustration of Ultrafiltration Cell with control temperature.

Experimental runs were operated at room temperature (25 ± 2 °C). Before each run, membranes were first compacted by filtering distilled water through the membrane at a pressure of 1 bar for 60 minutes. For each experimental work, a new circular membrane sheet having area of 13.85 cm^2 was placed inside the ultrafiltration cell. Pure water flux (J_0) was determined for initial water characteristic. The pure water flux was evaluated by weighing permeate collected at a specific time. The permeate fluxes (J) was determined by measuring the volume of permeate collected at 5 minutes intervals for 120 minutes. Then the volumes of permeates were weighed (W). The flux was calculated according to (Eq. 1):

$$J = \frac{W}{(Axt)} \tag{1}$$

Permeate fluxes, and blocking mechanisms were observed by adding crude glycerin to the feed tank for half tank capacity. Further, the UF cell was operated at a dead-end mode at the variation of the transmembrane pressure / TMP (3,16 - 4,83 bar), temperature (51,63 - 68,36 °C) and pH (6,32 - 9,67). pH adjustment was conducted by adding a 0.1 N HCl or 0.1 N NaOH. Sampling for permeate flux determination was carried out every 10 minutes for 60 minutes.

2.3. Analysis

UF performance for glycerin purification from the feed solution was evaluated through the rejection of FFA and impurities. The rejection (R) was calculated using Eq. (2).

$$R = \left(1 - \frac{C_p}{C_f}\right) x100\,\% \quad (2)$$

The composition of permeate was analyzed by using Gas Chromatography (Shimadzu TQ8030).

3. Model of Blocking Mechanism

Hermia's model defined the fouling mechanism especially in the porous membrane with dead-end system filtration. In more specific, the model highlighted the fouling mechanism which dominates in the entire of the process. This model applied a common power-law equation to describe the blocking mechanism and written in equation (3) [10,12].

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (3)$$

complete pore blocking illustrates that each solute is assumed to participate in blocking the entrance of the membrane pores completely. With the assumption that every solute stays on previously deposited solute, it is represented of intermediate pore blocking. Standard pore blocking describes that each solute is deposited to the internal pore wall. Determination based on the accumulation of the solute on the membrane surface is representative of cake/ gel formation [7]. Further, linearization of blocking mechanism according to equation (1) is presented in Table 1.

Table 1. Linearization equation of blocking models based on Hermia's model [13]

Pore Blocking Models	*Linearization Equation*	*Physical Concept*
Standard Blocking	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore Blocking + Surface Deposit
Intermediate Blocking	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore Constriction
Complete Blocking	$\ln J = \ln J_o - K_c t$	Formation of surface deposit
Gel/Cake Formation	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore Blocking

4. Results and Discussion

In this paper, flux decline, rejection, and the blocking mechanism were observed in various variations of process parameters such as Trans Membrane Pressure (TMP), temperature, and pH. For flux decline study and blocking mechanism, filtrate flow in dead-end filtration module was observed for 60 minutes, and then the filtrate was sampled every 5 minutes. Collected filtrate was then analyzed for its composition. The composition data were used to determine the rejection of impurities (FFA and MONG) in raw glycerin.

4.1. Flux decline and rejection

4.1.1. Effect of Trans Membrane Pressure (TMP) on permeate fluxes

Ultrafiltration process is one method to separate substances which have different of molecular size using Trans Membrane pressure (TMP) as a driving force. The fluxes increase along with the increase on TMP indicating that the flux is proportional to TMP. This finding was supported by Kim and DiGiano [14]. Fig 2. shows the flux response against the TMP. Generally, the flux decline over the time is caused by the impurities deposited on the surface and inside pore of the membrane.

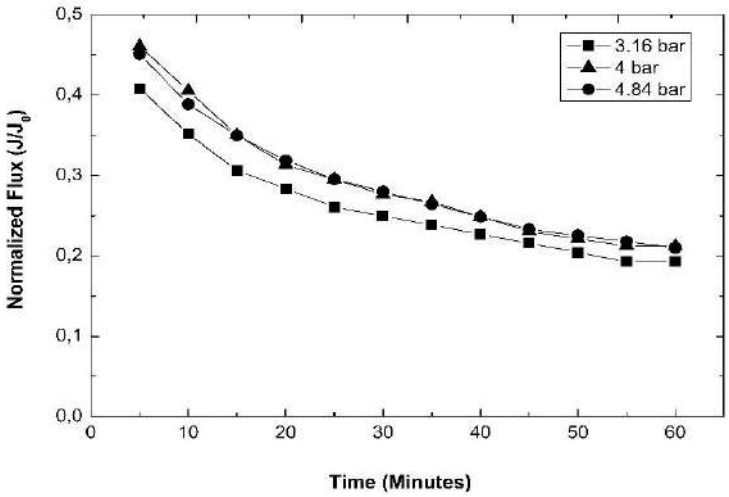

Fig 2. Influence of TMP on fluxes of glycerin-rich solutions.

The figure confirms the correlation between flux and TMP wherein increasing on TMP causes an increase in the flux. The higher normalized flux at higher TMP is achieved at a pressure range of 3,16 – 4 bar. In contrast, at a range of 4 – 4,84 bar, the effect of adjustment TMP on the positive impact on the flux is not significant indicating that the TMP has a slight impact on increasing flux. Adjusting TMP to the higher point actually lead to an increase in flux but it still cannot affect the pattern of flux decline. This is confirmed by the flux decline pattern in Figure 2 showing similarity pattern at the various variations of TMP. A significant flux decline in the early stages of the UF process a range of 0 – 25 minutes and then

continued with the stationary states of flux decline at a range of 30 – 60 minute are observed. This phenomenon indicates that the process more influenced by mass transfer mechanism than by TMP its self [12]. According to the phenomenon, when the TMP is set to a higher point, it directly affects the increase of the flux. This leads to a more severe condition of flux decline as the result of increases in deposits and impurities quantity. The impurities carried away by the glycerin-rich solution that flows through to membrane matrix and presumably deposited both on membrane surface as well as inside the pore of the membrane [9,12].

This phenomenon is conceivable because of the nature of the raw material (glycerin) and the majority of impurity (FFA) in raw glycerin. Glycerin has high viscosity, and it is much different from Newtonian fluids such as water. The high viscosity of glycerin causes the molecular arrangement in glycerin has more limited spatial molecular space. Besides that, the properties of FFA tend to be hydrophobic and insoluble in polar compounds. The hydrophobic characteristic is on the contrary to the hydrophilic properties of the membrane properties used in this study. It is accomplished that hydrophobic properties of the impurity (FFA) can increase repulsion forces on the membrane which ultimately influences the flux trend that occurs during the filtration process (mass transfer mechanism).

4.1.2. Temperature effect on permeate fluxes

Effect of temperature on flux decline is presented in Fig. 3. Observations show the temperature has more influence than the TMP on the flux decline qualitatively. The condition occurs because increasing the temperature can directly trigger the viscosity reduction. This makes the fluid more freely to flow as a result of increasing in molecular spatial space in higher temperature condition [15]. In addition, increasing the temperature can lead to an increase of the polymer bonding mobility inside the membrane matrix [9,16]. Hence, the resistant that caused by both fluid and membrane against each other reduce with increasing of the temperature.

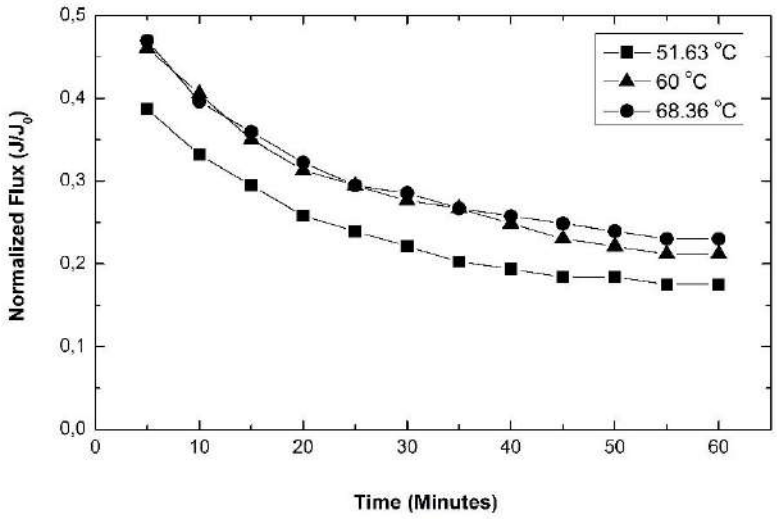

Fig 3. Influence of temperature on flux decline of the glycerin-rich solution

In addition, Fig. 3. shows the trend of flux response against temperature indicating that at a range of 51,63 ºC – 60 ºC, the increasing temperature has a positive effect towards the flux. On the contrary, in a range of 60 ºC – 68,36 ºC the effect of temperature is insignificant. Dhabhai et al. [3] found that the temperature does not influence the decrease of the raw glycerin viscosity at temperatures above 60 °C. Although the viscosity of glycerin which can directly affect fluid resistance to the membrane can be reduced, it does not have a positive effect on the pattern of flux decrease as shown in TMP. This condition denotes that characteristic and properties of impurity (FFA) plays a key role in the pattern of flux decrease. Moreover, the flux can directly increase along with decreasing in viscosity which can lead to increasing of impurities concentrations both on the surface and inside pore of the membrane. This phenomenon also confirms that the process is dominated by the mass transfer mechanism.

4.1.3. Effect of pH on permeate fluxes

Fig. 4 shows the responses of flux against different pH condition. The pH was observed in a range of 6,33 – 9,67. The results show that the flux decreases the acidic state is greater than in the alkaline state. Fatty acid as impurities which is contained in a glycerin-rich solution has the nature that remained as the undissociated molecule in the presence of an acidic environment. Fatty acid molecules can interact with acid to form the larger molecules via an agglomerate process with another molecule of fatty acid [8, 10]. The larger molecule that was formed can increase the adsorption of foulant molecule. The adsorption is formed on membrane surface as well as on the entrance of the membrane pore and then causes high flux decline and membrane fouling [8,17-18]. Sequentially, the flux decline follows the order of pH 7> pH 6,33> pH 9>pH 8 and the highest flux decline is found at pH 7. The pH 7 has higher flux decline than that at pH 6,33 which is

related to dissociation and undissociation effect where the pH 7 should have lower flux decline. The condition is most likely due to the fatty acid state that not fully undissociated at pH 7. This causes clots of some molecules is not formed and still at single molecule form. The single molecule of fatty acid can pass through into membrane pore since the average size of the single fatty acid molecule is four times smaller than the membrane pore size and triggers the blocking inside the wall of membrane pore. Irregularities also occur at pH 8 where the flux decline is smaller than the flux decline at pH 9. The reason for this phenomenon may due to the dissociated molecules of fatty acids (at pH 9 the fatty acid molecules almost completely dissociate) blockage the micropores of the membrane. The blocking at micropores is possible in PES-based UF membranes because it is an asymmetric porous membrane [19].

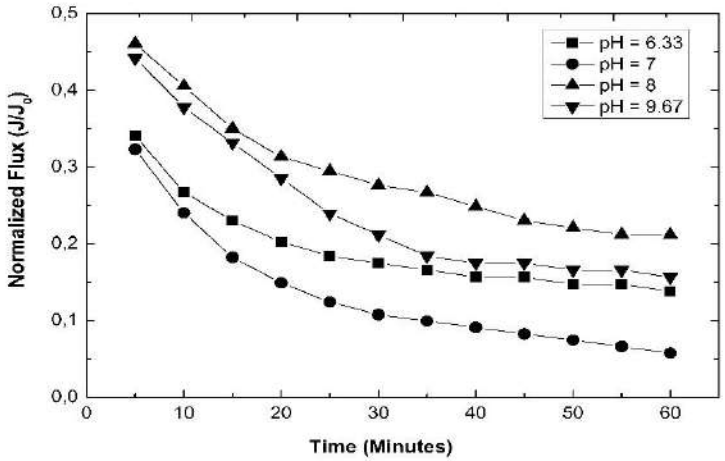

Fig. 4. Effect of pH on Flux decline of glycerin-rich solutions

4.1.4. Rejection

The impurities rejection data is given in Table 2.

Table 2. Summary of rejection data in various variations of process parameters.

No.	Pressure (bar)	Temperature ˚C	pH	Rejection (%)	
				FFA	Total Impurities
1.	3,16	60	8	48,10	48,50
2.	4	60	8	54,17	32,11
3.	4,84	60	8	57,63	52,86
4.	4	51,63	8	44,32	33,25
5.	4	60	8	54,17	32,11

6.	4	68,37	8	45,35	43,56
7.	4	60	6,33	30,70	21,18
8.	4	60	7	70,98	68,33
9.	4	60	8	54,17	32,11
10.	4	60	9,67	25,82	24,22

The Table shows a different trend in each variation of the operating condition. For TMP variation, the rejection increases with increasing on TMP. The rejection of FFA content in the filtrate at 4,84 bar and 3,16 bar are 57,63% and 48,1%, respectively. This condition takes place because in higher TMP some small foulant molecules may be penetrated into the membrane pore and form a deposit, thus causing a shrink on the size of membrane pore which leads to an increase in rejection of impurity. For temperature variation, the trend of rejection has a tendency to be similar to TMP variation where higher temperature process has greater rejection than lower temperature. The rejection of impurities is 33,25% at 51,63 ^{o}C while at 68,37 ^{o}C the rejection reaches 43,56%. This is likely due to the effect of increasing temperature which can directly affect the increase in flux and causes an increasing the impurities that flow through the membrane pore. It is similar to the condition that occurs in TMP variation. Rejection behaviour at pH variation has a different kind than the other operating parameter. The highest result is 70,98% at pH 7, and the lowest result is 25,82% at pH 9,67. This behaviour may occur due to the nature of the impurities, as described in section 4.1.3.

4.2. Blocking Mechanism

The constant of blocking mechanism and the corresponding correlation coefficients (R^2) during filtration is listed in Table 3. According to the Table, increasing on TMP reduces the flux decline. Its condition also applies to temperature as confirmed by the smaller value of the constants along with increases of TMP and temperature. Cake formation is predicted as a dominated blocking mechanism during the filtration process for both TMP and temperature variations. In the cake formation, the foulant is firstly adsorbed on the membrane surface, penetrate into the membrane pore and then form a layer that can cause a more severe decrease in flux even from the early step of filtration. The fatty acid may be the component responsible for severe fouling [7]. In biodiesel industries, glycerin was a by-product from the transesterification reaction which consists of palmitic acid (C16: 0), stearic acid (C18: 0) and most of the oleic acid that has double bond carbon chain (C18: 1) [20].

Table 3. Fitted Hermia's model for various process parameters.

Parameters	n = 0 cake formation		n = 1 Intermediate blocking		n = 1.5 Standard blocking		n = 2 Complete blocking	
	k_{cf}	R^2	k_i	R^2	k_s	R^2	k_c	R^2
Pressure								
3,16 bar	0,4098	0,9848	0,0585	0,9031	0,0164	0,8171	0,0191	0,7051
4 bar	0,3508	0,9891	0,0546	0,9291	0,0159	0,8588	0,0192	0,7613
4,84 bar	0,3400	0,9920	0,0532	0,9249	0,0155	0,8499	0,0187	0,7483
Temperature								
51,63 ˚C	0,5329	0,9782	0,0692	0,9026	0,0185	0,8204	0,0208	0,7084
60 ˚C	0,3508	0,9891	0,0546	0,9291	0,0159	0,8588	0,0192	0,7613
68,36 ˚C	0,2872	0,9737	0,0476	0,8892	0,0142	0,8136	0,0176	0,7184
pH								
6,33	0,4090	0,9840	0,0580	0,9030	0,0160	0,8170	0,0190	0,7050
7	4,4480	0,9187	0,2468	0,9917	0,0453	0,9557	0,0365	0,8307
8	0,3400	0,9920	0,0532	0,9249	0,0155	0,8499	0,0187	0,7483
9,67	0,6982	0,9742	0,0862	0,9443	0,0225	0,8935	0,0247	0,8068

In addition, Table 3 shows the value of k (constant) at acidic state that tends to be higher than in alkaline state. It demonstrates that the resistance of the fluid to the membrane is larger and causing more severe fouling than in alkaline state. The nature of fatty acids which is in undissociation at acidic environment may be responsible for that condition. Under this environment, the fatty acid would be clumping each other. Mah et al. (2012) reported that the droplets of a mixture of palm oil and oleic acid at pH 2 (very acidic condition) lead to significantly increase in droplet size and even reach twice in size over the original droplet size. Therefore, setting pH under acidic conditions can lead to agglomeration of foulant molecules.

Fig. 5. exhibits the blocking mechanism that occurs in the various variations of pH. Generally, the mechanism is dominated by the cake formation, except for pH 7 as supported with the highest R^2 value for pH 6,33; 8; and 9,67. The similar result was reported by Amin et al. [7] and Mah et al. [11] confirming that cake formation was the dominant mechanism in pH variation. The different condition at pH 7, as seen in the value of k (constant for blocking mechanism) is much greater than another pH. Moreover, the highest R^2 value in the intermediate blocking mechanism is found. Fig. 5 (b) and fig. 5 (c) confirm that in the initial conditions of filtration until 10 minutes, both intermediate blocking and standard blocking mechanism occur. Then, in 15 minutes until 45 minutes only the intermediate blocking mechanism is observed, and for 50 minutes afterwards only standard blocking contributes to the flux decline. In intermediate blocking, the solutes/particles which accumulated on the membrane surface and on the entrance of membrane pore is possible to overlap another solute that has already deposited on the membrane surface. The foulant is then pile up each other in irregularity

arrangement [7] and trigger other mechanisms such as standard blocking to occur during the filtration process. Standard blocking mechanism is believed to be responsible for a significant flux decline as in that condition the impurities molecule penetrates to the inside wall of the membrane pore and make a deposit which can be lead to plugging on the active area of the membrane pore [21,22]. This strengthens the evidence that fatty acids which are still dissociated at pH 7 entering the pore and causes blockages in the membrane pore.

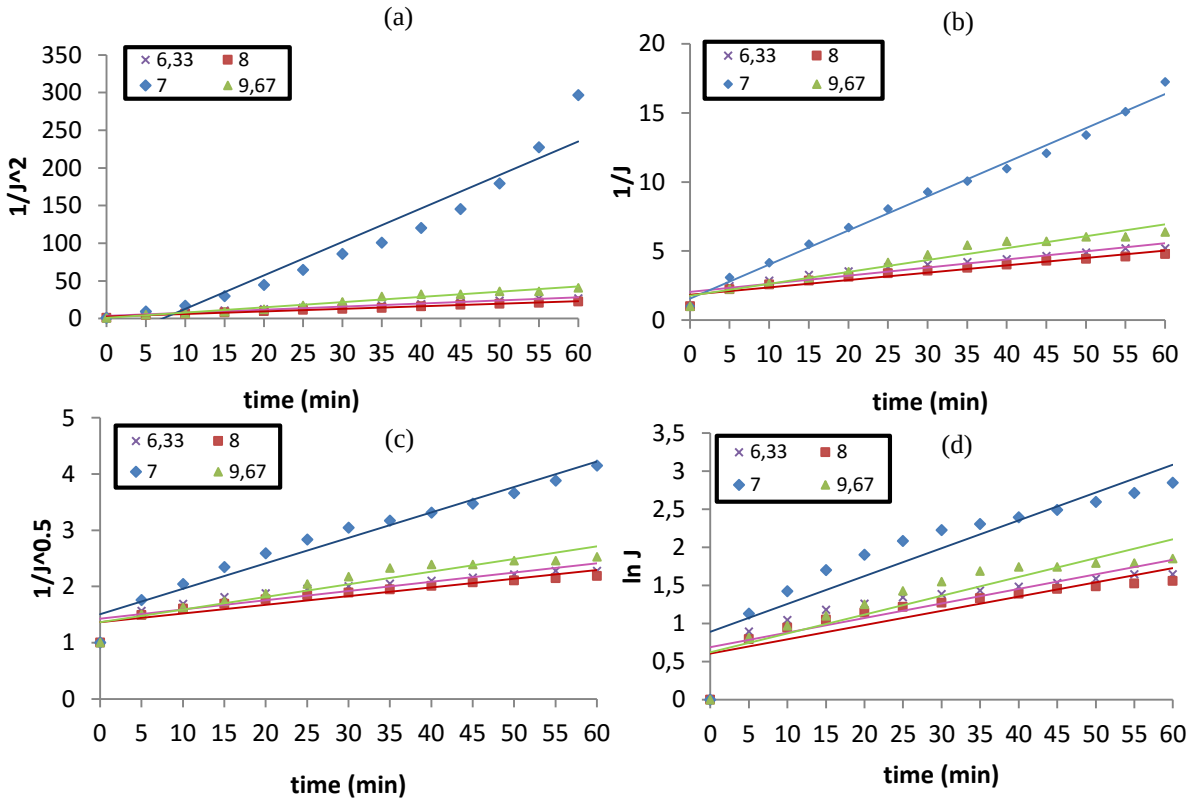

Fig. 5. Hermia's model fitting for the experimental data: (a) Cake formation, (b) Intermediate blocking, (c) Standard blocking, (d) Complete blocking

At high pH, especially for pH 9 above, the fatty acid molecule is fully dissociated and become surfactants with a negative charge with a hydrophilic head and hydrophobic tail. If there is an interaction between fatty acids and membranes, it forms a negative charge induction to the membrane. Thus the repulsive force between the fatty acid and the membrane may change. It conditions also can cause changes in fluid resistance to the membrane [8].

5. Conclusions

The study of flux decline, rejection and blocking mechanism during UF process using 1 kDa PES membrane with various variations process parameters (TMP, T, and pH) to the glycerin-rich solution (raw glycerin) from the biodiesel industry were conducted. Some concluding observations from the investigation are given below.

- It was found that flux decline was severe significantly in all variation of process parameter due to a deposit of impurities.
- Both pressure and temperature did not give significant effect to the flux decline due to dominating of the mass transfer mechanism which is caused by the nature of impurities its self.
- Both pressure and temperature had a similar trend of rejection that in higher process parameters the rejection becomes greater, whereas at pH variation behaviour of rejection is determined by the nature of impurities.
- Hermia's blocking law model found to fit well to the experimental data. The best-fit experiment data was cake layer formation mechanism for all process variation except for pH 7 where the intermediate blocking takes the lead in early stages and then followed by standard blocking.

Nomenclatures

C_f	Concentration FFA/impurities in the feed, ppm
C_p	Concentration FFA/impurities in the permeate, ppm
J	Permeate Fluxe, L/m^2. hr
J_0	Initial Flux, L/m^2. hr
R	Rejection, %
k	constant of blocking mechanism
n	value that represents a blocking mechanism, n = 0 (cake layer formation), n = 1 (intermediate blocking), n = 1.5 (standard blocking), and n = 2 (complete blocking).
R^2	the corresponding correlation coefficients
t	filtration time (h)
V	permeated volume (L),

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Nita Aryanti <nita.aryanti@che.undip.ac.id>

Paper ID CE19004 /Review of a paper, First Round Result with Rejection/

2 messages

Jestec <Jestec@taylors.edu.my> Sun, Jun 2, 2019 at 10:25 AM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

Dear Author

The **first round** of the review process has been completed.

5 reviewers have reviewed your paper.

3 accepted with minor corrections **1** accepted with major modifications, but **1** rejected your work

The Review panel decision is to conditionally accept the paper with Major Corrections.

This is to give you opportunity to improve the quality of your paper to be up to a journal article level.

Attached herewith, please find one/two/three/four/five/six reviewers' reports.

Please notice the following:

1- Address all the concerns/recommendations of the reviewers

2- All additions/corrections are to be highlighted in red color in the revised paper.

3- Send an outlining as one file (refer to the attachment) how did you address each reviewers' concern/recommendations.

4- In order to complete the review process on time, we highly appreciate it if we can receive the revised paper within **five weeks** from today.

Best regards

JESTEC Editor

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Nita Aryanti <nita.aryanti@che.undip.ac.id> Thu, Jun 20, 2019 at 3:43 PM
To: harivram@gmail.com

Nita Aryanti, Ph.D.
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REVIEW FORM

Title of paper: JESTEC CE19004 - PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

For sections A & B, please tick a number from 0 to 5, where 0 = strongly disagree and 5 = strongly agree.

A. Technical aspects

1. The paper is within the scope of the Journal.	☐ 0	✓ 1	☐ 2	☐ 3	☐ 4	☐ 5
2. The paper is original.	✓ 0	☐ 1	☐ 2	☐ 3	☐ 4	☐ 5
3. The paper is free of technical errors.	✓ 0	☐ 1	☐ 2	☐ 3	☐ 4	☐ 5

B. Communications aspects

1. The paper is clearly readable.	✓ 0	☐ 1	☐ 2	☐ 3	☐ 4	☐ 5
2. The figures are clear & do clearly convey the intended message.	✓ 0	☐ 1	☐ 2	☐ 3	☐ 4	☐ 5
3. The length of the paper is appropriate.	☐ 0	✓ 1	☐ 2	☐ 3	☐ 4	☐ 5

C. Comments to the authors (You may use another sheet of paper.)

Review of JESTEC CE19004 "PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE"

This is a very poor prepared manuscript, and must be REJECTED. It has no novelty, and it is also carelessly planned, as the authors used a commercial membrane with 1000 Da MWCO (molecular weight cut-off) to filter glycerol (92 Da, much smaller molecule, compared to the diameter of the membrane's pores). Furthermore, the membrane was not modified at all, or supplemented with any pretreatment, in order to achieve rejection >90% (maximum rejection in this manuscript was 70%). The analyses on the fouling behavior were mundane, where the reported results were of flux decline due to fouling, affected by the usual suspects, e.g. transmembrane pressure (TMP), temperature and pH. The effect of pH to the fouling behavior was not clear, as the trend was fluctuating up and down and up and down again. No idea of improvement was suggested in this manuscript in order to achieve better performance, for rejection and/or flux. The Hermia model in this manuscript was selected without clear reason or right justification. The manuscript was poorly written, with typos, inconsistencies, lack of references, and redundancies everywhere. It is agonizing to read this manuscript. Detailed 78 comments are attached in the next page.

D. Recommendation (Tick one)

1. Accepted without modifications.	☐
2. Accepted with minor corrections.	☐
3. Accepted with major modification.	☐
4. Rejected.	✓

E. Comments to the editors (These comments will not be sent to the authors)

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1. Please use dot, instead of comma, for writing numbers with decimals.
2. Please use degree sign ° to describe “degree”, and do not use superscripted zero “0”, superscripted uppercase “O”, or superscripted lowercase “o”!
3. Please write “min” or “mins” in the whole manuscript, to describe “minute” or “minutes”.
4. Please write “h” in the whole manuscript, to describe “hour” or “hours”.
5. Do not replace the word “or” using the symbol “/” !!
6. Do not use unit with the “/” character! For example use “L m^{-2} h^{-1}” instead of “L/m^2.hr)
7. Abstract: please write “transmembane pressure (TMP)”, and then write it consistently as TMP, TMP and TMP.
8. Abstract: “…Experiments were carried out at…”
9. Abstract: The flux decline phenomenon is very common, very usual. No novelty here!
10. Abstract: The current range of TMP, temperature and pH is too short. It might be widened, such as 1-5 bar, 25-70 °C, and 5-10, respectively.
11. Abstract: “…free fatty acid (FFA)…”
12. Section 1 paragraph 1: Please mention what are the components classified as MONG. It should be written as NGOM (non-glycerol organic matter, all in lowercase), instead of MONG that is grammatically incorrect.
13. Section 1 paragraph 1: What are the disadvantages of crude glycerin? Add more references!
14. Section 1 paragraph 1: …free fatty acid (FFA), fatty acid methyl ester (FAME, or biodiesel)…
15. Section 1 paragraph 1: Add space to split the word “alcoholand”
16. Section 1 paragraph 2: You mentioned about “other purification processes”, but no references at all !!
17. Section 1 paragraph 2: Cite Y. Wang et al, J. Membr. Sci. 363 (2010) 149-159 and Y. Wang et al, J. Membr. Sci. 378 (2011) 339-350 that explored pervaporation as a new process to handle and purify viscous and hygroscopic fluid (ethylene glycol), which is quite similar to glycerin.

18. Section 1 paragraph 3: "...ultrafiltration (UF)…", and then please write consistently UF, UF, and UF throughout the entire manuscript!
19. Section 1 paragraph 3: "Separation of glycerin from FAME by UF and microfiltration…"
20. Section 1 paragraph 3: What is the reference number for the citation "[Saleh]" ???
21. Section 1 paragraph 3: Please use uppercase A for the beginning of the sentence "A similar result was also found by Wang et al. [6]"
22. Section 1 paragraph 3: ASTM stands for what? Please write it down.
23. Section 1 paragraph 3: Please consistently write FFA, FFA, and FFA throughout the entire manuscript!
24. Section 1 paragraph 3: The proper name of the polymer is "polyethersulfone", with lowercase l, and with "f" instead of "ph", NOT "poyethersulphone"
25. Section 1 paragraph 3: Describe the details on the results and findings from Mah et al [10, 11]
26. Section 2 paragraph 1: Delete the word "polyethersulphone" and leave the PES word. Add space before the word "(Snyder Filtration XV).
27. Section 2.1 paragraph 1: You use a membrane with relatively wide pore (1000 Da MWCO) to separate glycerol (92 Da) from water (18 Da) and other small molecules??? Such a FATAL error in planning the experiment.
28. Section 2.2 paragraph 2: Delete "ultrafiltration", leave the "UF". Please write consistently UF, UF, and UF throughout the entire manuscript!
29. Figure 1: What is the hexagon in circle? Describe!
30. Section 2.2 paragraph 2: "…for 60 mins…"
31. Section 2.2 paragraph 2: "…inside the UF cell…"
32. Section 2.2 paragraph 2: "…collected for 120 mins, with interval of 5 mins…"
33. Section 2.2 paragraph 2: Permeate FLUX! Not "fluxes"
34. Equation 1: remove the "x"
35. Section 2.2 paragraph 3: delete "transmembrane pressure" and then write it consistently as TMP, TMP and TMP.
36. Section 2.2 paragraph 3: "…carried out for 60 mins, with interval of 10 mins."
37. Section 2.3 paragraph 1: "…calculated by using Eq. 2."
38. Section 2.3 paragraph 1: "gas chromatography (GC, Shimadzu TQ8030)."
39. Section 2.3 paragraph 1: Where is the standard curve, or calibration curve of the analysis of FFA, FAME, glycerin, etc. by using GC? What would be the retention time of those components? What would be the temperature of the GC column?
40. Section 3 paragraph 1: What is the reason and justification of using the Hermia model? Write it down!
41. Section 2.3 paragraph 2: Use uppercase "C" for the beginning of Section 2.3 paragraph 2!
42. Section 2.3 paragraph 2: Change "/" with "or"
43. Section 2.3 paragraph 2: Equation 1? This is wrong, maybe you refer to Equation 3?
44. Table 1: Please use lowercase letters in all words, except for the beginning of the sentences
45. Section 4: Delete "transmembrane pressure", and then write it consistently as TMP, TMP and TMP.
46. Section 4: "…sampled every 5 mins… for its composition by using GC."
47. Title of Section 4.1.1: Delete "transmembrane pressure", and then write it consistently as TMP, TMP and TMP.
48. Section 4.1.1 paragraph 1: "UF process is one method to…using TMP as a driving force"
49. Section 4.1.1 paragraph 1: Add more references, and not just use reference [14], because the phenomenon of the flux decline (in Section 4.1.1 paragraph 1) is so mainstream, very common, the shall be more than ten references for this aspect, cite five more references!
50. Figure 2: Where is J_0? How much is J_0? Why there is no $J/J_0= 1$ at t= 0 mins???
51. Change the label of x axis in Figures 2, 3, 4, 5 with "mins"

52. Figure 2: Insignificant change between the trend of the normalized flux at 4 and 4.84 bar. Explain! Add more TMP, between 1-5 bar!
53. Section 4.1.1 beginning of paragraph 2: Which figure confirms the correlation between flux and TMP?
54. Section 4.1.1 paragraph 2: "30-60 mins"
55. Section 4.1.1 paragraph 2: Delete the sentence started with "According to… the flux", because it is very redundant and confusing!
56. Section 4.1.1 paragraph 2: "…as the result of the increasing deposit and impurities…"
57. Section 4.1.1 paragraph 2: "The impurities were carried away…"
58. Section 4.1.1 paragraph 3: How high is the viscosity of glycerin? Where is the data, and the reference(s)?? State it in the unit of Pa.s, or centipoises (cP) also acceptable
59. Section 4.1.1 paragraph 3: Add references for "limited spatial molecular space", "hydrophobic characteristic", "tend to be hydrophobic and insoluble.."
60. Section 4.1.2 paragraph 1: "The condition occurs because increased temperature can… Hence, the resistance caused by both…is reduced by the increased temperature."
61. Figure 3: Insignificant change between the trend of the normalized flux at 60 and 68 °C. Explain! Add more variation of temperature, namely 25-70 °C.
62. Figure 4: Inconsistent trend, up and down and up and down again… unclear and confusing. Explain!
63. Please repeat all the experiments with a replicate (duplo) or two replicates (triplo), because all the results in Figures 2, 3, and 4 are insignificant, not worth mentioning
64. Section 4.1.3 paragraph 1: "…agglomeration… The larger molecules that were formed may increase the…"
65. Section 4.1.3 paragraph 1: What do you mean with "dissociation and undissociation"? It makes me dizzy! And no references to back up! Is this real life, or is it fantasy?
66. Section 4.1.3 paragraph 1: "Not fully undissociated at pH 7", "Irregularities at pH 8" WHATTT? Where are the references to back this bewildering statement?
67. Section 4.1.4 paragraph 1: "…Causing a shrink on the size…" What is the reason? Or where is the data, and where are the REFERENCES??
68. Table 2: Maximum rejection of mediocre 70%, due to filtering small molecules by using wide and sparse sieve… What a poorly planned experiment! The least you can do is chemically crosslink the membrane in order to decrease the pore size (hence the MWCO). Or even please perform thermal annealing for the membrane!
69. Table 3: Where are the fitting for all the data shown in Table 3?? There should be a set of 12 (twelve) plots!
70. Section 4.2 paragraph 2: "…which tend to dissociate at acidic environment…"
71. Section 4.2 paragraph 3: Please change "minutes" to mins!
72. Section 4.2 paragraph 3: "The foulant is the piled up… in irregular…"
73. Section 4.2 paragraph 3: Which "evidence"??? What "evidence"???
74. Section 4.2 paragraph 4: Add references that support the negative charge induction caused by the interaction between fatty acid and membrane!
75. Section 4.2 paragraph 4: "This condition may also cause changes in the fluid resistance to the membrane [8]."
76. Conclusion: You use a membrane with relatively wide pore (1000 Da MWCO) to separate glycerol (92 Da) from water (18 Da) and other small molecules??? Such a FATAL error in planning the experiment. This study is not worth studying.
77. Nomenclature: Please use UPPERCASE for the letters in the beginning of a sentence!
78. Nomenclature: Permeate FLUX! Not "fluxE"

REVIEW FORM

Title of paper: PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

For sections A & B, please tick a number from 0 to 5, where 0 = strongly disagree and 5 = strongly agree.

A. Technical aspects

1. The paper is within the scope of the Journal.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
2. The paper is original.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
3. The paper is free of technical errors.	☐ 0	☐ 1	☐ 2	☐ 3	☑ 4	☐ 5

B. Communications aspects

1. The paper is clearly readable.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
2. The figures are clear & do clearly convey the intended message.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
3. The length of the paper is appropriate.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5

C. Comments to the authors (You may use another sheet of paper.)

The paper addresses a very important topic in the context of global policies to promote and develop the circular economy, minimizing the amount of technological waste and recovering useful products.
The authors carried out a detailed study of the theoretical aspects of membrane separation, and analyzed the current state of experimental research in this field. The research is original and well structured, the experimental results are clearly expressed and analyzed in detail, thus allowing for easy understanding of the methodology, phenomena and data interpretation.
Also, the authors have carefully used the English language; there are very few language errors, for which I have indicated corrective suggestions in the attached word document.
I propose that the paper be published in JESTEC after complying with the suggested corrections.

D. Recommendation (Tick one)

1. Accepted without modifications.	☐
2. Accepted with minor corrections.	☑
3. Accepted with major modification.	☐
4. Rejected.	☐

E. Comments to the editors (These comments will not be sent to the authors)

The manuscript is of high scientific level, it is elaborated with professionalism, clearly expressed and very useful for the scientific and market environment. There are very few language errors, I indicated the proper corrections in the attached document. I propose that the paper be accepted for publication after making minor corrections as indicated.

REVIEW FORM

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C. Comments to the authors (You may use another sheet of paper.)

Please see my comment in the original manuscript using the track changes function

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4. Rejected.	☐

E. Comments to the editors (These comments will not be sent to the authors)

Journal of Engineering Science and Technology
Vol. XX, No. Y (Year) PPP - QQQ

PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

Abstract

Raw glycerin as a by-product of the transesterification process has low economic value and limited applications. Under this condition, purification of raw glycerin is required to increase the quality of glycerin. Membrane process using ultrafiltration membrane is an alternative to purify the glycerin. However, flux decline behaviour during the ultrafiltration process is a major limitation. In this research, flux decline, rejection, and blocking mechanism at various Trans Membrane Pressure (TMP), temperature, and pH were observed. Experimental runs was carried out at the variation of the transmembrane pressure/TMP (3,16 – 4,83 bar), temperature (51,63 – 68,36 ºC), and pH (6,32 – 9,67). The research showed that the flux decline was significant at all variation of the process parameter. This condition was caused by the presence of small size impurities such as Free Fatty Acid which can lead to clogging inside the membrane pore. Both TMP and temperature had no significant effect to flux decline. Rejection value was proportional to TMP and temperature while at pH variation the rejection was determined by the characteristic of impurities. Hermia's model was selected to analyze the blocking mechanism during filtration. It was confirmed that the mechanism was dominated by cake formation for all process parameters except for pH 7. At pH 7, the mechanism was controlled by intermediate blocking at an early stage and then followed by standard blocking. This research demonstrated that membrane separation via ultrafiltration process was capable of removing some impurities up to 68,33% for total impurities and up to 70,98% for the free fatty acid.

Keywords: Glycerin, Purification, Ultrafiltration, Fouling, Blocking Mechanism.

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1. Introduction

Production of biodiesel generates crude glycerin as a by-product. It was reported that production of 10 kg biodiesel produced 1 kg of crude glycerin [1]. Crude glycerin from biodiesel production has low economic value since the glycerin product is mixed with impurities in its heavy phase. On the other hand, glycerin is raw material for many industries such as pharmacy, food, cosmetic, cigarette, automotive, textile or chemical industry. In addition, pure glycerin is potential for bio-lubricant, additive and an alternative fuel by adjusting the combustion cycle [2]. As a by-product, glycerin is found in its crude form (crude glycerin) which is contain many impurities and Matter Organic Non-Glycerol (MONG) at various concentration. Application of crude glycerin has many disadvantages, and high cost since it contains many contaminants such as water, inorganic salts and other organic materials (Free Fatty acid (FFA), Fatty Acid Methyl Ester (FAME/biodiesel), alcohol and tri-, di-,mono-glyceride) [3].

In general, crude glycerin is purified by distillation. However, the low vapour pressure of glycerin and its temperature sensitivity causes degradation or polymerization of glycerin, and hence vacuum distillation is applied more frequently than the normal distillation [4]. As a consequence, application of vacuum distillation is expensive due to the high energy requirement to create vacuum condition and evaporate glycerin [3,4]. Other purification processes such as adsorption, ion exchange, saponification, acidification, neutralization (pre-treatment), extraction and drying have been implemented to obtain high purity glycerin. Nevertheless, the usage of chemicals and energy requirement has a consequence of high cost.

Purification of glycerin by membrane technology has been developed and studied due to its ease of process and can minimize energy requirement by utilizing concentration difference, electron potential and hydroscopic pressure [4, 5]. One type of the membrane for purification or separation glycerin is Ultrafiltration (UF). Separation of glycerin from FAME by UF and microfiltration ceramic membrane was studied [Saleh]. The research confirmed that the biodiesel met the ASTM Standard for glycerin content. a similar result was also found by Wang et al. [6]. Experiments focused on glycerin purification have been performed. Dhabbai et al. [3] investigated purification of crude glycerol using a sequential physicochemical treatment, membrane filtration, and activated charcoal adsorption. It was reported that result of maximum glycerol content was 97.5 wt% with acid value and free fatty acid (FFA) content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Other studies focused on the application of UF for glycerin model of glycerin separation. Amin et al. [7] evaluated UF fouling characteristic for filtration of mixture pure glycerin having 15% w/w and found that the flux decline involved cake layer model as well as pore blocking model. In addition, separation of glycerin mixed with fatty acids (palmitic, stearic, and oleic acids) by polyethersulphone (PES) UF membrane was also studied [8]. It was reported that the PES membrane exhibited severe fouling for all types of fatty acids in solution with glycerol–water. Similar study by Amin et al. [9] investigated glycerin-rich fatty acid solutions confirming that the adition of fatty acid had an effect on significant flux decline. Mah et al [10, 11] studied on UF of palm oil-oleic acid-glycerin mixture and evaluated the fouling mechanism, flux decline, fouling pattern and the UF performance.

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2. Materials and Method

2.1. Materials

Raw glycerin supplied from Biodiesel Plant of PT SMART Tbk, Tarjun, Indonesia was used as a raw material. The raw glycerin composed of glycerin 38,53%, FFA 45,01% and MONG other than FFA of 16,47%. In this research, PES flat sheet UF membrane (Synder Filtration XV) having 1 kDa molecular weight cut-off was purchased from Sterlitech Corp, USA.

2.2. Ultrafiltration Membrane

Experimental runs were carried out by a laboratory-scale Ultrafiltration Cell equipped with compressor and instrumentation control as illustrated in Fig. 1.

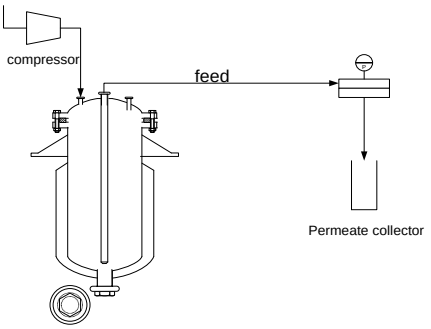

Fig 1. Schematic Illustration of Ultrafiltration Cell with control temperature.

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Experimental runs were operated at room temperature (25 ± 2 ºC). Before each run, membranes were first compacted by filtering distilled water through the membrane at a pressure of 1 bar for 60 minutes. For each experimental work, a new circular membrane sheet having area of 13.85 cm^2 was placed inside the ultrafiltration cell. Pure water flux (J_0) was determined for initial water characteristic. The pure water flux was evaluated by weighing permeate collected at a specific time. The permeate fluxes (J) was determined by measuring the volume of permeate collected at 5 minutes intervals for 120 minutes. Then the volumes of permeates were weighed (W). The flux was calculated according to (Eq. 1):

Commented [.6]: What is the flux unit?

Commented [.7]: Volume or mass?

$$J = \frac{W}{(Axt)} \quad (1)$$

Permeate fluxes, and blocking mechanisms were observed by adding crude glycerin to the feed tank for half tank capacity. Further, the UF cell was operated at a dead-end mode at the variation of the transmembrane pressure / TMP (3,16 - 4,83 bar), temperature (51,63 - 68,36 °C) and pH (6,32 - 9,67). pH adjustment was conducted by adding a 0.1 N HCl or 0.1 N NaOH. Sampling for permeate flux determination was carried out every 10 minutes for 60 minutes.

Commented [.8]: What are the justification of these values? Why not using exact value rather than decimal point.

2.3. Analysis

UF performance for glycerin purification from the feed solution was evaluated through the rejection of FFA and impurities. The rejection (R) was calculated using Eq. (2).

$$R = \left(1 - \frac{C_p}{C_f}\right) x100\% \quad (2)$$

The composition of permeate was analyzed by using Gas Chromatography (Shimadzu TQ8030).

Commented [.9]: Provide detail of the column type and analysis condition

3. Model of Blocking Mechanism

Hermia's model defined the fouling mechanism especially in the porous membrane with dead-end system filtration. In more specific, the model highlighted the fouling mechanism which dominates in the entire of the process. This model applied a common power-law equation to describe the blocking mechanism and written in equation (3) [10,12].

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (3)$$

Complete pore blocking illustrates that each solute is assumed to participate in blocking the entrance of the membrane pores completely. With the assumption that every solute stays on previously deposited solute, it is represented of intermediate pore blocking. Standard pore blocking describes that each solute is deposited to the internal pore wall. Determination based on the accumulation of the solute on the membrane surface is representative of cake/ gel formation [7]. Further, linearization of blocking mechanism according to equation (1) is presented in Table 1.

Table 1. Linearization equation of blocking models based on Hermia's model [13]

Pore Blocking Models	*Linearization Equation*	*Physical Concept*
Standard Blocking	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore Blocking + Surface Deposit
Intermediate Blocking	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore Constriction
Complete Blocking	$\ln J = \ln J_o - K_c t$	Formation of surface deposit
Gel/Cake Formation	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore Blocking

Commented [.10]: Describe the symbol found in the equation

4. Results and Discussion

In this paper, flux decline, rejection, and the blocking mechanism were observed in various variations of process parameters such as TMP, temperature, and pH. For flux decline study and blocking mechanism, filtrate flow in dead-end filtration module was observed for 60 minutes, and then the filtrate was sampled every 5 minutes. Collected filtrate was then analyzed for its composition. The composition data were used to determine the rejection of impurities (FFA and MONG) in raw glycerin.

4.1. Flux decline and rejection

4.1.1. Effect of Trans Membrane Pressure (TMP) on permeate fluxes

Ultrafiltration process is one method to separate substances which have different of molecular size using TMP as a driving force. The fluxes increase along with the increase on TMP indicating that the flux is proportional to TMP. This finding was supported by Kim and DiGiano [14]. Fig 2. shows the flux response against the TMP. Generally, the flux decline over the time is caused by the impurities deposited on the surface and inside pore of the membrane.

Commented [.11]: Why flux for 4 bar and 4.84 bar almost have the same value? it is not proportional then.

Commented [.12]: Provide the fixed value of pH and Temp at varied TMP

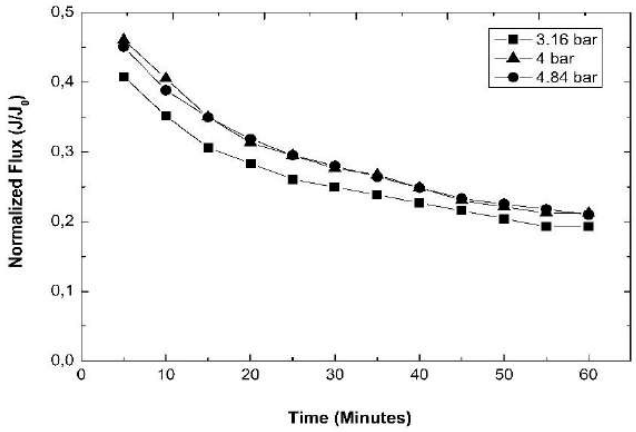

Fig 2. Influence of TMP on fluxes of glycerin-rich solutions.

The figure confirms the correlation between flux and TMP wherein increasing on TMP causes an increase in the flux. The higher normalized flux at higher TMP is achieved at a pressure range of 3,16 – 4 bar. In contrast, at a range of 4 – 4,84 bar, the effect of adjustment TMP on the positive impact on the flux is not significant indicating that the TMP has a slight impact on increasing flux. Adjusting TMP to the higher point actually lead to an increase in flux but it still cannot affect the pattern of flux decline. This is confirmed by the flux decline pattern in Figure 2 showing similarity pattern at the various variations of TMP. A significant flux decline in the early stages of the UF process a range of 0 – 25 minutes and then

continued with the stationary states of flux decline at a range of 30 – 60 minute are observed. This phenomenon indicates that the process more influenced by mass transfer mechanism than by TMP its self [12]. According to the phenomenon, when the TMP is set to a higher point, it directly affects the increase of the flux. This leads to a more severe condition of flux decline as the result of increases in deposits and impurities quantity. The impurities carried away by the glycerin-rich solution that flows through to membrane matrix and presumably deposited both on membrane surface as well as inside the pore of the membrane [9,12].

This phenomenon is conceivable because of the nature of the raw material (glycerin) and the majority of impurity (FFA) in raw glycerin. Glycerin has high viscosity, and it is much different from Newtonian fluids such as water. The high viscosity of glycerin causes the molecular arrangement in glycerin has more limited spatial molecular space. Besides that, the properties of FFA tend to be hydrophobic and insoluble in polar compounds. The hydrophobic characteristic is on the contrary to the hydrophilic properties of the membrane properties used in this study. It is accomplished that hydrophobic properties of the impurity (FFA) can increase repulsion forces on the membrane which ultimately influences the flux trend that occurs during the filtration process (mass transfer mechanism).

4.1.2. Temperature effect on permeate fluxes

Effect of temperature on flux decline is presented in Fig. 3. Observations show the temperature has more influence than the TMP on the flux decline qualitatively. The condition occurs because increasing the temperature can directly trigger the viscosity reduction. This makes the fluid more freely to flow as a result of increasing in molecular spatial space in higher temperature condition [15]. In addition, increasing the temperature can lead to an increase of the polymer bonding mobility inside the membrane matrix [9,16]. Hence, the resistant that caused by both fluid and membrane against each other reduce with increasing of the temperature.

Commented [.13]: Give the fixed value of pH and pressure at this varied temperature

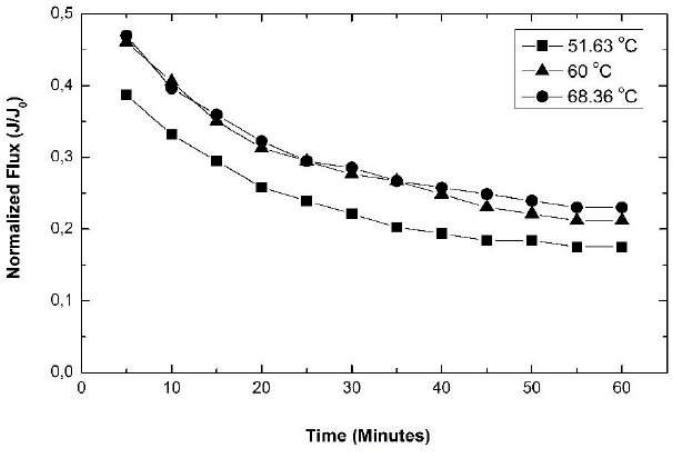

Fig 3. Influence of temperature on flux decline of the glycerin-rich solution

Commented [.14]: What is the initial pH of the solution? Why not used a sample at initial temperature as the control?

In addition, Fig. 3. shows the trend of flux response against temperature indicating that at a range of 51,63 ºC – 60 ºC, the increasing temperature has a positive effect towards the flux. On the contrary, in a range of 60 ºC – 68,36 ºC the effect of temperature is insignificant. Dhabhai et al. [3] found that the temperature does not influence the decrease of the raw glycerin viscosity at temperatures above 60 °C. Although the viscosity of glycerin which can directly affect fluid resistance to the membrane can be reduced, it does not have a positive effect on the pattern of flux decrease as shown in TMP. This condition denotes that characteristic and properties of impurity (FFA) plays a key role in the pattern of flux decrease. Moreover, the flux can directly increase along with decreasing in viscosity which can lead to increasing of impurities concentrations both on the surface and inside pore of the membrane. This phenomenon also confirms that the process is dominated by the mass transfer mechanism.

4.1.3. Effect of pH on permeate fluxes

Fig. 4 shows the responses of flux against different pH condition. –The pH was observed in a range of 6,33 – 9,67. The results show that the flux decreases the acidic state is greater than in the alkaline state. Fatty acid as impurities which is contained in a glycerin-rich solution has the nature that remained as the undissociated molecule in the presence of an acidic environment. Fatty acid molecules can interact with acid to form the larger molecules via an agglomerate process with another molecule of fatty acid [8, 10]. The larger molecule that was formed can increase the adsorption of foulant molecule. The adsorption is formed on membrane surface as well as on the entrance of the membrane pore and then causes high flux decline and membrane fouling [8,17-18]. Sequentially, the flux decline follows the order of pH 7> pH 6,33> pH 9>pH 8 and the highest flux decline is found at pH 7. The pH 7 has higher flux decline than that at pH 6,33 which is

Commented [.15]: Give fixed value of pressure and temperature

Commented [.16]: What is the initial pH of the feed sample

Commented [.17]: Why using pH 6.33 and 9.67?

related to dissociation and undissociation effect where the pH 7 should have lower flux decline. The condition is most likely due to the fatty acid state that not fully undissociated at pH 7. This causes clots of some molecules is not formed and still at single molecule form. The single molecule of fatty acid can pass through into membrane pore since the average size of the single fatty acid molecule is four times smaller than the membrane pore size and triggers the blocking inside the wall of membrane pore. Irregularities also occur at pH 8 where the flux decline is smaller than the flux decline at pH 9. The reason for this phenomenon may due to the dissociated molecules of fatty acids (at pH 9 the fatty acid molecules almost completely dissociate) blockage the micropores of the membrane. The blocking at micropores is possible in PES-based UF membranes because it is an asymmetric porous membrane [19].

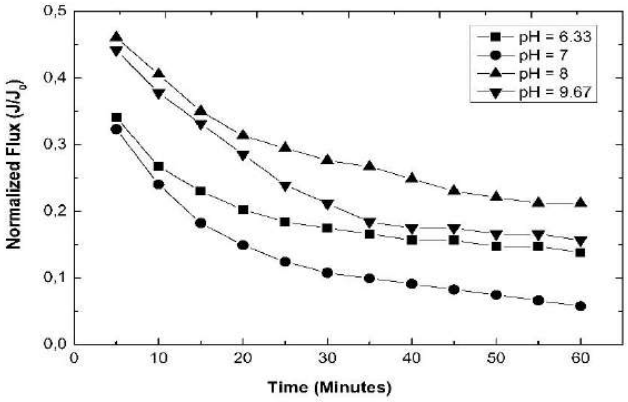

Fig. 4. Effect of pH on Flux decline of glycerin-rich solutions

4.1.4. Rejection

Commented [.18]: Benchmark and discussed the rejection obtained in this study with other publication for glycerine rejection.

The impurities rejection data is given in Table 2.

Table 2. Summary of rejection data in various variations of process parameters.

No.	Pressure (bar)	Temperature ˚C	pH	Rejection (%)	
				FFA	Total Impurities
1.	3,16	60	8	48,10	48,50
2.	4	60	8	54,17	32,11
3.	4,84	60	8	57,63	52,86
4.	4	51,63	8	44,32	33,25
5.	4	60	8	54,17	32,11

6.	4	68,37	8	45,35	43,56
7.	4	60	6,33	30,70	21,18
8.	4	60	7	70,98	68,33
9.	4	60	8	54,17	32,11
10.	4	60	9,67	25,82	24,22

~~The~~ Table 2 shows a different trend in each variation of the operating condition. For TMP variation, the rejection increases with increasing on TMP. The rejection of FFA content in the filtrate at 4,84 bar and 3,16 bar are 57,63% and 48,1%, respectively. This condition takes place because in higher TMP some small foulant molecules may be penetrated into the membrane pore and form a deposit, thus causing a shrink on the size of membrane pore which leads to an increase in rejection of impurity. For temperature variation, the trend of rejection has a tendency to be similar to TMP variation where higher temperature process has greater rejection than lower temperature. The rejection of impurities is 33,25% at 51,63 ^{o}C while at 68,37 ^{o}C the rejection reaches 43,56%. This is likely due to the effect of increasing temperature which can directly affect the increase in flux and causes an increasing the impurities that flow through the membrane pore. It is similar to the condition that occurs in TMP variation. Rejection behaviour at pH variation has a different kind than the other operating parameter. The highest result is 70,98% at pH 7, and the lowest result is 25,82% at pH 9,67. This behaviour may occur due to the nature of the impurities, as described in section 4.1.3.

4.2. Blocking Mechanism

The constant of blocking mechanism and the corresponding correlation coefficients (R^2) during filtration is listed in Table 3. According to the Table 3, increasing on TMP reduces the flux decline. Its condition also applies to temperature as confirmed by the smaller value of the constants along with increases of TMP and temperature. Cake formation is predicted as a dominated blocking mechanism during the filtration process for both TMP and temperature variations. In the cake formation, the foulant is firstly adsorbed on the membrane surface, penetrate into the membrane pore and then form a layer that can cause a more severe decrease in flux even from the early step of filtration. The fatty acid may be the component responsible for severe fouling [7]. In biodiesel industries, glycerin was a by-product from the transesterification reaction which consists of palmitic acid (C16: 0), stearic acid (C18: 0) and most of the oleic acid that has double bond carbon chain (C18: 1) [20].

Table 3. Fitted Hermia's model for various process parameters.

Parameters	n = 0 cake formation		n = 1 Intermediate blocking		n = 1.5 Standard blocking		n = 2 Complete blocking	
	k_{cf}	R^2	k_i	R^2	k_s	R^2	k_c	R^2
Pressure								
3,16 bar	0,4098	0,9848	0,0585	0,9031	0,0164	0,8171	0,0191	0,7051
4 bar	0,3508	0,9891	0,0546	0,9291	0,0159	0,8588	0,0192	0,7613
4,84 bar	0,3400	0,9920	0,0532	0,9249	0,0155	0,8499	0,0187	0,7483
Temperature								
51,63 ˚C	0,5329	0,9782	0,0692	0,9026	0,0185	0,8204	0,0208	0,7084
60 ˚C	0,3508	0,9891	0,0546	0,9291	0,0159	0,8588	0,0192	0,7613
68,36 ˚C	0,2872	0,9737	0,0476	0,8892	0,0142	0,8136	0,0176	0,7184
pH								
6,33	0,4090	0,9840	0,0580	0,9030	0,0160	0,8170	0,0190	0,7050
7	4,4480	0,9187	0,2468	0,9917	0,0453	0,9557	0,0365	0,8307
8	0,3400	0,9920	0,0532	0,9249	0,0155	0,8499	0,0187	0,7483
9,67	0,6982	0,9742	0,0862	0,9443	0,0225	0,8935	0,0247	0,8068

In addition, Table 3 shows the value of k (constant) at acidic state that tends to be higher than in alkaline state. It demonstrates that the resistance of the fluid to the membrane is larger and causing more severe fouling than in alkaline state. The nature of fatty acids which is in undissociation at acidic environment may be responsible for that condition. Under this environment, the fatty acid would be clumping each other. Mah et al. (2012) reported that the droplets of a mixture of palm oil and oleic acid at pH 2 (very acidic condition) lead to significantly increase in droplet size and even reach twice in size over the original droplet size. Therefore, setting pH under acidic conditions can lead to agglomeration of foulant molecules.

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Fig. 5. exhibits the blocking mechanism that occurs in the various variations of pH. Generally, the mechanism is dominated by the cake formation, except for pH 7 as supported with the highest R^2 value for pH 6,33; 8; and 9,67. The similar result was reported by Amin et al. [7] and Mah et al. [11] confirming that cake formation was the dominant mechanism in pH variation. The different condition at pH 7, as seen in the value of k (constant for blocking mechanism) is much greater than another pH. Moreover, the highest R^2 value in the intermediate blocking mechanism is found. Fig. 5 (b) and fig. 5 (c) confirm that in the initial conditions of filtration until 10 minutes, both intermediate blocking and standard blocking mechanism occur. Then, in 15 minutes until 45 minutes only the intermediate blocking mechanism is observed, and for 50 minutes afterwards only standard blocking contributes to the flux decline. In intermediate blocking, the solutes/particles which accumulated on the membrane surface and on the entrance of membrane pore is possible to overlap another solute that has already deposited on the membrane surface. The foulant is then pile up each other in irregularity

arrangement [7] and trigger other mechanisms such as standard blocking to occur during the filtration process. Standard blocking mechanism is believed to be responsible for a significant flux decline as in that condition the impurities molecule penetrates to the inside wall of the membrane pore and make a deposit which can be lead to plugging on the active area of the membrane pore [21,22]. This strengthens the evidence that fatty acids which are still dissociated at pH 7 entering the pore and causes blockages in the membrane pore.

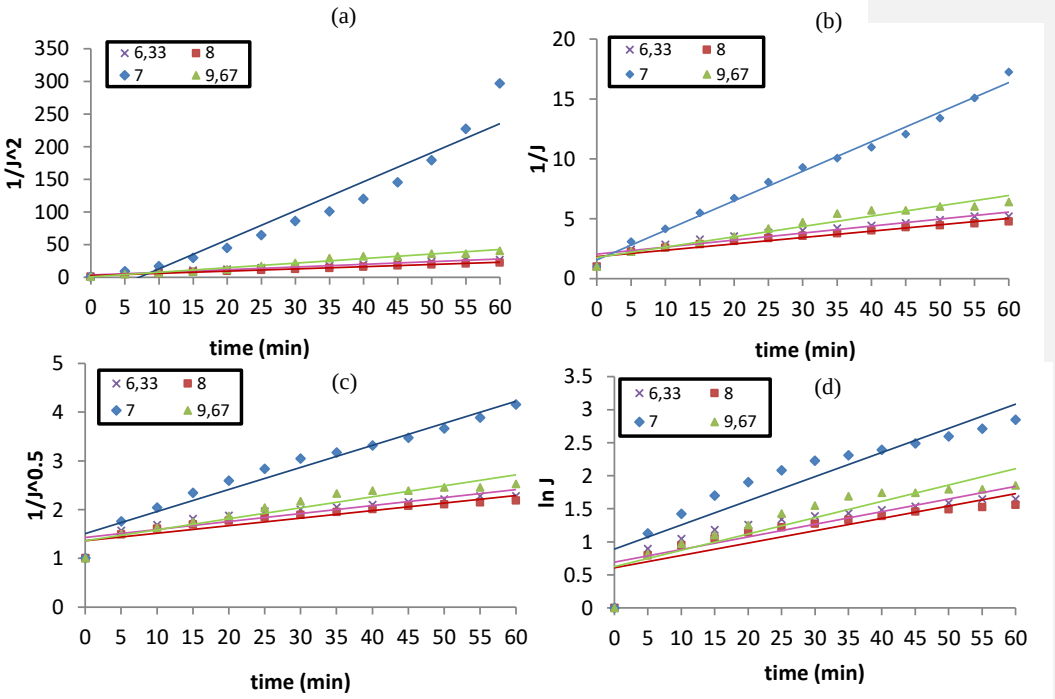

Fig. 5. Hermia's model fitting for the experimental data: (a) Cake formation, (b) Intermediate blocking, (c) Standard blocking, (d) Complete blocking

At high pH, especially for pH 9 above, the fatty acid molecule is fully dissociated and become surfactants with a negative charge with a hydrophilic head and hydrophobic tail. If there is an interaction between fatty acids and membranes, it forms a negative charge induction to the membrane. Thus the repulsive force between the fatty acid and the membrane may change. It conditions also can cause changes in fluid resistance to the membrane [8].

5. Conclusions

The study of flux decline, rejection and blocking mechanism during UF process using 1 kDa PES membrane with various variations process parameters (TMP, T, and pH) to the glycerin-rich solution (raw glycerin) from the biodiesel industry were conducted. Some concluding observations from the investigation are given below.

- It was found that flux decline was severe significantly in all variation of process parameter due to a deposit of impurities.
- Both pressure and temperature did not give significant effect to the flux decline due to dominating of the mass transfer mechanism which is caused by the nature of impurities its self.
- Both pressure and temperature had a similar trend of rejection that in higher process parameters the rejection becomes greater, whereas at pH variation behaviour of rejection is determined by the nature of impurities.
- Hermia's blocking law model found to fit well to the experimental data. The best-fit experiment data was cake layer formation mechanism for all process variation except for pH 7 where the intermediate blocking takes the lead in early stages and then followed by standard blocking.

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Nomenclatures

C_f	Concentration FFA/impurities in the feed, ppm
C_p	Concentration FFA/impurities in the permeate, ppm
J	Permeate Fluxe, L/m^2. hr
J_0	Initial Flux, L/m^2. hr
R	Rejection, %
k	constant of blocking mechanism
n	value that represents a blocking mechanism, n = 0 (cake layer formation), n = 1 (intermediate blocking), n = 1.5 (standard blocking), and n = 2 (complete blocking).
R^2	the corresponding correlation coefficients
t	filtration time (h)
V	permeated volume (L),

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REVIEW FORM

Title of paper: PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

For sections A & B, please tick a number from 0 to 5, where 0 = strongly disagree and 5 = strongly agree.

A. Technical aspects

1. The paper is within the scope of the Journal.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
2. The paper is original.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
3. The paper is free of technical errors.	☐ 0	☐ 1	☐ 2	☐ 3	☑ 4	☐ 5

B. Communications aspects

1. The paper is clearly readable.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
2. The figures are clear & do clearly convey the intended message.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
3. The length of the paper is appropriate.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5

C. Comments to the authors (You may use another sheet of paper.)

-Minor grammatical errors and typing errors such as spacing, capital letters at beginning of sentence, etc .
-Introduction, para. 3 "…and microfiltration ceramic membrane was studied [Saleh]", "Mah et al [10, 11] studied…"
-Ultrafiltration Membrane, para. 2 "..at 5 minutes intervals.."
-*x* in Equation (1) and (2) looks like a variable. It should be multiplication? Please check the font used.
-Referencing: " Mah et al. (2012) reported.."

D. Recommendation (Tick one)

1. Accepted without modifications.	☐
2. Accepted with minor corrections.	☑
3. Accepted with major modification.	☐
4. Rejected.	☐

E. Comments to the editors (These comments will not be sent to the authors)

Recommended

REVIEW FORM

Title of paper:

For sections A & B, please tick a number from 0 to 5, where 0 = strongly disagree and 5 = strongly agree.

A. Technical aspects

1. The paper is within the scope of the Journal.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
2. The paper is original.	☐ 0	☐ 1	☐ 2	☑ 3	☐ 4	☐ 5
3. The paper is free of technical errors.	☐ 0	☐ 1	☐ 2	☑ 3	☐ 4	☐ 5

B. Communications aspects

1. The paper is clearly readable.	☐ 0	☐ 1	☐ 2	☑ 3	☐ 4	☐ 5
2. The figures are clear & do clearly convey the intended message.	☐ 0	☐ 1	☐ 2	☐ 3	☑ 4	☐ 5
3. The length of the paper is appropriate.	☐ 0	☐ 1	☐ 2	☐ 3	☑ 4	☐ 5

C. Comments to the authors (You may use another sheet of paper.)

This paper studied in the flux decline happened in the ultrafiltration applied for glycerol purification. The study provided a better understanding on the behavior of system of ultrafiltration dealing with glycerol and its impurity for several parameters at various range. There are some comments which required author have to address.

1. In the introduction, what are the current limitations of using UF for glycerol purification? what is the objective of this study? Or what is this study trying to improve? Reduce the effect of flux decline or just gaining an understand the effect of flux decline when some dependent variables were varied.
2. In the introduction, ref. [8] reported that using PES exhibited a severe fouling in the present of fatty acid in crude glycerol. A justification is needed for reasons why this study still used PES with very small cut-off 1 kDa.
3. For all equations in the manuscript, after each equation, please specify each papameter, its name, and unit.
4. In the method section, Gas Chromatography was used for analysis. Operating condition for this analysis applied for glycerol must be mentioned here.
5. Various is an adjective of variation. So please choose one, not 'various variation'.
6. The paragraph right after the results and discussion, 'For flux decline study and blocking mechanism… in raw glycerin.' This part should be moved to method section.
7. Since the objectives of this study was missing in the introduction. The conclusion should say if the objectives are achieved.
8. Is using UF a good solution for glycerol purification? Since flux decline occurs very soon after the system start for all studied parameters at various range.

D. Recommendation (Tick one)

1. Accepted without modifications. ☐
2. Accepted with minor corrections. ☐

3. Accepted with major modification. ☑

4. Rejected. ☐

E. Comments to the editors (These comments will not be sent to the authors)

This paper need to improve more its formatting.

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REVISION of Paper ID CE19004 /Review of a paper, First Round Result with Rejection/

1 message

Nita Aryanti <nita.aryanti@che.undip.ac.id> Sat, Jul 6, 2019 at 12:48 AM
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Dear editor of JESTEC,

We revised and corrected our paper according to the reviewer comments as file attached. In addition, we send outline of our answer of all reviewer comments and recommendations.
Thank you.

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On Sun, Jun 2, 2019 at 10:25 AM Jestec <Jestec@taylors.edu.my> wrote:

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>
> **5** reviewers have reviewed your paper.
>
> **3** accepted with minor corrections **1** accepted with major modifications, but **1** rejected your work
>
> The Review panel decision is to conditionally accept the paper with Major Corrections.
>
> This is to give you opportunity to improve the quality of your paper to be up to a journal article level.
>
> Attached herewith, please find one/two/three/four/five/six reviewers' reports.
>
> Please notice the following:

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PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

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Abstract

Crude glycerin as a by-product of the transesterification process has low economic value and limited applications. Under this condition, purification of crude glycerin is required to increase the quality of glycerin. Membrane process using ultrafiltration membrane is an alternative to purify the glycerin. However, flux decline behaviour during the ultrafiltration process is a major limitation. Since specific information of blocking information in ultrafiltration of glycerin rich solution was not found, this research seek to focus on separation of glycerin rich solution from its impurities. In this research, flux decline, rejection, and blocking mechanism at various Trans Membrane Pressure (TMP), temperature, and pH were observed. Experiments were carried out at the variation of the TMP (3.2 – 4.8 bar), temperature (51.63 – 68.36 °C), and pH (6.32 – 9.67). The research showed that the flux decline was significant at all variations of the process parameter. This condition was caused by the presence of small size impurities such as free fatty acid (FFA), which can lead to clogging inside the membrane pore. Both TMP and temperature had no significant effect on flux decline. Rejection value was proportional to TMP and temperature while at pH variation, the rejection was determined by the characteristic of impurities. Hermia's model was selected to analyse the blocking mechanism during filtration. It was confirmed that the mechanism was dominated by cake formation for all process parameters except for pH 7. At pH 7, the mechanism was controlled by intermediate blocking at an early stage and then followed by standard blocking. This research demonstrated that the ultrafiltration process was capable of removing some impurities of crude glycerin up to 68.33% and 70.98% for total impurities and FFA, respectively. However, processs development such as feed pretreatment or membrane modification is suggested to improve rejection and reduce the membrane fouling.

Keywords: Glycerin, Purification, Ultrafiltration, Fouling, Blocking Mechanism.

1. Introduction

Production of biodiesel generates crude glycerin as a by-product. It was reported that the production of 10 kg biodiesel produced 1 kg of crude glycerin [1]. Crude glycerin from biodiesel production has low economic value since the glycerin product is mixed with impurities in its heavy phase. On the other hand, glycerin is the raw material for many industries such as pharmacy, food, cosmetic, cigarette, automotive, textile or chemical industry. In addition, pure glycerin is potential for bio-lubricant, additive and an alternative fuel by adjusting the combustion cycle [2]. As a by-product, glycerin is found in its crude form (crude glycerin or raw glycerin) which contain many impurities and matter organic non-glycerol (NGOM) at various concentrations. The NGOM found in crude glycerin is fatty acid methyl esters (FAME), fatty acid ethyl esters, free fatty acids (FFA) and glycerides. Application of crude glycerin has many disadvantages such as low fuel value, require purification to increase its fuel value and high cost [1,3,4,5]. Crude glycerin contains many contaminants such as water, inorganic salts and other organic materials (FFA, FAME or biodiesel, alcohol (methanol), unreacted palm oil and triglyceride, diglyceride, monoglyceride) [3,10].

In general, crude glycerin is purified by distillation. However, the low vapour pressure of glycerin and its temperature sensitivity causes degradation or polymerisation of glycerin, and hence, vacuum distillation is applied more frequently than the normal distillation [4]. As a consequence, application of vacuum distillation was expensive due to the high energy required to create vacuum condition and evaporate glycerin [3,4]. Other purification processes such as adsorption, ion exchange, saponification, acidification, neutralisation (pre-treatment), extraction and drying have been implemented to obtain high purity glycerine [6]. Nevertheless, the usage of chemicals and energy requirement has a consequence of high cost.

Purification of glycerin by membrane technology has been developed and studied due to its process simplicity and can minimise energy requirement by utilising concentration difference, electron potential and hydroscopic pressure [4, 7]. One type of the membrane for purification or separation glycerin is Ultrafiltration (UF). Separation of glycerin from FAME by UF and microfiltration ceramic membrane was studied [8]. The research confirmed that the biodiesel met the American Society for Testing and Materials (ASTM D6751-09) standard for glycerin content. A similar result was also found by Wang et al. [9]. Experiments focused on glycerin purification have been performed. Dhabbai et al. [3] investigated purification of crude glycerol using a sequential physicochemical treatment, membrane filtration, and activated charcoal adsorption. It was reported that the result of maximum glycerol content was 97.5 wt% with acid value and FFA content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Other studies focused on the application of UF for glycerin model of glycerin separation. Amin et al. [10] evaluated UF fouling characteristic for filtration of pure mixture glycerin having 15% w/w and found that the flux decline involved cake layer model as well as pore blocking model. In addition, the separation of glycerin mixed with fatty acids (palmitic, stearic, and oleic acids) by polyethersulphone (PES) UF membrane was also studied [11]. It was reported that the PES membrane exhibited severe fouling for all types of fatty acids in solution with glycerol–water. A similar study by Amin et al. [12] investigated glycerin-rich fatty acid solutions confirming that the addition of fatty acid affected significant flux decline. Mah et al [13, 14] studied on UF of palm oil-oleic acid-

glycerin mixture and performance. It was found that cake formation was the blocking mechanism that occurs during UF process based on prediction using Hermia's model and the smallest flux decline occurred at palm oil (PO) and oleic acid (OA) mixtures. Blocking behaviour between PO and OA was different, where for PO blocking was occurred only at the surface while for OA blocking reached inside the pore of the membrane. Observation of the influence of pH was also carried out. It presented that flux decline was getting worse in the presence of the acidic environment.

To the best of our knowledge, the applications of PES UF for separation or of glycerin used pure glycerin or mixture of pure glycerin with impurities as UF feed. This research focused on the use of crude glycerin from biodiesel plant as UF feed to study the possibility and performance of UF membrane in the purification of original crude glycerin. The crude glycerin contains many impurities consist of water inorganic salt from catalyst residue, methanol, unreacted palm oil (mono-, di- and triglycerides), free fatty acids, lipids, methyl esters, as well as a various other NGOM. By using the PES UF membrane, compounds having high molecular weight were separated and retained in retentate and glycerin permeated to the membrane. In more specific, the objective of the research was to study the effect of process parameter (TMP, temperature and pH) on membrane performance (flux and rejection) for purification of crude glycerin. In addition, investigation of the blocking mechanism of the UF membrane in crude glycerin purification was addressed.

2. Materials and Methods

2.1. Materials

Crude glycerin was supplied from Biodiesel Plant of PT SMART Tbk, Tarjun, Indonesia was used as a raw material. The crude glycerin composed glycerin with concentration of 82.17 %, 10.56% FFA and NGOM other than FFA of 7.27%. The crude glycerin was then mixed with demineralised water at ratio 1:1 to form 50% glycerine solution. In this research, PES flat sheet UF membrane (Synder Filtration XV) having 1 kDa molecular weight cut-off was purchased from Sterlitech Corp, USA. It was reported that UF membrane having 30 kDa pore size was able to separate oleic acid (as a model of fatty acid) in a mixture of pure glycerin, oleic acid and palm oil [13,14]. In this research, UF membrane having 1 kDa pore size which was smaller than 30 kDa was selected to increase UF performance in separating impurities such as FFA and palm oil.

2.2. UF Membrane

Experiments were carried out by a laboratory-scale UF Cell equipped with compressor and instrumentation control as illustrated in Fig. 1.

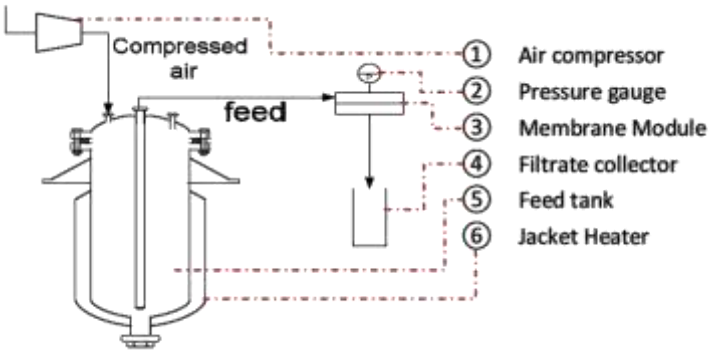

Fig. 1. Schematic illustration of UF cell with temperature control.

Experimental runs were operated at room temperature (25 ± 2 °C). Before each run, membranes were first compacted by filtering distilled water through the membrane at a pressure of 1 bar for 60 mins. For each experimental work, a new circular membrane sheet having area of 13.85 cm^2 was placed inside the UFcell. Pure water flux (J_0) was determined for initial water characteristic. The pure water flux was evaluated by weighing permeate collected at a specific time. The permeate flux (J) was determined by collecting permeate for 120 mins, with interval of 5 mins. Then, permeates were weighed (W), and its weight was converted into volume (V). Both pure water flux and permeate flux were calculated according to (Eq. 1)

$$J = \frac{V}{A \cdot t} \tag{1}$$

In eq. (1), J can be represented as J_0 or water flux ($L.m^{-2}.h^{-1}$) and J or permeate flux ($L.m^{-2}.h^{-1}$), V is volume of permeate (L) and A is membrane area (m^{-2}).

Permeate fluxes, and blocking mechanisms were observed by adding crude glycerin to the feed tank for half tank capacity. Further, the UF cell was operated at a dead-end mode at the variation of the transmembrane pressure (TMP) at 3.2 – 4.8 bar, temperature (51.63 - 68,36°C) and pH (6.32 – 9.67).The value of process parameters was selected according to optimisation of each process parameters in the previous study. The pH adjustment was conducted by adding a 0.1 N HCl or 0.1 N NaOH. Sampling for permeate flux determination was carried out for 60 mins, with interval of 10 mins.

2.3. Analysis

UF performance for glycerin purification from the feed solution was evaluated through the rejection of FFA and impurities. The rejection (R) was calculated by using eq. (2).

$$R = \frac{C_f - C_p}{C_f} \tag{2}$$

In equation (2), R (%) is rejection of FFA or impurities, C_f (mg/L)is concentration of FFA or impurities in feed, C_p (mg/L) is concentration of FFA or impurities in the permeate. The composition of permeate was analyzed by using gas chromatography and mass spectrometry (GCMS, Shimadzu TQ8030) on Rxi-1ms column (30m × 250 micrometers × 0.25 micrometre, Restek Corp, USA) with injection temperature at 250 ºC and FID detector at 300 ºC, Nitrogen at 74.5 kPa and Helium as the carrier.

2.4. Model of Blocking Mechanism

Hermia's model defined the fouling mechanism, especially in the porous membrane with dead-end system filtration. In more specific, the model highlighted the fouling mechanism which dominates in the entire of the process. This model applied a common power-law equation to describe the blocking mechanism and written in Eq. (3) [13,15].

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{3}$$

In eq. (3), t is filtration time, k is filtration constant and V is filtrate volume. Complete pore blocking illustrates that each solute is assumed to participate in blocking the entrance of the membrane pores completely. With the assumption that every solute stays on previously deposited solute, it is represented of intermediate pore blocking. Standard pore blocking describes that each solute is deposited to the internal pore wall. Determination based on the accumulation of the solute on the membrane surface is representative of cake or gel formation [10]. Mah et al. [13] and Amin et al. [10] concluded that Hermia's model was fit well with the experimental data for predicting the blocking mechanism during UF. It was confirmed by the value of R^2 which is mostly above 0.9 for appropriate model. In addition, optimising process parameters, analysing the transition of each fouling mechanism and predict cleaning or replacing membrane during operation can be predicted based on Hermia's model [13]. Further, linearisation of blocking mechanism according to equation (3) is presented in Table 1.

Table 1. Linearization equation of blocking models based on Hermia's model [16]

Pore Blocking Models	Linearization Equation	Physical Concept
Standard Blocking	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore Blocking + Surface Deposit
Intermediate Blocking	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore Constriction
Complete Blocking	$\ln J = \ln J_o - K_c t$	Formation of surface deposit
Gel or Cake Formation	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore Blocking

In Table 1, K_s, K_i, K_c and K_{cf} are constants of standard blocking ($h^{-1/2}$ $m^{-1/2}$), intermediate blocking (m^{-1}), complete blocking (h^{-1}) and gel or cake formation (h/m^2), respectively.

3. Result and Discussion

In this paper, flux decline, rejection, and the blocking mechanism were observed in various of the process parameters such as TMP, temperature, and pH.

3.1. Flux decline and rejection

3.1.1. Effect of TMP on Permeate Flux

UF process is one method to separate substances which have different molecular size using TMP as a driving force. The fluxes increase along with the increase on TMP, indicating that the flux is proportional to TMP as long as the resistance between the membrane and the fluid are not significant [10, 14, 17-20]. Fig 2. shows the flux response against the TMP at pH 5.27 and temperature 60 ºC. Generally, the flux decline over time is caused by the impurities deposited on the surface and inside the membrane pores.

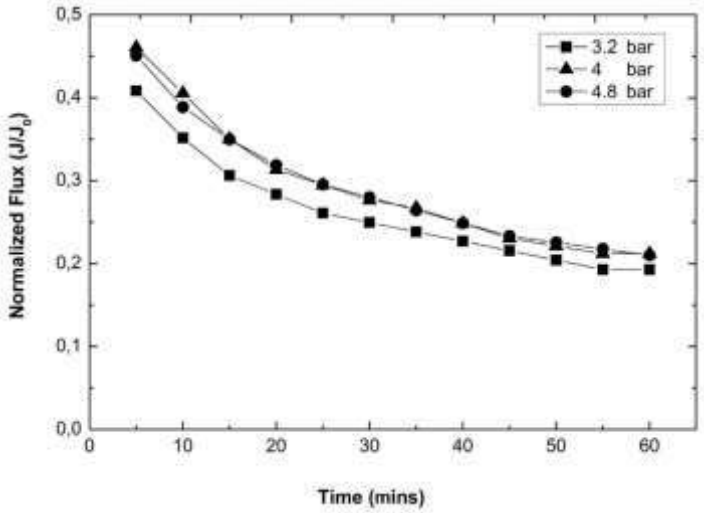

Fig. 2. Influence of TMP on fluxes of glycerin-rich solutions at pH of 5.27 and Temperature of 60 ºC

Fig. 2 confirms the correlation between flux and TMP, wherein increasing TMP causes an increase in the flux. The higher normalised flux at higher TMP is achieved at a pressure range of 3.2 – 4 bar. In contrast, at a range of 4 – 4.84 bar, the effect of adjustment TMP on the positive impact on the flux is not significant, indicating that the TMP had a slight effect on increasing flux. This condition reveals an increase in resistance between the membrane and the fluid that caused by

polarisation of impurities on the membrane surface [12, 14]. Based on Darcy's law, flux was not only depended on TMP but also influenced by the resistance between the membrane and the fluid [20].

Adjusting TMP to a higher point lead to an increase in flux, but it still cannot affect the pattern of flux decline. This is confirmed by the flux decline pattern in Figure 2 showing similarity pattern at the variations of TMP. A significant flux decline in the early stages of the UF process a range of 0 – 25 mins and then continued with the stationary states of flux decline at a range of 30 – 60 mins are observed. This phenomenon indicates that the process more influenced by mass transfer mechanism than by TMP it's self [15]. This leads to a more severe condition of flux decline as the result of the deposits increase and impurities quantity. The impurities were carried away by the glycerin-rich solution that flows through to membrane matrix and presumably deposited both on membrane surface as well as inside the pore of the membrane [12,15].

This phenomenon is conceivable because of the nature of the raw material (glycerin) and the majority of impurity (FFA) in crude glycerin. Glycerin has a high viscosity. The viscosity for pure glycerine was found as 1.5 Pa.s [1] and for crude glycerine containing 80% of glycerine, the viscosity was above 20 mPa.s at reference temperature [21]. The fluid characteristic is much different from Newtonian fluids such as water that only has viscosity about 1 mPa.s at 20 ^{o}C [21]. The high viscosity of glycerine indicates that the molecular spatial space of glycerin is denser, as like as molecular space of liquid phase that is also denser than the gases phase molecular space [18]. This is due to the existence of a highly branched network of hydrogen bonds formed by three hydrophilic hydroxyl groups [22]. Besides that, the properties of FFA tend to be hydrophobic and insoluble in polar compounds [11]. The hydrophobicity of the FFA has different characteristic to the hydrophilic properties of the membrane used in this study. It is accomplished that hydrophobic properties of the impurity (FFA) can increase repulsion forces on the membrane, which ultimately influences the flux trend that occurs during the filtration process (mass transfer mechanism).

3.1.2. Temperature Effect on Permeate Flux

Effect of various temperature (at pH of 8, TMP of 4 bar) on flux decline is presented in Fig. 3. Observations show the temperature has more influence than the TMP on the flux decline qualitatively. The condition occurs because the increased temperature can directly trigger the viscosity reduction. This makes the fluid more freely to flow as a result of increasing in molecular spatial space in higher temperature condition [22]. In addition, increasing the temperature can lead to an increase of the polymer bonding mobility inside the membrane matrix [12,23]. Hence, the resistance caused by both fluid and membrane against each other is reduced by the increased temperature.

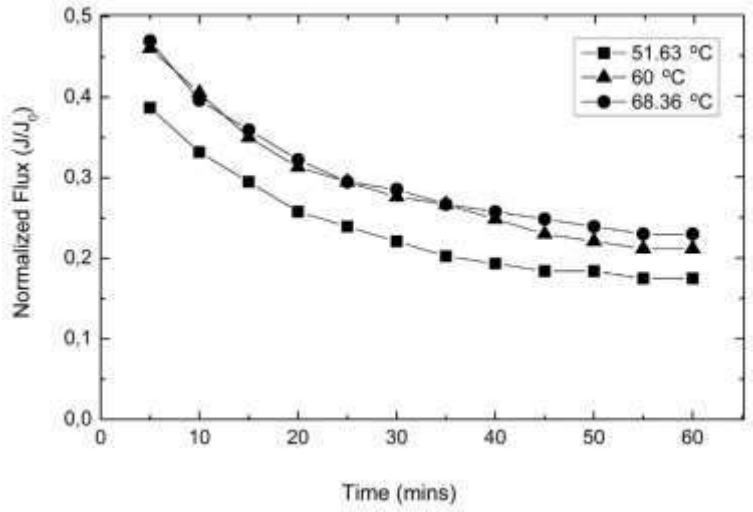

Fig. 3. Influence of temperature on flux decline of the glycerin-rich solution (pH = 8, TMP = 4 bar).

In addition, Fig. 3. shows the trend of flux response against temperature indicating that at a range of 51.63 °C – 60 °C, the increasing temperature has a positive effect on the flux. On the contrary, in a range of 60 °C – 68.36 °C the effect of temperature is insignificant.

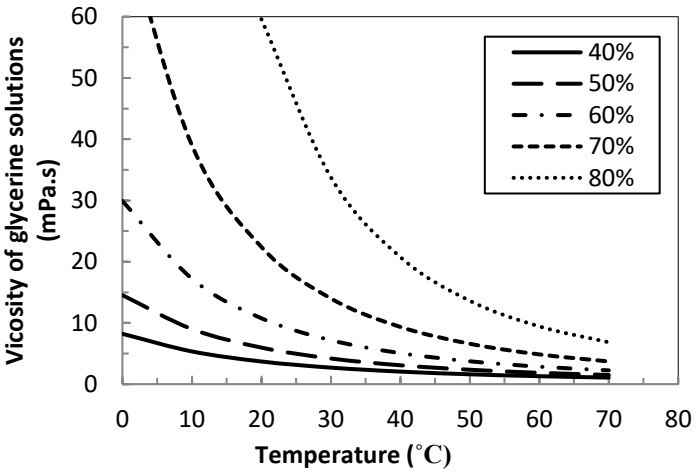

Fig.4. Viscosity of glycerine solution with increased temperature. Drawn from data calculation using viscosity-temperature correlation equation based on Arrhenius form. Source: [21]

Dhabhai et al. [3] found that the temperature did not influence the decrease of the raw glycerin viscosity at temperatures above 60 °C. It was presumably the cause

of the minor effect of temperature above 60 °C. Figure 4 supports the finding confirming that the viscosity change at temperature above 60°C is insignificant. Although the viscosity of glycerin which can directly affect fluid resistance to the membrane can be reduced, it does not have a positive effect on the pattern of flux decrease as shown in TMP. This condition denotes that characteristic and properties of impurity (FFA) plays a key role in the pattern of flux decrease. Moreover, the flux can directly increase along with decreasing in viscosity which can lead to increasing of impurities concentrations both on the surface and inside pore of the membrane. This phenomenon also confirms that the process is dominated by the mass transfer mechanism.

3.1.3. Effect of pH on Permeate Flux

Fig. 5 shows the responses of flux against different pH condition at TMP of 4 and temperature of 60 ºC. The pH was observed in a range of 6.33 – 9.67 where the feed sample pH was 5.27. The results show that the flux decreases the acidic state greater than those in the alkaline state. Fatty acids are impurities in a glycerin-rich solution. Based on pH condition of its environment, the fatty acid has the nature that remained as the undissociated molecule in the presence of an acidic environment and could be dissociated in an alkaline environment. A large amount of undissociated would cause severe fouling and flux decline [14, 11, 24].]Fatty acid molecules can interact with acid to form the larger molecules via an agglomeration process with another molecule of fatty acid [11,13]. The larger molecule that was formed may increase the adsorption of foulant molecule. The adsorption is formed on the membrane surface as well as on the entrance of the membrane pore and then causes high flux decline and membrane fouling [11,24-25]. Sequentially, the flux decline follows the order of pH 7> pH 6.33> pH 9.67>pH 8 and the highest flux decline is found at pH 7. Similar trend was also reported by Mah et al. [14]. According to dissociation and undissociation effect, at pH of 6.33, the flux decline should be the highest and at pH 9 the flux decline was the lowest. However, flux value at pH 7 shows higher flux decline than those at pH 6.33. This is most likely due to the fatty acid state that not fully dissociated at pH 7 [11]. In the dissociated state, fatty acid does not form clots and find as single molecule form [24]. The single molecule of fatty acid can pass through into membrane pore since the average size of the single fatty acid molecule is four times smaller than the membrane pore size [10] and then triggers the blocking inside the wall of membrane pore. At pH 9, this phenomenon may be due to the fact that dissociated molecules of fatty acids (at pH 9 the fatty acid molecules almost completely dissociate) blockage the micropores of the membrane. The blocking at micropores is possible in PES-based UF membranes because it is an asymmetric porous membrane [26].

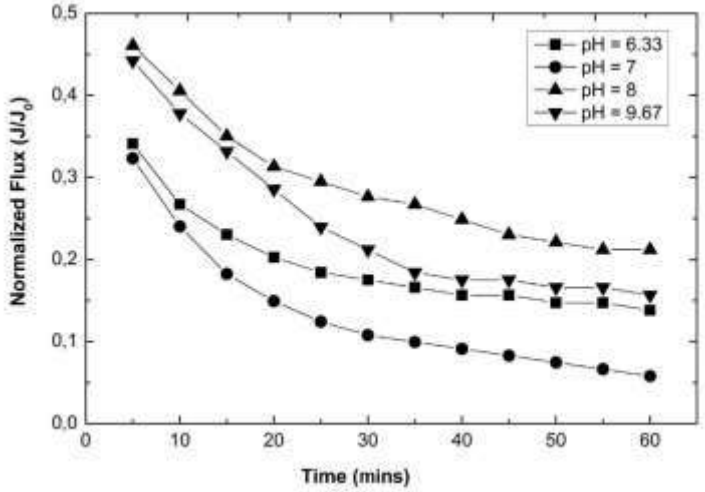

Fig. 5. Effect of pH on Flux decline of glycerin-rich solutions (TMP = 4, Temperature = 60 ºC).

3.1.4. Rejection

Rejection behaviour for glycerine-rich solution was observed by Mah et al. [14] and Amin et al. [10]. Amin et al. [10] reported that the 25 kDa of PES and 30 kDa UF (at TMP 2 bar and temperature 40 ºC) found that membrane could reject 35.59 to 41.41% of FFA. In addition, it was found that the FFA rejection for hydrophobic membrane was higher than the hydrophilic membrane. Moreover, Mah et al. [14] used 30 kDa UF membrane and PO+OA mixture as a foulant under the operating condition at TMP 2 bar, temperature 60 ºC and pH 2-9. It was found that the best rejection of impurities is 97.95% at pH 2.

Table 2. Summary of rejection data in various variations of process parameters.

No.	Pressure (bar)	Temperature (°C)	pH	Rejection (%)	
				FFA	Total impurities
1.	3.2	60	8	48.10	48.50
2.	4	60	8	54.17	32.11
3.	4.8	60	8	57.63	52.86
4.	4	51.63	8	44.32	33.25
5.	4	60	8	54.17	32.11
6.	4	68.37	8	45.35	43.56
7.	4	60	6.33	30.70	21.18
8.	4	60	7	70.98	68.33
9.	4	60	8	54.17	32.11
10.	4	60	9.67	25.82	24.22

Table 2 shows a different trend in each variation of the operating condition. For TMP variation, the rejection increases with increasing on TMP. The rejection of FFA content in the filtrate at 4.8 bar and 3.2 bar are 57.63% and 48.1%, respectively. This condition takes place because in higher TMP some small foulant molecules may be penetrated the membrane pore and form a deposit, thus causing significantly reduce on the size of membrane pore which leads to an increase in rejection of impurity [14, 27]. For temperature variation, the trend of rejection tends to be similar to TMP variation where a higher temperature process has greater rejection than lower temperature. The rejection of impurities is 33.5% at 51.63 °C while at 68.37 °C the rejection reaches 43,56%. This is likely due to the effect of increasing temperature which can directly affect the increase in flux and causes an increase the impurities that flow through the membrane pore [12]. It is similar to the condition that occurs in TMP variation. Rejection behaviour at pH variation has a different kind than the other operating parameter. The highest result is 70.98% at pH 7, and the lowest result is 25.82% at pH 9.67. This behaviour may occur due to the nature of the impurities, as described in section 3.1.3.

The result of impurities rejection at each variation in this study is higher than impurities rejection reported by Amin et al. [12]. In this study, the highest result is 70.98% rejection of FFA whereas the highest result by Amin et al. [12] is 41.41%. It is proved that using smaller membrane pore size give a positive impact on impurities rejection. In case of the result reported by Mah et al. [14] that shows higher rejection (about 97,95 at pH 2) than the result in this study might be explained by the type of impurities which is contained in glycerine and its operation condition. Previous researchers used PO+OA mixture as foulant that has a larger molecular and droplet size than FFA. The larger molecule and droplet size can lead to increasing on the rejection of impurities [14]. Further, TMP that was also used lower than TMP that was used in this study. The lower TMP can decrease penetrating possibility by impurities to membrane pore [12,15].

3.2. Blocking Mechanism

The constant of the blocking mechanism and the corresponding correlation coefficients (R^2) during filtration is listed in Table 3. According to the Table, increasing TMP reduces the flux decline. Its condition also applies to temperature as confirmed by the smaller value of the constants along with increases of TMP and temperature. Cake formation is predicted as a dominated blocking mechanism during the filtration process for both TMP and temperature variations. In the cake formation, the foulant is firstly adsorbed on the membrane surface, penetrate the membrane pore and then form a layer that can cause a more severe decrease in flux even from the early step of filtration. The fatty acid may be the component responsible for severe fouling [10]. In biodiesel industries, glycerin was a by-product from the transesterification reaction which consists of palmitic acid (C16: 0), stearic acid (C18: 0) and most of the oleic acid that has double bond carbon chain (C18: 1) [28].

In addition, Table 3 shows the value of k (constant) at an acidic state that tends to be higher than in the alkaline state. It demonstrates that the resistance of the fluid to the membrane is larger and causing more severe fouling than in the alkaline state. The nature of fatty acids which tend to undissociated at acidic

environment may be responsible for that condition. Under this environment, the fatty acid would be clumping each other [11]. Mah et al. [14] reported that the droplets of a mixture of palm oil and oleic acid at pH 2 (very acidic condition) lead to significant increase in droplet size and even reach twice in size over the original droplet size. Therefore, setting pH under acidic conditions can lead to agglomeration of foulant molecules.

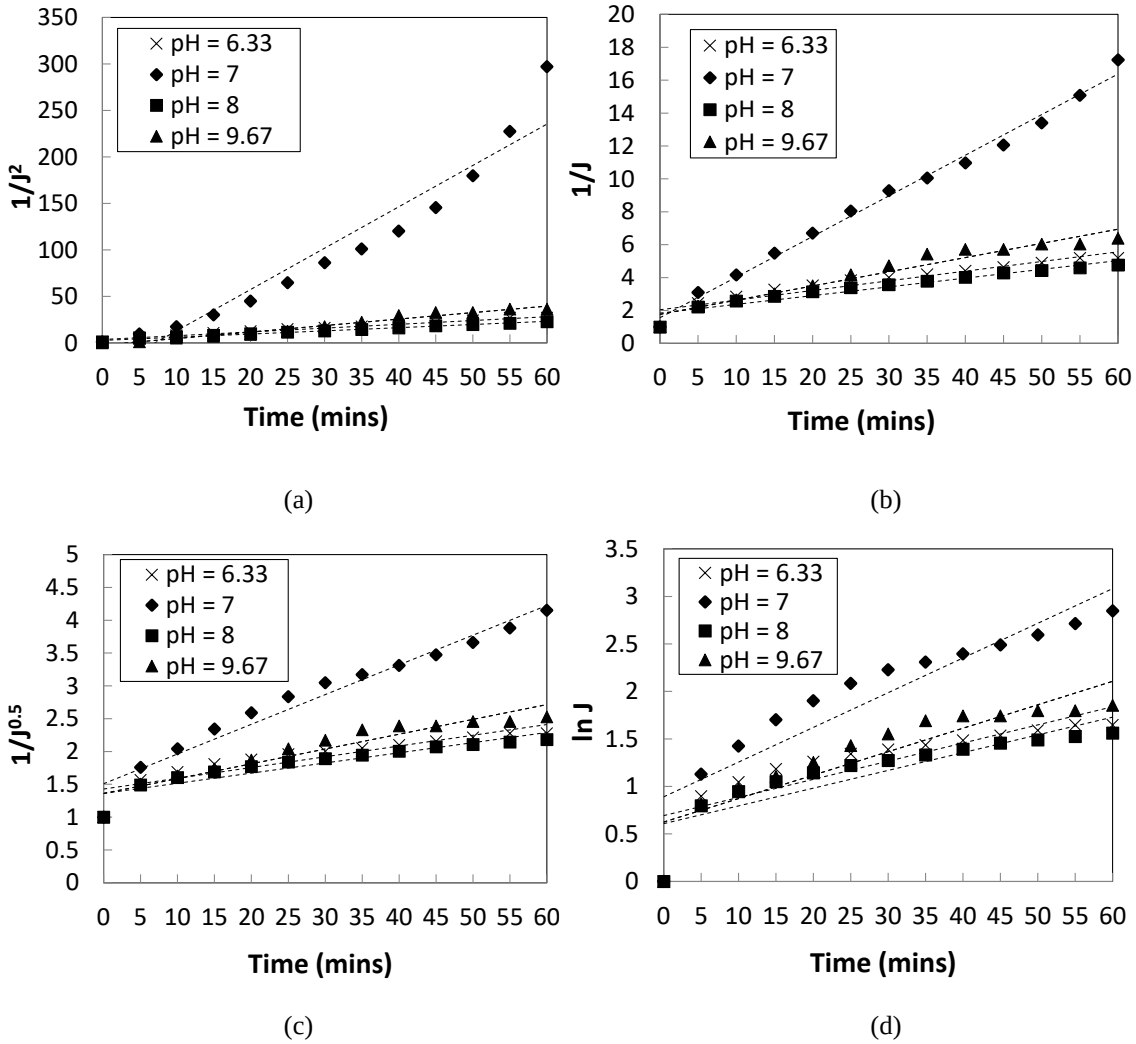

Fig. 6. Hermia's model fitting for the experimental data: (a) Cake formation, (b) Intermediate blocking, (c) Standard blocking, (d) Complete blocking (P = 4 bar, T= 60 °C)

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Table 3. Summary of rejection data in various variations of process parameters.

Parameters	n=0 Cake Formation		n=1 Intermediate Blocking		n=1.5 Standard Blocking		n=2 Complete Blocking	
	K_{cf}	R^2	K_i	R^2	K_s	R^2	K_c	R^2
Pressure								
3.2 bar	0.4098	0.9848	0.0585	0.9031	0.0164	0.8171	0.0191	0.7051
4 bar	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
4.8 bar	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
Temperature								
51.63 °C	0.5329	0.9782	0.0692	0.9026	0.0185	0.8204	0.0208	0.7084
60 °C	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
68.36 °C	0.2872	0.9737	0.0476	0.8892	0.0142	0.8136	0.0176	0.7184
pH								
6.33	0.4090	0.9840	0.0580	0.9030	0.0160	0.8170	0.0190	0.7050
7	4.4480	0.9187	0.2468	0.9917	0.0453	0.9557	0.0365	0.8307
8	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
9.67	0.6982	0.9742	0.0862	0.9443	0.0225	0.8935	0.0247	0.8068

Fig. 6. exhibits the blocking mechanism that occurs in the various variations of pH. Generally, the mechanism is dominated by the cake formation, except for pH 7 as supported with the highest R^2 value for pH 6.33, 8 and 9.67. The similar result was reported by Amin et al. [10] and Mah et al. [14] confirming that cake formation was the dominant mechanism in pH variation. The different condition at pH 7, as seen in the value of k (constant for blocking mechanism) is much greater than at another pH. Moreover, the highest R^2 value in the intermediate blocking mechanism is found. Fig. 5 (b) and fig. 5 (c) confirm that in the initial conditions of filtration until 10 mins, both intermediate blocking and standard blocking mechanism occur. Then, in 15 mins until 45 mins only the intermediate blocking mechanism is observed, and for 50 mins afterwards only standard blocking contributes to the flux decline. In intermediate blocking, the solutes or particles which accumulated on the membrane surface and the entrance of membrane pore are possible to overlap another solute that has already deposited on the membrane surface. The foulant is the pilled up each other in irregular arrangement [10] and triggers other mechanisms such as standard blocking to occur during the filtration process. Standard blocking mechanism is believed to be responsible for a significant flux decline as in that condition the impurities molecule penetrates to the inside wall of the membrane pore and make a deposit which can be lead to plugging on the active area of the membrane pore [29,30]. This strengthens the previous statement that fatty acids which are not fully dissociated at pH 7enterthe pore and cause blockages in the membrane pore.

At high pH, especially for pH 9 above, the fatty acid molecule is fully dissociated and become surfactants with a hydrophilic head and hydrophobic tails which have negative charge [31]. If there was an interaction between fatty acids and membranes, it formed a negative charge induction to the membrane [10, 32]. Thus the repulsive force between the fatty acid and the membrane may change. This condition may also cause changes in the fluid resistance to the membrane [11].

4. Conclusions

The study of flux decline, rejection and blocking mechanism during UF process using 1 kDa PES membrane with various variations process parameters (TMP, temperature, and pH) to the glycerin-rich solution from the biodiesel industry were conducted. It was found that flux decline was severe significantly in all variation of process parameter due to a deposit of impurities. Both pressure and temperature did not give significant effect to the flux decline due to the domination of the mass transfer mechanism which is caused by the nature of impurities its self. In addition, the pressure and temperature had a similar trend of rejection that in higher process parameters the rejection becomes greater, whereas at pH variation behaviour of rejection is determined by the nature of impurities. Hermia's blocking law model found to fit well to the experimental data. The best-fit experiment data was cake layer formation mechanism for all process variation except for pH 7 where the intermediate blocking takes the lead in early stages and then followed by standard blocking. In order to improve the UF performance, preliminary treatment of crude glycerin or modification of the membrane surface is required. This treatment is expected can reduce the membrane fouling specifically due to FFA characteristic.

Nomenclatures

A	Membrane area, m^2
C_f	Concentration ofFFA or impurities in the feed, mg/L
C_p	Concentration of FFA or impurities in the permeate, mg/L
J	Permeate Flux, $L.m^{-2}.\ h^{-1}$
J_0	Initial Flux, $L.m^{-2}.\ h^{-1}$
k	Constant of blocking mechanism
K_c	constants of complete blocking (h^{-1})
K_{cf}	constants of gel or cake formation (h/m^2)
K_i	constants of intermediate blocking (m^{-1})
K_s	constants of standard blocking ($h^{-1/2}\ m^{-1/2}$)
n	Value that represents a blocking mechanism, n = 0 (cake layer formation), n = 1 (intermediate blocking), n = 1.5 (standard blocking), and n = 2 (complete blocking)
R	Rejection, %
R^2	The corresponding correlation coefficients
t	Filtration time (h)
V	Permeated volume (L)
W	Weight of permeate (g)

Abbreviations

ASTM	American Society for Testing and Materials
FFA	Free Fatty Acid
GC	Gas Chromatography
TMP	Trans Membrane Pressure
UF	Ultrafiltration

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OUTLINING HOW THE ISSUES ARE ADDRESSED

Title of paper: PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

1. Address all the concerns/recommendations of the reviewers.
2. All amendments made are to be highlighted in red color in the revised paper.

Reviewer # 1

Final Recommendation	Accepted without modification	Accepted with minor corrections	Accepted with major modification	Rejected
Please tick	☐	☐	☐	☑

Comments	Addressed (Y/N)	Reply/Action taken
1. Please use dot, instead of comma, for writing numbers with decimals.	Y	All comma in numbers with decimal have been changed with dot.
2. Please use degree sign ° to describe "degree", and do not use superscripted zero "0", superscripted uppercase "O", or superscripted lowercase "o"!	Y	All sign describing degree have been changed with " ° "
3. Please write "min" or "mins" in the whole manuscript, to describe "minute" or "minutes	Y	All words minutes have changed with mins
4. Please write "h" in the whole manuscript, to describe "hour" or "hours".	Y	Description of 'hour' or 'hours' have been change into 'h'
5. Do not replace the word "or" using the symbol "/" !!	Y	All symbol "/" have been replaced by "or"
6. Do not use unit with the "/" character! For example use "L m^{-2} h^{-1}" instead of "L/m^2.hr)	Y	All unit have been edited.
7. Abstract: please write "transmembane pressure (TMP)", and then write it consistently as TMP, TMP and TMP.	Y	Transmembrane pressure has been changed into TMP in the whole manuscropt.
8. Abstract: "…Experiments were carried out at…"	Y	It has been corrected
9. Abstract: The flux decline phenomenon is very common, very usual. No novelty here!	Y	We modified the abstract and add some suggetion for improvement.
10. Abstract: The current range of TMP, temperature and pH is too short. It might be widened, such as 1-5 bar, 25-70 °C, and 5-10, respectively.	N	We select the current TMP according to result of optimization variable study in the previous research.
11. Abstract: "…free fatty acid (FFA)…"	Y	It has been corrected
12. Section 1 paragraph 1: Please mention what are the components classified as MONG. It should be written as NGOM (non-glycerol organic matter, all in lowercase), instead of MONG that is grammatically incorrect.	Y	It has been corrected

13. Section 1 paragraph 1: What are the disadvantages of crude glycerin? Add more references!	Y	Disadvantage of crude glycerin has been written and more references have been added
14. Section 1 paragraph 1: …free fatty acid (FFA), fatty acid methyl ester (FAME, or biodiesel)…	Y	It has been corrected
15. Section 1 paragraph 1: Add space to split the word "alcoholand"	Y	It has been corrected
16. Section 1 paragraph 2: You mentioned about "other purification processes", but no references at all !!	Y	It has been corrected
17. Section 1 paragraph 2: Cite Y. Wang et al, J. Membr. Sci. 363 (2010) 149-159 and Y. Wang et al, J. Membr. Sci. 378 (2011) 339-350 that explored pervaporation as a new process to handle and purify viscous and hygroscopic fluid (ethylene glycol), which is quite similar to glycerin.	N	Thank you for the suggestion. However, we think that the paper you're suggested is not similar to our process. Hence, we cite other reference that we think is similar with our concept.
18. Section 1 paragraph 3: "...ultrafiltration (UF)…", and then please write consistently UF, UF, and UF throughout the entire manuscript!	Y	It has been changed and all ultrafiltration have been replaced by UF
19. Section 1 paragraph 3: "Separation of glycerin from FAME by UF and microfiltration…"	Y	It has been corrected
20. Section 1 paragraph 3: What is the reference number for the citation "[Saleh]" ???	Y	It has been edited and corrected. Saleh is the reference no 8.
21. Section 1 paragraph 3: Please use uppercase A for the beginning of the sentence "A similar result was also found by Wang et al. [6]"	Y	It has been correcetd
22. Section 1 paragraph 3: ASTM stands for what? Please write it down.	Y	The ASTM has been defined
23. Section 1 paragraph 3: Please consistently write FFA, FFA, and FFA throughout the entire manuscript!	Y	It has been corrected
24. Section 1 paragraph 3: The proper name of the polymer is "polyethersulfone", with lowercase l, and with "f" instead of "ph", NOT "poyethersulphone"	Y	It has been corrected
25. Section 1 paragraph 3: Describe the details on the results and findings from Mah et al [10, 11]	Y	The fnding has been written in detail
26. Section 2 paragraph 1: Delete the word "polyethersulphone" and leave the PES word. Add space before the word "(Snyder Filtration XV).	Y	It has been corrected
27. Section 2.1 paragraph 1: You use a membrane with relatively wide pore (1000 Da MWCO) to separate glycerol (92 Da) from water (18 Da) and other small molecules??? Such a FATAL error in planning the experiment.	N	In this research we did not aim to separate glycerol from water with 1kDa membrane. We separated gliceryne rich solution containing glicerin, water and impurities by UF membrane. Glycerin and water which has having smaller molecular weight than the membrane pore will pass to the UF membrane. On the other hand, the impurities was retained by the UF.

28. Section 2.2 paragraph 2: Delete “ultrafiltration”, leave the “UF”. Please write consistently UF, UF, and UF throughout the entire manuscript!	Y	It has been corrected
29. Figure 1: What is the hexagon in circle? Describe!	Y	We edited the image for better visualization and illustration
30. Section 2.2 paragraph 2: “…for 60 mins…”	Y	It has been corrected
31. Section 2.2 paragraph 2: “…inside the UF cell…”	Y	It has been corrected
32. Section 2.2 paragraph 2: “…collected for 120 mins, with interval of 5 mins…”	Y	It has been corrected
33. Section 2.2 paragraph 2: Permeate FLUX! Not “fluxes”	Y	It has been corrected
34. Equation 1: remove the “x”		
35. Section 2.2 paragraph 3: delete “transmembrane pressure” and then write it consistently as TMP, TMP and TMP.	Y	It has been corrected
36. Section 2.2 paragraph 3: “…carried out for 60 mins, with interval of 10 mins.”	Y	It has been corrected
37. Section 2.3 paragraph 1: “…calculated by using Eq. 2.”	Y	It has been corrected
38. Section 2.3 paragraph 1: “gas chromatography (GC, Shimadzu TQ8030).”	Y	It has been corrected
39. Section 2.3 paragraph 1: Where is the standard curve, or calibration curve of the analysis of FFA, FAME, glycerin, etc. by using GC? What would be the retention time of those components? What would be the temperature of the GC column?	Y	Temperature of the GC column has been added. We had the standard curve. However, we apologize that we could not add the standard curve in this manuscript since too may images should be added.
40. Section 3 paragraph 1: What is the reason and justification of using the Hermia model? Write it down!	Y	The reason af using the Hermia model has been written in detail
41. Section 2.3 paragraph 2: Use uppercase “C” for the beginning of Section 2.3 paragraph 2!	Y	It has been corrected
42. Section 2.3 paragraph 2: Change “/” with “or”	Y	It has been corrected
43. Section 2.3 paragraph 2: Equation 1? This is wrong, maybe you refer to Equation 3?	Y	It has been corrected
44. Table 1: Please use lowercase letters in all words, except for the beginning of the sentences	Y	It has been corrected
45. Section 4: Delete “transmembrane pressure”, and then write it consistently as TMP, TMP and TMP.	Y	It has been corrected
46. Section 4: “…sampled every 5 mins… for its composition by using GC.”	Y	It has been corrected
47. Title of Section 4.1.1: Delete “transmembrane pressure”, and then write it consistently as TMP, TMP and TMP.	Y	It has been corrected
48. Section 4.1.1 paragraph 1: “UF process is one method to…using TMP as a driving force”	Y	It has been corrected
49. Section 4.1.1 paragraph 1: Add more references, and not just use reference [14], because the phenomenon of the flux decline (in Section 4.1.1 paragraph 1) is so mainstream, very common, the shall be more than ten references for this aspect, cite five more references!	Y	We explained in more detail regarding the comment of reciewer and add more reference.

50. Figure 2: Where is J_0? How much is J_0? Why there is no J/J_0= 1 at t= 0 mins???	Y and N	We had add the J_0 value. We did not visualize the graph from J/J_0 = 1 because the different between each parameter could not be observed if we draw graph from J/J_0=1
51. Change the label of x axis in Figures 2, 3, 4, 5 with "mins"	Y	All the label of x-axis has been edited.
52. Figure 2: Insignificant change between the trend of the normalized flux at 4 and 4.84 bar. Explain! Add more TMP, between 1-5 bar!	Y and N	We have add explanation in the paragraph to confirm the insignificant change. However, we could not add more TMP from 1-5 bar since we did not have enough data on the range of TMP.
53. Section 4.1.1 beginning of paragraph 2: Which figure confirms the correlation between flux and TMP?	Y	It has been corrected. It supposed to be written as Fig.2.
54. Section 4.1.1 paragraph 2: "30-60 mins"	Y	It has been corrected
55. Section 4.1.1 paragraph 2: Delete the sentence started with "According to… the flux", because it is very redundant and confusing!	Y	It has been changed
56. Section 4.1.1 paragraph 2: "…as the result of the increasing deposit and impurities…"	Y	It has been corrected
57. Section 4.1.1 paragraph 2: "The impurities were carried away…"	Y	It has been corected
58. Section 4.1.1 paragraph 3: How high is the viscosity of glycerin? Where is the data, and the reference(s)?? State it in the unit of Pa.s, or centipoises (cP) also acceptable	Y	We add viscosity of crude glycerin according to the reference and calculated the viscosity of glycerin rich solution
59. Section 4.1.1 paragraph 3: Add references for "limited spatial molecular space", "hydrophobic characteristic", "tend to be hydrophobic and insoluble.."	Y	It has been corrected
60. Section 4.1.2 paragraph 1: "The condition occurs because increased temperature can… Hence, the resistance caused by both…is reduced by the increased temperature."	Y	It has been corrected
61. Figure 3: Insignificant change between the trend of the normalized flux at 60 and 68 °C. Explain! Add more variation of temperature, namely 25-70 °C.	Y and N	We add more explaination in the paragraph. However, we could not add more variation of temperature
62. Figure 4: Inconsistent trend, up and down and up and down again… unclear and confusing. Explain!	Y	We add more discussion with supporting reference
63. Please repeat all the experiments with a replicate (duplo) or two replicates (triplo), because all the results in Figures 2, 3, and 4 are insignificant, not worth mentioning	Y	Actually in the provided data
64. Section 4.1.3 paragraph 1: "…agglomeration… The larger molecules that were formed may increase the…"	Y	It has been corrected

65. Section 4.1.3 paragraph 1: What do you mean with "dissociation and undissociation"? It makes me dizzy! And no references to back up! Is this real life, or is it fantasy?	Y	We add discussion in detail supported with the succifient reference
66. Section 4.1.3 paragraph 1: "Not fully undissociated at pH 7", "Irregularities at pH 8" WHATTT? Where are the references to back this bewildering statement?	Y	We supported the statement with the succifient reference
67. Section 4.1.4 paragraph 1: "…Causing a shrink on the size…" What is the reason? Or where is the data, and where are the REFERENCES??	Y	The reference has been added and the reason has been expalined in the paragraph.
68. Table 2: Maximum rejection of mediocre 70%, due to filtering small molecules by using wide and sparse sieve… What a poorly planned experiment! The least you can do is chemically crosslink the membrane in order to decrease the pore size (hence the MWCO). Or even please perform thermal annealing for the membrane!	N	As previously expalined in answering comment no 27, we separated gliceryne rich solution containing glicerin, water and impurities by UF membrane. Glycerin and water which has having smaller molecular weight than the membrane pore will pass to the UF membrane. On the other hand, the impurities was retained by the UF. We aplogize that we can not do expremient with chemically crosslink the membrane since it will far from our research objective.
69. Table 3: Where are the fitting for all the data shown in Table 3?? There should be a set of 12 (twelve) plots!	N	We could not present all the fitting data in this manuscript since it will generate very long table that will not interest the reader.
70. Section 4.2 paragraph 2: "…which tend to dissociate at acidic environment…"	Y	It has been corrected
71. Section 4.2 paragraph 3: Please change "minutes" to mins!	Y	It has been corrected
72. Section 4.2 paragraph 3: "The foulant is the piled up… in irregular…"	Y	It has been corrected
73. Section 4.2 paragraph 3: Which "evidence"??? What "evidence"???	Y	We add more discussion to confirm the evidence
74. Section 4.2 paragraph 4: Add references that support the negative charge induction caused by the interaction between fatty acid and membrane!	Y	We add references to support the statement
75. Section 4.2 paragraph 4: "This condition may also cause changes in the fluid resistance to the membrane [8]."	Y	It has been corrected
76. Conclusion: You use a membrane with relatively wide pore (1000 Da MWCO) to separate glycerol (92 Da) from water (18 Da) and other small molecules??? Such a FATAL error in planning the experiment. This study is not worth studying.	N	As previously expalined in answering comment no 27 and no 68, we separated gliceryne rich solution containing glicerin, water and impurities by UF membrane. Glycerin and water which has having

		smaller molecular weight than the membrane pore will pass to the UF membrane. On the other hand, the impurities was retained by the UF.
77. Nomenclature: Please use UPPERCASE for the letters in the beginning of a sentence!	Y	It has been corrected
78. Nomenclature: Permeate FLUX! Not "fluxE"	Y	It has been corrected

(Please add more rows if needed)

Reviewer # 2

Final Recommendation Please tick	**Accepted without modification**	**Accepted with minor corrections**	**Accepted with major modification**	**Rejected**
	☐	☑	☐	☐

Comments	**Addressed (Y/N)**	**Reply/Action taken**
• Some typos and gramatical errors as detailed in the corrected manuscript	Y	All the typo, gramatical errors has been corrected and some words have been changed acording to the reviewer suggestions
• Please define all the parameters in the equations (1), (2), (3) and in Table 1, not only in Nomenclature	Y	All the parameters in equation (1), (2), (3) and in Table 1 are defined.
• Please add A, K, W. In Nomenclature	Y	We add the variable A, K, and W in nomenclature

(Please add more rows if needed)

Reviewer # 3

Final Recommendation Please tick	**Accepted without modification**	**Accepted with minor corrections**	**Accepted with major modification**	**Rejected**
	☐	☑	☐	☐

Comments	**Addressed (Y/N)**	**Reply/Action taken**
• Transmembrane pressure is changed to TMP	Y	It has been corrected
• Use dot instead of comma for the decimal point	Y	Decimal point has been changed into dot
• Numbering of citation by [Saleh]	Y	Citation of Saleh is numbered
• Please provide the research gap addressed in this study at the end of introduction chapter	Y	Further paragraph addressed the reseach gap has been added
• Check font format of Fig. 1	Y	Font format on Fig. 1 has been checked and changed
• What is the flux unit?	Y	Flux unit has been added
• Volume or mass in sentence "Then the volumes of permeates were weighed (W)"	Y	The sentence is changed into "Then the permeates were weighed (W)"

• What are the justification of these values? Why not using exact value rather than decimal point.	Y	We add more detail explanation in the paragraph. We select the current values according to result of optimization variable study in the previous research.
• Provide detail of the column type and analysis condition of GC	Y	Detail of the column and analysis condition of GC has been provided
• Describe the symbol found in the equation in Table 1	Y	All symbols have been described
• Why flux for 4 bar and 4.84 bar almost have the same value? it is not proportional then.	Y	
• Provide the fixed value of pH and Temp at varied TMP	Y	The fixed value of pH and temperature have been provided
• Give the fixed value of pH and pressure at this varied temperature	Y	The fixed value of pH and pressure have been provided
• What is the initial pH of the solution? Why not used a sample at initial temperature as the control?	Y	We add the initial pH of solution.
• Give fixed value of pressure and temperature	Y	The value of pressure and temperature have been given
• What is the initial pH of the feed sample	Y	The initial pH of feed sample is given
• Why using pH 6.33 and 9.67?	Y	We select the current pH according to result of optimization variable study in the previous research.
• Benchmark and discussed the rejection obtained in this study with other publication for glycerine rejection.	Y	We add a paragraph for discussed the rejection of and FFA. In our paper, we only investigated the rejection of glycerin

(Please add more rows if needed)

Reviewer # 4

Final Recommendation Please tick	**Accepted without modification**	**Accepted with minor corrections**	**Accepted with major modification**	**Rejected**
	☐	☑	☐	☐

Comments	**Addressed (Y/N)**	**Reply/Action taken**
• Minor grammatical errors and typing errors such as spacing, capital letters at beginning of sentence, etc .	Y	All errors have been corrected
• Introduction, para. 3 "…and microfiltration ceramic membrane was studied [Saleh]", "Mah et al [10, 11] studied…"	Y	Referrence of Saleh has been added and citation is edited.
• Ultrafiltration Membrane, para. 2 "..at 5 minutes intervals.."	Y	It has been corrected
• x in Equation (1) and (2) looks like a variable. It should be multiplication? Please check the font used.	Y	x is multiplication. The equation is edited
• Referencing: " Mah et al. (2012) reported.."	Y	The citation has been added

(Please add more rows if needed)

Reviewer # 5				
Final Recommendation Please tick	**Accepted without modification** ☐	**Accepted with minor corrections** ☐	**Accepted with major modification** ☑	**Rejected** ☐

Comments	Addressed (Y/N)	Reply/Action taken
• In the introduction, what are the current limitations of using UF for glycerol purification? what is the objective of this study? Or what is this study trying to improve? Reduce the effect of flux decline or just gaining an understand the effect of flux decline when some dependent variables were varied.	Y	New paragraph has been added to explain in more detail
• In the introduction, ref. [8] reported that using PES exhibited a severe fouling in the present of fatty acid in crude glycerol. A justification is needed for reasons why this study still used PES with very small cut-off 1 kDa.	Y	A justification according to selestion of PES pore size is added in section 2.1.
• For all equations in the manuscript, after each equation, please specify each papameter, its name, and unit.	Y	Name and unit of each parameter in equation has been specified
• In the method section, Gas Chromatography was used for analysis. Operating condition for this analysis applied for glycerol must be mentioned here.	Y	We add in more detail the operating condition of Gas Chromatography
• Various is an adjective of variation. So please choose one, not 'various variation'.	Y	The word has been changed as "various"
• The paragraph right after the results and discussion, 'For flux decline study and blocking mechanism… in raw glycerin.' This part should be moved to method section.	Y	This part is removed since the detail has been explained in Materials and Method section
• Since the objectives of this study was missing in the introduction. The conclusion should say if the objectives are achieved.	Y	The objective is added in introduction and the conclusion is corrected

• Is using UF a good solution for glycerol purification? Since flux decline occurs very soon after the system start for all studied parameters at various range.	Y	We add the explanation on the conclusion

(Please add more rows if needed)

Reviewer # 6

Final Recommendation Please tick	Accepted without modification ☐	Accepted with minor corrections ☐	Accepted with major modification ☐	Rejected ☐

Comments	Addressed (Y/N)	Reply/Action taken
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(Please add more rows if needed)

Reviewer # 7

Final Recommendation Please tick	Accepted without modification ☐	Accepted with minor corrections ☐	Accepted with major modification ☐	Rejected ☐

Comments	Addressed (Y/N)	Reply/Action taken
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(Please add more rows if needed)

Reviewer # 8

Final Recommendation Please tick	Accepted without modification ☐	Accepted with minor corrections ☐	Accepted with major modification ☐	Rejected ☐

Comments	Addressed (Y/N)	Reply/Action taken
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(Please add more rows if needed)

Reviewer # 9

Final Recommendation Please tick	Accepted without modification ☐	Accepted with minor corrections ☐	Accepted with major modification ☐	Rejected ☐

Comments	Addressed (Y/N)	Reply/Action taken
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(Please add more rows if needed)

Reviewer # 10

Final Recommendation Please tick	Accepted without modification ☐	Accepted with minor corrections ☐	Accepted with major modification ☐	Rejected ☐

Comments	Addressed (Y/N)	Reply/Action taken
•		
•		
•		
•		

(Please add more rows if needed)

E-mail @che.undip.ac.id

Nita Aryanti <nita.aryanti@che.undip.ac.id>

Paper ID CE19004 /A progress of Review Process/

1 message

Jestec <Jestec@taylors.edu.my> Sun, Jul 7, 2019 at 6:28 PM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

Dear Author

This email is to confirm that your paper is currently undergoing the

☐ 1st ☑ 2nd ☐ 3rd round of the review process.

Thank you for your patience.

Best regards

JESTEC Editor

http://jestec.taylors.edu.my

E-mail @che.undip.ac.id

Nita Aryanti <nita.aryanti@che.undip.ac.id>

Paper ID CE19004 /Review of a paper, Second Round Result/

6 messages

Jestec <Jestec@taylors.edu.my> Sun, Aug 18, 2019 at 5:20 PM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

Dear Author

The second round of the review process has been completed.

5 reviewers reviewed your revised paper.

Reviewers #2 and 4	satisfied with the revision.
Reviewer # 1	rejected the revised paper again.
Reviewers #3 and 5	accepted the revised paper with minor/major corrections.

Attached herewith, please find one/two/three/four/five/six reviewers' reports.

Please notice the following:

1- Acknowledge the receipt of this email

2- Address all the concerns/recommendations of the reviewers

3- All additions/corrections are to be highlighted in red color in the revised paper.

4- Send a separate outlining how did you address each reviewers' concern/recommendations.

Best Regards

JESTEC Editor

http://jestec.taylors.edu.my

3 attachments

Review Report - 5 R1.docx
44K

Review Report - 1 R1.docx
50K

Review Report - 3 with Comment R1.docx
676K

Nita Aryanti <nita.aryanti@che.undip.ac.id> Sun, Aug 18, 2019 at 8:09 PM
To: harivram@gmail.com

[Quoted text hidden]

3 attachments

Review Report - 5 R1.docx
44K

Review Report - 1 R1.docx
50K

Review Report - 3 with Comment R1.docx
676K

Nita Aryanti <nita.aryanti@che.undip.ac.id> Sun, Aug 18, 2019 at 8:38 PM
To: Jestec <Jestec@taylors.edu.my>

Dear Jestec Editorial Team,

Thank you for your email. We will revise as suggested by the reviewer.
Acoording to this..what is the deadline for revision?

Many thanks.

Regards,
Nita
[Quoted text hidden]

Nita Aryanti <nita.aryanti@che.undip.ac.id> Sun, Aug 18, 2019 at 8:43 PM
To: Jestec <Jestec@taylors.edu.my>

Dear editor,

It was said that there was three reviewer reports. However, in attached file, there was only reports from reviewer 1 and reviewer 5, and I could not find report from reviewer 3.

Regards,
Nita

On Sun, 18 Aug 2019, 17:20 Jestec, <Jestec@taylors.edu.my> wrote:
[Quoted text hidden]

Jestec <Jestec@taylors.edu.my> Sun, Aug 18, 2019 at 10:09 PM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

2 to 3 weeks

Best Regards

JESTEC Editor

http://jestec.taylors.edu.my

[Quoted text hidden]
[Quoted text hidden]

Jestec <Jestec@taylors.edu.my> Sun, Aug 18, 2019 at 10:11 PM
To: Nita Aryanti <nita.aryanti@che.undip.ac.id>

Best Regards

JESTEC Editor

http://jestec.taylors.edu.my

From: Nita Aryanti [mailto:nita.aryanti@che.undip.ac.id]
Sent: Sunday, August 18, 2019 9:43 PM
To: Jestec <Jestec@taylors.edu.my>
Subject: Re: Paper ID CE19004 /Review of a paper, Second Round Result/

Dear editor,

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[Quoted text hidden]
[Quoted text hidden]

Review Report - 3 with Comment R1.docx
676K

REVIEW FORM

Title of paper: JESTEC CE19004.R1 - PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

For sections A & B, please tick a number from 0 to 5, where 0 = strongly disagree and 5 = strongly agree.

A. Technical aspects

1. The paper is within the scope of the Journal.	☐ 0	☐ 1	☐ 2	✓ 3	☐ 4	☐ 5
2. The paper is original.	☐ 0	☐ 1	✓ 2	☐ 3	☐ 4	☐ 5
3. The paper is free of technical errors.	☐ 0	☐ 1	✓ 2	☐ 3	☐ 4	☐ 5

B. Communications aspects

1. The paper is clearly readable.	☐ 0	☐ 1	✓ 2	☐ 3	☐ 4	☐ 5
2. The figures are clear & do clearly convey the intended message.	☐ 0	☐ 1	✓ 2	☐ 3	☐ 4	☐ 5
3. The length of the paper is appropriate.	☐ 0	☐ 1	☐ 2	✓ 3	☐ 4	☐ 5

C. Comments to the authors (You may use another sheet of paper.)

This is a modified version of the previously agonizing CE19004 manuscript. However, there are still some major changes need to be provided by the authors. There are a number of issues that have not addressed quite well by the authors, thus a REJECTION is still recommended. Detailed comments are in the following pages.

D. Recommendation (Tick one)

1. Accepted without modifications.	☐
2. Accepted with minor corrections.	☐
3. Accepted with major modification.	☐
4. Rejected.	√

E. Comments to the editors (These comments will not be sent to the authors)

Review of JESTEC CE19004.R1 - Purification of glycerin-rich solution from palm oil based production biodiesel by ultrafiltration membrane

This is a modified version of the previously agonizing CE19004 manuscript. However, there are still some major changes need to be provided by the authors. There are a number of issues that have not addressed quite well by the authors, thus a REJECTION is still recommended.

1. The title is not reflecting the content of the manuscript, if not misleading. No purification is achieved, as no results obtain >95% pure concentration (maximum rejection around 70%). Therefore, the TITLE MUST BE CHANGED to: "Fouling behavior of polyethersulphone ultrafiltration membrane in the separation of glycerin-rich solution as byproduct of palm-oil-based biodiesel production".
2. Abstract: The current range of TMP, temperature, and pH is too shallow. It might be widened but it was argued that those parameters were the result of optimization from previous research. Where is the reference?
3. Section 1, paragraph 1: How come reference #10 jumps up, and bypassing references number 6, 7, 8 and 9? Fix the sequence of the references!
4. Section 1, paragraph 1: The word "matter organic non-gycerol" is not appropriate. Change it to "non-glycerol organic matter (NGOM)".
5. Section 1, paragraph 2: Beside those aforementioned processes, there is also an emerging process to remove impurities (i.e. water) from viscous glycerin-like product is pervaporation. Cite Y. Wang et al, J. Membr. Sci. 363 (2010) 149-159 and Y. Wang et al, J. Membr. Sci. 378 (2011) 339-350.
   It was previously argued that the suggested reference are "not similar to our process", yet you cite processes having no membrane at all, e.g. adsorption, ion exchange, saponification, acidification, neutralization, extraction, and drying!!
   Pervaporation is a membrane-based process, and it is more similar to membrane ultrafiltration process, than those non-membrane processes. How absurd. Reference #23 is about pervaporation. If pervaporation is not similar to your process, then remove the reference #23.
6. Section 1, paragraph 4: What do you mean by "To the best of our knowledge, the applications of PES UF for separation or of glycerin used pure glycerin or mixture of pure glycerin with impurities as UF feed". Very confusing!
7. Section 1, paragraph 4: Similar works have been done before.
   Cite Bellona et al., Sep. Purif. Technol. 74 (2010) 44-54, "The effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes" https://dx.doi.org/10.1016/j.seppur.2010.05.005 that employed GE/Osmonics SEPA membrane (now Suez (GE) Sepa CF, http://www.sterlitech.com/ultrafiltration-uf-membrane-ympwsp1905.html) to separated several organic compounds (including glycerin).

   Cite Arenillas et al., J. Membr. Sci. Res. 3 (2017) 102-108 "Glycerin removal from ultrafiltration flat sheet membranes by filtration and soaking" https://dx.doi.org/10.22079/jmsr.2016.23080 that employed ultrafiltration membrane for removing glycerin.

8. Section 1, paragraph 4: Write reasons/justifications on why no pretreatment was taken, in order to obtain >95% pure concentration. Moreover, the title of this manuscript must be change. The word "purification" in the old title (and in Section 1, paragraph 4, the last three lines) must be removed, since the product is not really pure.
9. Section 2.1: You use a membrane with 1000 Da molecular weight cut-off, to separate glycerin (92 Da) from impurities. However you missed to write what are the impurities and their molecular weight. If the impurites are free fatty acids, most fatty acids such as lauric acid, stearic acid, cerotic acid, even docosahexaenoic acid with 22 carbons are around 300 Da only. This is the fundamental on why the ultrafiltration experiments in this study (without any initiative for modification taken) shall give rejection only 70%, since the permeate streams contains not just glycerin, but also 300 Da fatty acids, also water (highly likely). It is better to use UF with 200 Da MWCO, or employ some pretreatments. Write reasons/justifications on why no pretreatment was taken.
10. Section 2.4: Add the parameter "n" to the Table 1, and the caption of Figure 6. The Table 3 has the "n" parameter written in it.
11. Table 1: in the column of "Physical Concept", use uppercase S and D for the 3rd line (Formation of Surface Deposit).
12. Section 3.1.1, paragraph 4: Any data for contact angle of free fatty acids that reflect their hydrophobic properties?
13. Figure 4, Y-axis: "glycerin", not "glycerinE".
14. Figure 5: The irregular sequence of normalized flux (fluctuating trend of flux vs. pH 6.33, 7.00, 8.00, and 9.67) was attempted to be justified by reference #11 (J. Food Eng. 101 (2010) 264-272), and #13 (Sep. Purif. Technol. 98 (2012) 419-431), with the theory of dissociation/undissociation of fatty acid. The discussion related to the irregularities for pH 6.33 and 7.00 has been written. However, the irregularities for pH 8.00 and 9.67 have not been discussed. Add the related discussion! What are the causes or reasons behind the imperfection of dissociation of fatty acids? Add the related discussion!
15. Section 3.1.3: Edit the excess square bracket
16. Abbreviation: add PO, OA, NGOM, FAME into the list
17. Reference #3: add a space to separate "andReaney" to be "and Reaney"
18. Reference #5: Be consistent! Remove the DOI in order to make the format of this reference is in unison with other references.
19. Reference #6: Be consistent! Remove the DOI in order to make the format of this reference is in unison with other references.
20. Reference #8: Be consistent! Remove the DOI in order to make the format of this reference is in unison with other references.
21. Reference #18: …2nd ed.
22. Reference #19: Be consistent! Remove the DOI, and also the "p" in "p.42-69", as this format is not in unison with other items in the list of references.
23. Reference #20: The name of the first author must be "van den Berg, G.B."
24. Reference #27: Be consistent! Check the manuscript preparation guide for writing the format of the reference. Is the requirement stated to use the abbreviated name of the journal, or to use the full

name of the journal? Reference #27 is much different with references #1 to #32. Or, maybe reference #27 is the right one (using abbreviated name), and the format of other references must be changed. Check and recheck it.

25. Reference #31: …6th ed
26. Reference #31: Use uppercase M and uppercase S for “Journal of Membrane Science”. Or, for “J. Membr. Sci.”.

Journal of Engineering Science and Technology
Vol. XX, No. Y (Year) PPP - QQQ

PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

Abstract

Crude glycerin as a by-product of the transesterification process has low economic value and limited applications. Under this condition, purification of crude glycerin is required to increase the quality of glycerin. Membrane process using ultrafiltration membrane is an alternative to purify the glycerin. However, flux decline behaviour during the ultrafiltration process is a major limitation. Since specific information of blocking information in ultrafiltration of glycerin rich solution was not found, this research seek to focus on separation of glycerin rich solution from its impurities. In this research, flux decline, rejection, and blocking mechanism at various Trans Membrane Pressure (TMP), temperature, and pH were observed. Experiments were carried out at the variation of the TMP (3.2 – 4.8 bar), temperature (51.63 – 68.36 °C), and pH (6.32 – 9.67). The research showed that the flux decline was significant at all variations of the process parameter. This condition was caused by the presence of small size impurities such as free fatty acid (FFA), which can lead to clogging inside the membrane pore. Both TMP and temperature had no significant effect on flux decline. Rejection value was proportional to TMP and temperature while at pH variation, the rejection was determined by the characteristic of impurities. Hermia's model was selected to analyse the blocking mechanism during filtration. It was confirmed that the mechanism was dominated by cake formation for all process parameters except for pH 7. At pH 7, the mechanism was controlled by intermediate blocking at an early stage and then followed by standard blocking. This research demonstrated that the ultrafiltration process was capable of removing some impurities of crude glycerin up to 68.33% and 70.98% for total impurities and FFA, respectively. However, processs development such as feed pretreatment or membrane modification is suggested to improve rejection and reduce the membrane fouling.

Keywords: Glycerin, Purification, Ultrafiltration, Fouling, Blocking Mechanism.

1. Introduction

Production of biodiesel generates crude glycerin as a by-product. It was reported that the production of 10 kg biodiesel produced 1 kg of crude glycerin [1]. Crude glycerin from biodiesel production has low economic value since the glycerin product is mixed with impurities in its heavy phase. On the other hand, glycerin is the raw material for many industries such as pharmacy, food, cosmetic, cigarette, automotive, textile or chemical industry. In addition, pure glycerin is potential for bio-lubricant, additive and an alternative fuel by adjusting the combustion cycle [2]. As a by-product, glycerin is found in its crude form (crude glycerin or raw glycerin) which contain many impurities and matter organic non-glycerol (NGOM) at various concentrations. The NGOM found in crude glycerin is fatty acid methyl esters (FAME), fatty acid ethyl esters, free fatty acids (FFA) and glycerides. Application of crude glycerin has many disadvantages such as low fuel value, require purification to increase its fuel value and high cost [1,3,4,5]. Crude glycerin contains many contaminants such as water, inorganic salts and other organic materials (FFA, FAME or biodiesel, alcohol (methanol), unreacted palm oil and triglyceride, diglyceride, monoglyceride) [3,10].

In general, crude glycerin is purified by distillation. However, the low vapour pressure of glycerin and its temperature sensitivity causes degradation or polymerisation of glycerin, and hence, vacuum distillation is applied more frequently than the normal distillation [4]. As a consequence, application of vacuum distillation was expensive due to the high energy required to create vacuum condition and evaporate glycerin [3,4]. Other purification processes such as adsorption, ion exchange, saponification, acidification, neutralisation (pre-treatment), extraction and drying have been implemented to obtain high purity glycerine [6]. Nevertheless, the usage of chemicals and energy requirement has a consequence of high cost.

Purification of glycerin by membrane technology has been developed and studied due to its process simplicity and can minimise energy requirement by utilising concentration difference, electron potential and hydroscopic pressure [4, 7]. One type of the membrane for purification or separation glycerin is Ultrafiltration (UF). Separation of glycerin from FAME by UF and microfiltration ceramic membrane was studied [8]. The research confirmed that the biodiesel met the American Society for Testing and Materials (ASTM D6751-09) standard for glycerin content. A similar result was also found by Wang et al. [9]. Experiments focused on glycerin purification have been performed. Dhabbai et al. [3] investigated purification of crude glycerol using a sequential physicochemical treatment, membrane filtration, and activated charcoal adsorption. It was reported that the result of maximum glycerol content was 97.5 wt% with acid value and FFA content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Other studies focused on the application of UF for glycerin model of glycerin separation. Amin et al. [10] evaluated UF fouling characteristic for filtration of pure mixture glycerin having 15% w/w and found that the flux decline involved cake layer model as well as pore blocking model. In addition, the separation of glycerin mixed with fatty acids (palmitic, stearic, and oleic acids) by polyethersulphone (PES) UF membrane was also studied [11]. It was reported that the PES membrane exhibited severe fouling for all types of fatty acids in solution with glycerol–water. A similar study by Amin et al. [12] investigated glycerin-rich fatty acid solutions confirming that the addition of fatty acid affected significant flux decline. Mah et al [13, 14] studied on UF of palm oil-oleic acid-

glycerin mixture and performance. It was found that cake formation was the blocking mechanism that occurs during UF process based on prediction using Hermia's model and the smallest flux decline occurred at palm oil (PO) and oleic acid (OA) mixtures. Blocking behaviour between PO and OA was different, where for PO blocking was occurred only at the surface while for OA blocking reached inside the pore of the membrane. Observation of the influence of pH was also carried out. It presented that flux decline was getting worse in the presence of the acidic environment.

To the best of our knowledge, the applications of PES UF for separation or of glycerin used pure glycerin or mixture of pure glycerin with impurities as UF feed. This research focused on the use of crude glycerin from biodiesel plant as UF feed to study the possibility and performance of UF membrane in the purification of original crude glycerin. The crude glycerin contains many impurities consist of water inorganic salt from catalyst residue, methanol, unreacted palm oil (mono-, di- and triglycerides), free fatty acids, lipids, methyl esters, as well as a various other NGOM. By using the PES UF membrane, compounds having high molecular weight were separated and retained in retentate and glycerin permeated to the membrane. In more specific, the objective of the research was to study the effect of process parameter (TMP, temperature and pH) on membrane performance (flux and rejection) for purification of crude glycerin. In addition, investigation of the blocking mechanism of the UF membrane in crude glycerin purification was addressed.

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For the research gap, what are the different on the current study with other/previous studies?

2. Materials and Methods

2.1. Materials

Crude glycerin was supplied from Biodiesel Plant of PT SMART Tbk, Tarjun, Indonesia was used as a raw material. The crude glycerin composed glycerin with concentration of 82.17 %, 10.56% FFA and NGOM other than FFA of 7.27%. The crude glycerin was then mixed with demineralised water at ratio 1:1 to form 50% glycerine solution. In this research, PES flat sheet UF membrane (Synder Filtration XV) having 1 kDa molecular weight cut-off was purchased from Sterlitech Corp, USA. It was reported that UF membrane having 30 kDa pore size was able to separate oleic acid (as a model of fatty acid) in a mixture of pure glycerin, oleic acid and palm oil [13,14]. In this research, UF membrane having 1 kDa pore size which was smaller than 30 kDa was selected to increase UF performance in separating impurities such as FFA and palm oil.

2.2. UF Membrane

Experiments were carried out by a laboratory-scale UF Cell equipped with compressor and instrumentation control as illustrated in Fig. 1.

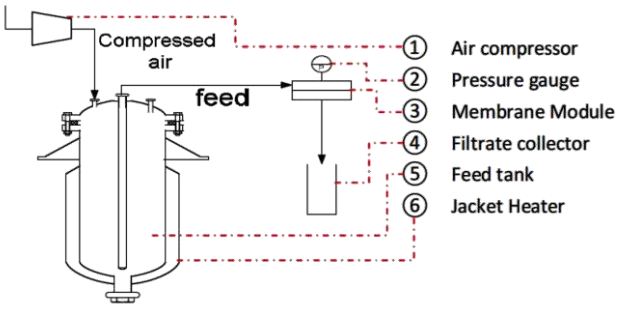

Fig. 1. Schematic illustration of UF cell with temperature control.

Experimental runs were operated at room temperature (25 ± 2 °C). Before each run, membranes were first compacted by filtering distilled water through the membrane at a pressure of 1 bar for 60 mins. For each experimental work, a new circular membrane sheet having area of 13.85 cm^2 was placed inside the UFcell. Pure water flux (J_0) was determined for initial water characteristic. The pure water flux was evaluated by weighing permeate collected at a specific time. The permeate flux (J) was determined by collecting permeate for 120 mins, with interval of 5 mins. Then, permeates were weighed (W), and its weight was converted into volume (V). Both pure water flux and permeate flux were calculated according to (Eq. 1)

Commented [.2]: Density is used to convert from mass to volume? How do you get the density value?

$$J = \frac{V}{A \cdot t} \quad (1)$$

In eq. (1), J can be represented as J_0 or water flux ($L.m^{-2}.h^{-1}$) and J or permeate flux ($L.m^{-2}.h^{-1}$), V is volume of permeate (L) and A is membrane area (m^2).

Permeate fluxes, and blocking mechanisms were observed by adding crude glycerin to the feed tank for half tank capacity. Further, the UF cell was operated at a dead-end mode at the variation of the transmembrane pressure (TMP) at 3.2 – 4.8 bar, temperature (51.63 - 68.36°C) and pH (6.32 – 9.67).The value of process parameters was selected according to optimisation of each process parameters in the previous study. The pH adjustment was conducted by adding a 0.1 N HCl or 0.1 N NaOH. Sampling for permeate flux determination was carried out for 60 mins, with interval of 10 mins.

Commented [.3]: Add citation/ref

2.3. Analysis

UF performance for glycerin purification from the feed solution was evaluated through the rejection of FFA and impurities. The rejection (R) was calculated by using eq. (2).

$$R = \frac{C_f - C_p}{C_f} \quad (2)$$

In equation (2), R (%) is rejection of FFA or impurities, C_f (mg/L)is concentration of FFA or impurities in feed, C_p (mg/L) is concentration of FFA or impurities in the permeate. The composition of permeate was analyzed by using gas chromatography and mass spectrometry (GCMS, Shimadzu TQ8030) on Rxi-1ms column (30m × 250 micrometers × 0.25 micrometre, Restek Corp, USA) with injection temperature at 250 ºC and FID detector at 300 ºC, Nitrogen at 74.5 kPa and Helium as the carrier.

2.4. Model of Blocking Mechanism

Hermia's model defined the fouling mechanism, especially in the porous membrane with dead-end system filtration. In more specific, the model highlighted the fouling mechanism which dominates in the entire of the process. This model applied a common power-law equation to describe the blocking mechanism and written in Eq. (3) [13,15].

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{3}$$

In eq. (3), t is filtration time, k is filtration constant and V is filtrate volume. Complete pore blocking illustrates that each solute is assumed to participate in blocking the entrance of the membrane pores completely. With the assumption that every solute stays on previously deposited solute, it is represented of intermediate pore blocking. Standard pore blocking describes that each solute is deposited to the internal pore wall. Determination based on the accumulation of the solute on the membrane surface is representative of cake or gel formation [10]. Mah et al. [13] and Amin et al. [10] concluded that Hermia's model was fit well with the experimental data for predicting the blocking mechanism during UF. It was confirmed by the value of R^2 which is mostly above 0.9 for appropriate model. In addition, optimising process parameters, analysing the transition of each fouling mechanism and predict cleaning or replacing membrane during operation can be predicted based on Hermia's model [13]. Further, linearisation of blocking mechanism according to equation (3) is presented in Table 1.

Table 1. Linearization equation of blocking models based on Hermia's model [16]

Pore Blocking Models	Linearization Equation	Physical Concept
Standard Blocking	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore Blocking + Surface Deposit
Intermediate Blocking	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore Constriction
Complete Blocking	$\ln J = \ln J_o - K_c t$	Formation of surface deposit
Gel or Cake Formation	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore Blocking

In Table 1, K_s, K_i, K_c and K_{cf} are constants of standard blocking ($h^{-1/2}$ $m^{-1/2}$), intermediate blocking (m^{-1}), complete blocking (h^{-1}) and gel or cake formation (h/m^2), respectively.

3. Result and Discussion

In this paper, flux decline, rejection, and the blocking mechanism were observed in various of the process parameters such as TMP, temperature, and pH.

3.1. Flux decline and rejection

3.1.1. Effect of TMP on Permeate Flux

UF process is one method to separate substances which have different molecular size using TMP as a driving force. The fluxes increase along with the increase on TMP, indicating that the flux is proportional to TMP as long as the resistance between the membrane and the fluid are not significant [10, 14, 17-20]. Fig 2. shows the flux response against the TMP at pH 5.27 and temperature 60 °C. Generally, the flux decline over time is caused by the impurities deposited on the surface and inside the membrane pores.

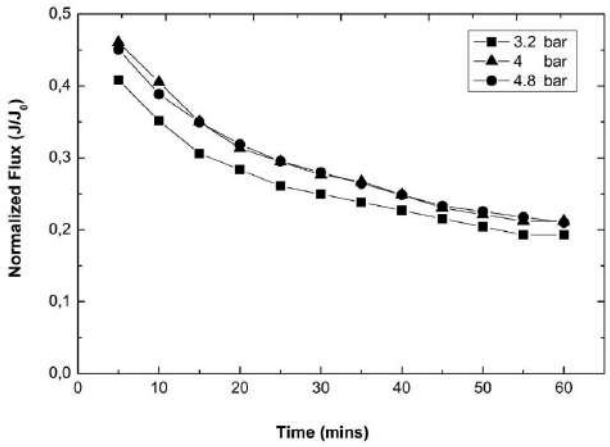

Fig. 2. Influence of TMP on fluxes of glycerin-rich solutions at pH of 5.27 and Temperature of 60 °C

Fig. 2 confirms the correlation between flux and TMP, wherein increasing TMP causes an increase in the flux. The higher normalised flux at higher TMP is achieved at a pressure range of 3.2 – 4 bar. In contrast, at a range of 4 – 4.84 bar, the effect of adjustment TMP on the positive impact on the flux is not significant, indicating that the TMP had a slight effect on increasing flux. This condition reveals an increase in resistance between the membrane and the fluid that caused by

polarisation of impurities on the membrane surface [12, 14]. Based on Darcy's law, flux was not only depended on TMP but also influenced by the resistance between the membrane and the fluid [20].

Adjusting TMP to a higher point lead to an increase in flux, but it still cannot affect the pattern of flux decline. This is confirmed by the flux decline pattern in Figure 2 showing similarity pattern at the variations of TMP. A significant flux decline in the early stages of the UF process a range of 0 – 25 mins and then continued with the stationary states of flux decline at a range of 30 – 60 mins are observed. This phenomenon indicates that the process more influenced by mass transfer mechanism than by TMP it's self [15]. This leads to a more severe condition of flux decline as the result of the deposits increase and impurities quantity. The impurities were carried away by the glycerin-rich solution that flows through to membrane matrix and presumably deposited both on membrane surface as well as inside the pore of the membrane [12,15].

This phenomenon is conceivable because of the nature of the raw material (glycerin) and the majority of impurity (FFA) in crude glycerin. Glycerin has a high viscosity. The viscosity for pure glycerine was found as 1.5 Pa.s [1] and for crude glycerine containing 80% of glycerine, the viscosity was above 20 mPa.s at reference temperature [21]. The fluid characteristic is much different from Newtonian fluids such as water that only has viscosity about 1 mPa.s at 20 ^{o}C [21]. The high viscosity of glycerine indicates that the molecular spatial space of glycerin is denser, as like as molecular space of liquid phase that is also denser than the gases phase molecular space [18]. This is due to the existence of a highly branched network of hydrogen bonds formed by three hydrophilic hydroxyl groups [22]. Besides that, the properties of FFA tend to be hydrophobic and insoluble in polar compounds [11]. The hydrophobicity of the FFA has different characteristic to the hydrophilic properties of the membrane used in this study. It is accomplished that hydrophobic properties of the impurity (FFA) can increase repulsion forces on the membrane, which ultimately influences the flux trend that occurs during the filtration process (mass transfer mechanism).

3.1.2. Temperature Effect on Permeate Flux

Effect of various temperature (at pH of 8, TMP of 4 bar) on flux decline is presented in Fig. 3. Observations show the temperature has more influence than the TMP on the flux decline qualitatively. The condition occurs because the increased temperature can directly trigger the viscosity reduction. This makes the fluid more freely to flow as a result of increasing in molecular spatial space in higher temperature condition [22]. In addition, increasing the temperature can lead to an increase of the polymer bonding mobility inside the membrane matrix [12,23]. Hence, the resistance caused by both fluid and membrane against each other is reduced by the increased temperature.

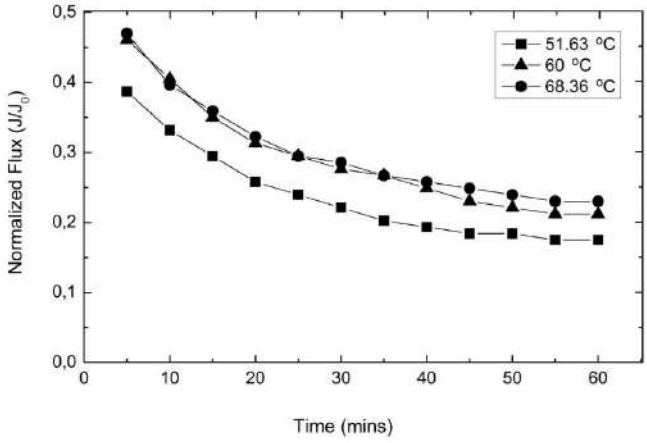

Fig. 3. Influence of temperature on flux decline of the glycerin-rich solution (pH = 8, TMP = 4 bar).

In addition, Fig. 3. shows the trend of flux response against temperature indicating that at a range of 51.63 °C – 60 °C, the increasing temperature has a positive effect on the flux. On the contrary, in a range of 60 °C – 68.36 °C the effect of temperature is insignificant.

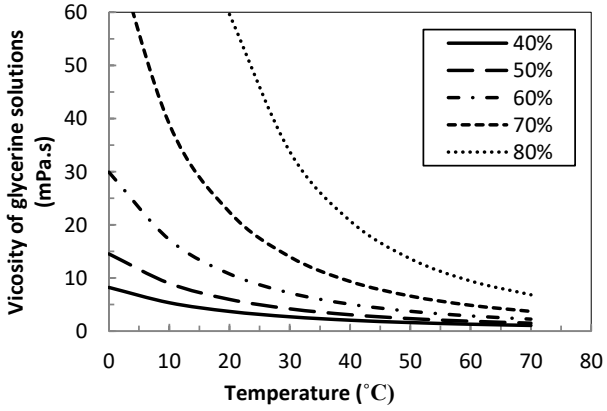

Fig.4. Viscosity of glycerine solution with increased temperature. Drawn from data calculation using viscosity-temperature correlation equation based on Arrhenius form. Source: [21]

Dhabhai et al. [3] found that the temperature did not influence the decrease of the raw glycerin viscosity at temperatures above 60 °C. It was presumably the cause

of the minor effect of temperature above 60 °C. Figure 4 supports the finding confirming that the viscosity change at temperature above 60°C is insignificant. Although the viscosity of glycerin which can directly affect fluid resistance to the membrane can be reduced, it does not have a positive effect on the pattern of flux decrease as shown in TMP. This condition denotes that characteristic and properties of impurity (FFA) plays a key role in the pattern of flux decrease. Moreover, the flux can directly increase along with decreasing in viscosity which can lead to increasing of impurities concentrations both on the surface and inside pore of the membrane. This phenomenon also confirms that the process is dominated by the mass transfer mechanism.

3.1.3. Effect of pH on Permeate Flux

Fig. 5 shows the responses of flux against different pH condition at TMP of 4 and temperature of 60 ºC. The pH was observed in a range of 6.33 – 9.67 where the feed sample pH was 5.27. The results show that the flux decreases the acidic state greater than those in the alkaline state. Fatty acids are impurities in a glycerin-rich solution. Based on pH condition of its environment, the fatty acid has the nature that remained as the undissociated molecule in the presence of an acidic environment and could be dissociated in an alkaline environment. A large amount of undissociated would cause severe fouling and flux decline [14, 11, 24].]Fatty acid molecules can interact with acid to form the larger molecules via an agglomeration process with another molecule of fatty acid [11,13]. The larger molecule that was formed may increase the adsorption of foulant molecule. The adsorption is formed on the membrane surface as well as on the entrance of the membrane pore and then causes high flux decline and membrane fouling [11,24-25]. Sequentially, the flux decline follows the order of pH 7> pH 6.33> pH 9.67>pH 8 and the highest flux decline is found at pH 7. Similar trend was also reported by Mah et al. [14]. According to dissociation and undissociation effect, at pH of 6.33, the flux decline should be the highest and at pH 9 the flux decline was the lowest. However, flux value at pH 7 shows higher flux decline than those at pH 6.33. This is most likely due to the fatty acid state that not fully dissociated at pH 7 [11]. In the dissociated state, fatty acid does not form clots and find as single molecule form [24]. The single molecule of fatty acid can pass through into membrane pore since the average size of the single fatty acid molecule is four times smaller than the membrane pore size [10] and then triggers the blocking inside the wall of membrane pore. At pH 9, this phenomenon may be due to the fact that dissociated molecules of fatty acids (at pH 9 the fatty acid molecules almost completely dissociate) blockage the micropores of the membrane. The blocking at micropores is possible in PES-based UF membranes because it is an asymmetric porous membrane [26].

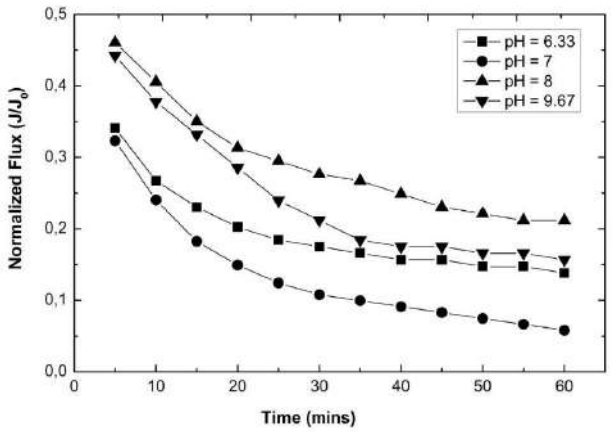

Fig. 5. Effect of pH on Flux decline of glycerin-rich solutions (TMP = 4, Temperature = 60 ºC).

3.1.4. Rejection

Rejection behaviour for glycerine-rich solution was observed by Mah et al. [14] and Amin et al. [10]. Amin et al. [10] reported that the 25 kDa of PES and 30 kDa UF (at TMP 2 bar and temperature 40 ºC) found that membrane could reject 35.59 to 41.41% of FFA. In addition, it was found that the FFA rejection for hydrophobic membrane was higher than the hydrophilic membrane. Moreover, Mah et al. [14] used 30 kDa UF membrane and PO+OA mixture as a foulant under the operating condition at TMP 2 bar, temperature 60 ºC and pH 2-9. It was found that the best rejection of impurities is 97.95% at pH 2.

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Table 2. Summary of rejection data in various variations of process parameters.

No.	Pressure (bar)	Temperature (°C)	pH	Rejection (%)	
				FFA	Total impurities
1.	3.2	60	8	48.10	48.50
2.	4	60	8	54.17	32.11
3.	4.8	60	8	57.63	52.86
4.	4	51.63	8	44.32	33.25
5.	4	60	8	54.17	32.11
6.	4	68.37	8	45.35	43.56
7.	4	60	6.33	30.70	21.18
8.	4	60	7	70.98	68.33
9.	4	60	8	54.17	32.11
10.	4	60	9.67	25.82	24.22

Table 2 shows a different trend in each variation of the operating condition. For TMP variation, the rejection increases with increasing on TMP. The rejection of FFA content in the filtrate at 4.8 bar and 3.2 bar are 57.63% and 48.1%, respectively. This condition takes place because in higher TMP some small foulant molecules may be penetrated the membrane pore and form a deposit, thus causing significantly reduce on the size of membrane pore which leads to an increase in rejection of impurity [14, 27]. For temperature variation, the trend of rejection tends to be similar to TMP variation where a higher temperature process has greater rejection than lower temperature. The rejection of impurities is 33.5% at 51.63 °C while at 68.37 °C the rejection reaches 43,56%. This is likely due to the effect of increasing temperature which can directly affect the increase in flux and causes an increase the impurities that flow through the membrane pore [12]. It is similar to the condition that occurs in TMP variation. Rejection behaviour at pH variation has a different kind than the other operating parameter. The highest result is 70.98% at pH 7, and the lowest result is 25.82% at pH 9.67. This behaviour may occur due to the nature of the impurities, as described in section 3.1.3.

The result of impurities rejection at each variation in this study is higher than impurities rejection reported by Amin et al. [12]. In this study, the highest result is 70.98% rejection of FFA whereas the highest result by Amin et al. [12] is 41.41%. It is proved that using smaller membrane pore size give a positive impact on impurities rejection. In case of the result reported by Mah et al. [14] that shows higher rejection (about 97.95 at pH 2) than the result in this study might be explained by the type of impurities which is contained in glycerine and its operation condition. Previous researchers used PO+OA mixture as foulant that has a larger molecular and droplet size than FFA. The larger molecule and droplet size can lead to increasing on the rejection of impurities [14]. Further, TMP that was also used lower than TMP that was used in this study. The lower TMP can decrease penetrating possibility by impurities to membrane pore [12,15].

3.2. Blocking Mechanism

The constant of the blocking mechanism and the corresponding correlation coefficients (R^2) during filtration is listed in Table 3. According to the Table, increasing TMP reduces the flux decline. Its condition also applies to temperature as confirmed by the smaller value of the constants along with increases of TMP and temperature. Cake formation is predicted as a dominated blocking mechanism during the filtration process for both TMP and temperature variations. In the cake formation, the foulant is firstly adsorbed on the membrane surface, penetrate the membrane pore and then form a layer that can cause a more severe decrease in flux even from the early step of filtration. The fatty acid may be the component responsible for severe fouling [10]. In biodiesel industries, glycerin was a by-product from the transesterification reaction which consists of palmitic acid (C16: 0), stearic acid (C18: 0) and most of the oleic acid that has double bond carbon chain (C18: 1) [28].

In addition, Table 3 shows the value of k (constant) at an acidic state that tends to be higher than in the alkaline state. It demonstrates that the resistance of the fluid to the membrane is larger and causing more severe fouling than in the alkaline state. The nature of fatty acids which tend to undissociated at acidic

environment may be responsible for that condition. Under this environment, the fatty acid would be clumping each other [11]. Mah et al. [14] reported that the droplets of a mixture of palm oil and oleic acid at pH 2 (very acidic condition) lead to significant increase in droplet size and even reach twice in size over the original droplet size. Therefore, setting pH under acidic conditions can lead to agglomeration of foulant molecules.

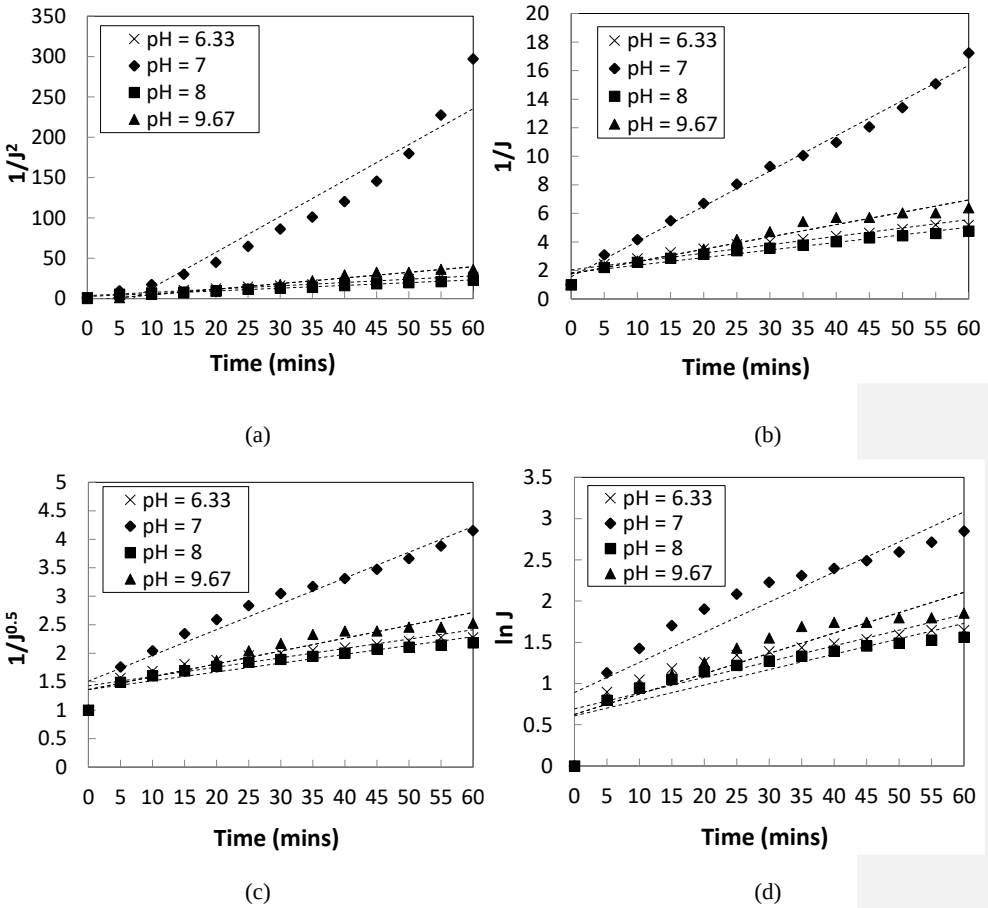

Fig. 6. Hermia's model fitting for the experimental data: (a) Cake formation, (b) Intermediate blocking, (c) Standard blocking, (d) Complete blocking (P = 4 bar, T= 60 °C)

Table 3. Summary of rejection data in various variations of process parameters.

Parameters	n=0 Cake Formation		n=1 Intermediate Blocking		n=1.5 Standard Blocking		n=2 Complete Blocking	
	K_{cf}	R^2	K_i	R^2	K_s	R^2	K_c	R^2
Pressure								
3.2 bar	0.4098	0.9848	0.0585	0.9031	0.0164	0.8171	0.0191	0.7051
4 bar	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
4.8 bar	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
Temperature								
51.63 °C	0.5329	0.9782	0.0692	0.9026	0.0185	0.8204	0.0208	0.7084
60 °C	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
68.36 °C	0.2872	0.9737	0.0476	0.8892	0.0142	0.8136	0.0176	0.7184
pH								
6.33	0.4090	0.9840	0.0580	0.9030	0.0160	0.8170	0.0190	0.7050
7	4.4480	0.9187	0.2468	0.9917	0.0453	0.9557	0.0365	0.8307
8	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
9.67	0.6982	0.9742	0.0862	0.9443	0.0225	0.8935	0.0247	0.8068

Fig. 6. exhibits the blocking mechanism that occurs in the various variations of pH. Generally, the mechanism is dominated by the cake formation, except for pH 7 as supported with the highest R^2 value for pH 6.33, 8 and 9.67. The similar result was reported by Amin et al. [10] and Mah et al. [14] confirming that cake formation was the dominant mechanism in pH variation. The different condition at pH 7, as seen in the value of k (constant for blocking mechanism) is much greater than at another pH. Moreover, the highest R^2 value in the intermediate blocking mechanism is found. Fig. 5 (b) and fig. 5 (c) confirm that in the initial conditions of filtration until 10 mins, both intermediate blocking and standard blocking mechanism occur. Then, in 15 mins until 45 mins only the intermediate blocking mechanism is observed, and for 50 mins afterwards only standard blocking contributes to the flux decline. In intermediate blocking, the solutes or particles which accumulated on the membrane surface and the entrance of membrane pore are possible to overlap another solute that has already deposited on the membrane surface. The foulant is the pilled up each other in irregular arrangement [10] and triggers other mechanisms such as standard blocking to occur during the filtration process. Standard blocking mechanism is believed to be responsible for a significant flux decline as in that condition the impurities molecule penetrates to the inside wall of the membrane pore and make a deposit which can be lead to plugging on the active area of the membrane pore [29,30]. This strengthens the previous statement that fatty acids which are not fully dissociated at pH 7enterthe pore and cause blockages in the membrane pore.

At high pH, especially for pH 9 above, the fatty acid molecule is fully dissociated and become surfactants with a hydrophilic head and hydrophobic tails which have negative charge [31]. If there was an interaction between fatty acids and membranes, it formed a negative charge induction to the membrane [10, 32]. Thus the repulsive force between the fatty acid and the membrane may change. This condition may also cause changes in the fluid resistance to the membrane [11].

4. Conclusions

The study of flux decline, rejection and blocking mechanism during UF process using 1 kDa PES membrane with various variations process parameters (TMP, temperature, and pH) to the glycerin-rich solution from the biodiesel industry were conducted. It was found that flux decline was severe significantly in all variation of process parameter due to a deposit of impurities. Both pressure and temperature did not give significant effect to the flux decline due to the domination of the mass transfer mechanism which is caused by the nature of impurities its self. In addition, the pressure and temperature had a similar trend of rejection that in higher process parameters the rejection becomes greater, whereas at pH variation behaviour of rejection is determined by the nature of impurities. Hermia's blocking law model found to fit well to the experimental data. The best-fit experiment data was cake layer formation mechanism for all process variation except for pH 7 where the intermediate blocking takes the lead in early stages and then followed by standard blocking. In order to improve the UF performance, preliminary treatment of crude glycerin or modification of the membrane surface is required. This treatment is expected can reduce the membrane fouling specifically due to FFA characteristic.

Nomenclatures

A	Membrane area, m^2
C_f	Concentration ofFFA or impurities in the feed, mg/L
C_p	Concentration of FFA or impurities in the permeate, mg/L
J	Permeate Flux, $L.m^{-2}. h^{-1}$
J_0	Initial Flux, $L.m^{-2}. h^{-1}$
k	Constant of blocking mechanism
K_c	constants of complete blocking (h^{-1})
K_{cf}	constants of gel or cake formation (h/m^2)
K_i	constants of intermediate blocking (m^{-1})
K_s	constants of standard blocking ($h^{-1/2}\, m^{-1/2}$)
n	Value that represents a blocking mechanism, n = 0 (cake layer formation), n = 1 (intermediate blocking), n = 1.5 (standard blocking), and n = 2 (complete blocking)
R	Rejection, %
R^2	The corresponding correlation coefficients
t	Filtration time (h)
V	Permeated volume (L)
W	Weight of permeate (g)

Abbreviations

ASTM	American Society for Testing and Materials
FFA	Free Fatty Acid
GC	Gas Chromatography
TMP	Trans Membrane Pressure
UF	Ultrafiltration

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Title of paper:

For sections A & B, please tick a number from 0 to 5, where 0 = strongly disagree and 5 = strongly agree.

A. Technical aspects

1. The paper is within the scope of the Journal.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☑ 5
2. The paper is original.	☐ 0	☐ 1	☐ 2	☑ 3	☐ 4	☐ 5
3. The paper is free of technical errors.	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	☐ 5

B. Communications aspects

1. The paper is clearly readable.	☐ 0	☐ 1	☐ 2	☑ 3	☐ 4	☐ 5
2. The figures are clear & do clearly convey the intended message.	☐ 0	☐ 1	☐ 2	☐ 3	☑ 4	☐ 5
3. The length of the paper is appropriate.	☐ 0	☐ 1	☐ 2	☐ 3	☑ 4	☐ 5

C. Comments to the authors (You may use another sheet of paper.)

This paper studied in the flux decline happened in the ultrafiltration applied for glycerol purification. The study provided a better understanding on the behavior of system of ultrafiltration dealing with glycerol and its impurity for several parameters at various range. There are some comments which required author have to address.

1. In the introduction, what are the current limitations of using UF for glycerol purification? what is the objective of this study? Or what is this study trying to improve? Reduce the effect of flux decline or just gaining an understand the effect of flux decline when some dependent variables were varied.
2. In the introduction, ref. [8] reported that using PES exhibited a severe fouling in the present of fatty acid in crude glycerol. A justification is needed for reasons why this study still used PES with very small cut-off 1 kDa.
3. For all equations in the manuscript, after each equation, please specify each papameter, its name, and unit.
4. In the method section, Gas Chromatography was used for analysis. Operating condition for this analysis applied for glycerol must be mentioned here.
5. Various is an adjective of variation. So please choose one, not 'various variation'.
6. The paragraph right after the results and discussion, 'For flux decline study and blocking mechanism… in raw glycerin.' This part should be moved to method section.
7. Since the objectives of this study was missing in the introduction. The conclusion should say if the objectives are achieved.
8. Is using UF a good solution for glycerol purification? Since flux decline occurs very soon after the system start for all studied parameters at various range.

D. Recommendation (Tick one)

1. Accepted without modifications. ☐
2. Accepted with minor corrections. ☑

3. Accepted with major modification. ☐

4. Rejected. ☐

E. Comments to the editors (These comments will not be sent to the authors)

This paper need to improve more its formatting.

After the round 1, the author has made some corrections according to my comments. Thank you. However, a very minor part of this article needed to correct is comment 5 above. The way of using various and variation is still not right. Please tell the author to make it correctly. Thank you.

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FOULING BEHAVIOR OF POLYETHERSULPHONE ULTRAFILTRATION MEMBRANE IN THE SEPARATION OF GLYCERIN-RICH SOLUTION AS BYPRODUCT OF PALM-OIL-BASED BIODIESEL PRODUCTION

Abstract

Crude glycerin as a by-product of the transesterification process has low economic value and limited applications. Under this condition, purification of crude glycerin is required to increase the quality of glycerin. Membrane process using ultrafiltration membrane is an alternative to purify the glycerin. However, flux decline behaviour during the ultrafiltration process is a major limitation. Since specific information of blocking information in ultrafiltration of glycerin rich solution was not found, this research seek to focus on separation of glycerin rich solution from its impurities. In this research, flux decline, rejection, and blocking mechanism at various Trans Membrane Pressure (TMP), temperature, and pH were observed. Experiments were carried out at the variation of the TMP (3.2 – 4.8 bar), temperature (51.63 – 68.36 °C), and pH (6.32 – 9.67). The research showed that the flux decline was significant at all variations of the process parameter. This condition was caused by the presence of small size impurities such as free fatty acid (FFA), which can lead to clogging inside the membrane pore. Both TMP and temperature had no significant effect on flux decline. Rejection value was proportional to TMP and temperature while at pH variation, the rejection was determined by the characteristic of impurities. Hermia's model was selected to analyse the blocking mechanism during filtration. It was confirmed that the mechanism was dominated by cake formation for all process parameters except for pH 7. At pH 7, the mechanism was controlled by intermediate blocking at an early stage and then followed by standard blocking. This research demonstrated that the ultrafiltration process was capable of removing some impurities of crude glycerin up to 68.33% and 70.98% for total impurities and FFA, respectively. However, process development such as feed pretreatment or membrane modification is suggested to improve rejection and reduce the membrane fouling.

Keywords: Glycerin, Purification, Ultrafiltration, Fouling, Blocking Mechanism.

1. Introduction

Production of biodiesel generates crude glycerin as a by-product. It was reported that the production of 10 kg biodiesel produced 1 kg of crude glycerin [1]. Crude glycerin from biodiesel production has low economic value since the glycerin product is mixed with impurities in its heavy phase. On the other hand, glycerin is the raw material for many industries such as pharmacy, food, cosmetic, cigarette, automotive, textile or chemical industry. In addition, pure glycerin is potential for bio-lubricant, additive and an alternative fuel by adjusting the combustion cycle [2]. As a by-product, glycerin is found in its crude form (crude glycerine or raw glycerin) which contain many impurities and non-glycerol organic matter (NGOM) at various concentrations. The NGOM found in crude glycerin is fatty acid methyl esters (FAME), fatty acid ethyl esters, free fatty acids (FFA) and glycerides. Application of crude glycerin has many disadvantages such as low fuel value, require purification to increase its fuel value and high cost [1,3,4,5]. Crudeglycerincontains many contaminants such as water, inorganic salts and other organic materials (FFA, FAME or biodiesel, alcohol (methanol), unreacted palm oil and triglyceride, diglyceride, monoglyceride) [3].

In general, crude glycerin is purified by distillation. However, the low vapour pressure of glycerin and its temperature sensitivity causes degradation or polymerisation of glycerin, and hence, vacuum distillation is applied more frequently than the normal distillation [4]. As a consequence, application of vacuum distillation was expensive due to the high energy required to create vacuum condition and evaporate glycerin [3,4]. Other purification processes such as ion exchange [6], acidification, neutralisation (pre-treatment) [7], extraction [8], pervaporation [9,10] adsorption, saponification, and drying [4] have been implemented to obtain high purity glycerine. Nevertheless, the usage of chemicals and energy requirement has a consequence of high cost.

Purification of glycerin by membrane technology has been developed and studied due to its process simplicity and can minimise energy requirement by utilising concentration difference, electron potential and hydroscopic pressure [4,11]. One type of the membrane for purification or separation glycerin is Ultrafiltration (UF). Separation of glycerin from FAME by UF and microfiltration ceramic membrane was studied [12]. The research confirmed that the biodiesel met the American Society for Testing and Materials (ASTM D6751-09) standard for glycerin content. A similar result was also found by Wang et al. [13]. Experiments focused on glycerin purification have been performed. Dhabbai et al. [3] investigated purification of crude glycerol using a sequential physicochemical treatment, membrane filtration, and activated charcoal adsorption. It was reported that the result of maximum glycerol content was 97.5 wt% with acid value and FFA content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Other studies focused on the application of UF for glycerin model of glycerin separation. Amin et al. [14] evaluated UF fouling characteristic for filtration of pure mixture glycerin having 15% w/w and found that the flux decline involved cake layer model as well as pore blocking model. In addition, the separation of glycerin mixed with fatty acids (palmitic, stearic, and oleic acids) by polyethersulphone (PES) UF membrane was also studied [15]. It was reported that the PES membrane exhibited severe fouling for all types of fatty acids in solution with glycerol–water. A similar study by Amin et al. [16] investigated glycerin-rich fatty acid solutions confirming that the addition of fatty acid affected significant flux decline. Mah et al [17, 18] studied on UF of palm oil-oleic acid-

glycerin mixture and performance. It was found that cake formation was the blocking mechanism that occurs during UF process based on prediction using Hermia's model and the smallest flux decline occurred at palm oil (PO) and oleic acid (OA) mixtures. Blocking behaviour between PO and OA was different, where for PO blocking was occurred only at the surface while for OA blocking reached inside the pore of the membrane. Observation of the influence of pH was also carried out. It presented that flux decline was getting worse in the presence of the acidic environment. This study using hydrophilic PES membrane to minimize fouling which is caused by interaction of hydrophobic site of FFA towards membrane material (surface and inner pore surface).

To the best of our knowledge, the applications of PES UF for separation impurities from glycerin used glycerin-rich solution from mixture of pure glycerin with addition of impurities as UF feed has not been investigated. The pore size of the membrane that was used in previous study also extremely larger (around 5 – 30 kDa) than the size of impurities [14,17]. Bellona et al. [19] investigated the effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes. It was found that organic foulant such as glycerin could be removed by NF membrane with rejection above 90%. However, applied operational pressure was certainly high. In addition, glycerin could not flow through the pore of NF membrane and caused the glycerin still mixed with the impurities. Arenillas et al. [20] studied removal glycerin from UF flat sheet membrane via filtration and soaking process. Their study was only focused on removal of glycerin contain in membrane matrix as the preservative. This research emphasised the use of crude glycerin from biodiesel plant as UF feed to study the possibility and performance of UF membrane 1 kDa in separation of impurities from industrial crude glycerin. The objectives of the research were to study the effect of process parameter (TMP, temperature and pH) on membrane performance (flux and rejection) for purification of crude glycerin. In more specific, this study was to gain deep understanding about the fouling behavior and blocking mechanism during UF process of industrial crude glycerin with 1 kDa UF membrane. The crude glycerin contains many impurities consist of water inorganic salt from catalyst residue, methanol, unreacted palm oil (mono-, di-andtriglycerides), free fatty acids, lipids, methyl esters, as well as a various other NGOM. By using the PES UF membrane, compound shaving high molecular weight were separated and retained in retentate and glycerin permeated to the membrane. In addition, investigation of the blocking mechanism of the UF membrane in crude glycerin purification was addressed.

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2. Materials and Methods

2.1. Materials

Crude glycerine was supplied from Biodiesel Plant of PT SMART Tbk, Tarjun, Indonesia was used as a raw material. The crude glycerin composed glycerin with concentration of 82.17 %, 10.56% FFA and NGOM other than FFAof 7.27%. The crude glycerin was then mixed with demineralised water at ratio 1:1 to form 50% glycerine solution. In this research, PES flat sheet UF membrane (Synder Filtration XV) having 1 kDa molecular weight cut-off was purchased from Sterlitech Corp, USA. It was reported that UF membrane having 30 kDa pore size was able to separate oleic acid (as a model of fatty acid) in a mixture of pure glycerin, oleic acid and palm oil [17,18]. In this research, UF membrane having 1 kDa pore size

which was smaller than 30 kDa was selected to increase UF performance in separating impurities such as FFA and palm oil.

2.2. UF Membrane

Experiments were carried out by a laboratory-scale UF Cell equipped with compressor and instrumentation control, as illustrated in Fig. 1.

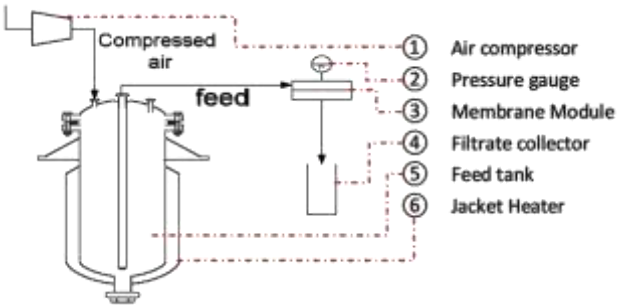

Fig. 1. Schematic illustration of UF cell with temperature control.

Experimental runs were operated at room temperature (25 ± 2 °C). Before each run, membranes were first compacted by filtering distilled water through the membrane at a pressure of 1 bar for 60 mins. For each experimental work, a new circular membrane sheet having area of 13.85 cm^2 was placed inside the UFcell. Pure water flux (J_0) was determined for initial water characteristic. The pure water flux was evaluated by weighing permeate collected at a specific time. The permeate flux (J) was determined by collecting permeate for 120 mins, with interval of 5 mins. Then, permeates were collected in glass graduated cylinder Pyrex™ 10 mL to measure the volume (V). Both pure water flux and permeate flux were calculated according to (Eq. 1)

$$J = \frac{V}{A \cdot t} \quad (1)$$

In eq. (1), J can be represented as J_0 or water flux ($L.m^{-2}.h^{-1}$) and J or permeate flux ($L.m^{-2}.h^{-1}$), V is volume of permeate (L) and A ismembrane area (m^2).

Permeate fluxes, and blocking mechanisms were observed by adding crude glycerin to the feed tank for half tank capacity. Further, the UF cell was operated at a dead-end mode at the variation of the transmembrane pressure (TMP) at3.2 – 4.8 bar, temperature (51.63 - 68.36°C) and pH (6.32 – 9.67). The value of process parameters was selected according to optimisation of each process parameters in our previous study. The pH adjustment was conducted by adding a 0.1 N HCl or 0.1 N NaOH. Sampling for permeate flux determination was carried out for 60 mins, with an interval of 10 mins. Flux decline, rejection, and the blocking mechanism were observed in various of the process parameters.

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2.3. Analysis

UF performance for glycerin purification from the feed solution was evaluated through the rejection of FFA and impurities. The rejection (R) was calculated by using eq. (2).

$$R = \frac{C_f - C_p}{C_f} \tag{2}$$

In equation (2), R (%) is rejection of FFA or impurities, C_f (mg/L)is concentration of FFA or impurities in feed, C_p(mg/L)is concentration of FFA or impurities in the permeate. The composition of permeate was analysed by using gas chromatography and mass spectrometry (GCMS, Shimadzu TQ8030). Column oven temperature is 65 ºC for 8 min, then the column temperature was ramped from 65 ºC to 250 ºC at 4 ºC/min and held for 20 min. Each sample (1 µL) was injected into Rxi-1ms column (30m × 250 micrometres × 0.25 micrometres, Restek Corp, USA) with linear velocity as flow control mode and injection that was used is split injection with ratio 20:1. The injection temperature is 250 °C where the operating pressure is 75,5 kPa with detector temperature held constant at 300 °C. Helium was used as the carrier gas at a flow rate of 1,2 mL/min and operation run time at 74 min.

2.4. Model of Blocking Mechanism

Hermia's model defined the fouling mechanism, especially in the porous membrane with dead-end system filtration. In more specific, the model highlighted the fouling mechanism which dominates in the entire of the process. This model applied a common power-law equation to describe the blocking mechanism and written in Eq. (3) [17,21].

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{3}$$

In eq. (3), t is filtration time (min), k is filtration constant, and V is filtrate volume (L). Complete pore blocking illustrates that each solute is assumed to participate in blocking the entrance of the membrane pores completely. With the assumption that every solute stays on previously deposited solute, it is represented of intermediate pore blocking. Standard pore blocking describes that each solute is deposited to the internal pore wall. Determination based on the accumulation of the solute on the membrane surface is representative of cake or gel formation [14]. Mah et al. [17] and Amin et al. [14]concluded that Hermia's model was fit well with the experimental data for predicting the blocking mechanism during UF. It was confirmed by the value of R^2 which is mostly above 0.9 for appropriate model. In addition, optimising process parameters, analysing the transition of each fouling mechanism and predict cleaning or replacing membrane during operation can be predicted based on Hermia's model [17]. Further, linearisation of blocking mechanism according to equation (3) is presented in Table 1.

Table 1. Linearization equation of blocking models based on Hermia's model [22]

Pore Blocking Models	n	Linearization Equation	Physical Concept
Standard Blocking	1.5	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore Blocking + Surface Deposit
Intermediate Blocking	1	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore Constriction
Complete Blocking	2	$\ln J = \ln J_o - K_c t$	Formation of Surface Deposit
Gel or Cake Formation	0	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore Blocking

In Table 1, K_s, K_i, K_c and K_{cf} are constants of standard blocking ($h^{-1/2}$ $m^{-1/2}$), intermediate blocking (m^{-1}), complete blocking (h^{-1}) and gel or cake formation (h/m^2), respectively.

3. Result and Discussion

3.1. Flux decline and rejection

3.1.1. Effect of TMP on Permeate Flux

UF process is one method to separate substances which have different molecular size using TMP as a driving force. The fluxes increase along with the increase on TMP, indicating that the flux is proportional to TMP as long as the resistance between the membrane and the fluid are not significant [14, 18, 23-26]. Fig 2. shows the flux response against the TMPat pH 5.27 and temperature 60 °C. Generally, the flux decline over time is caused by the impurities deposited on the surface and inside the membrane pores.

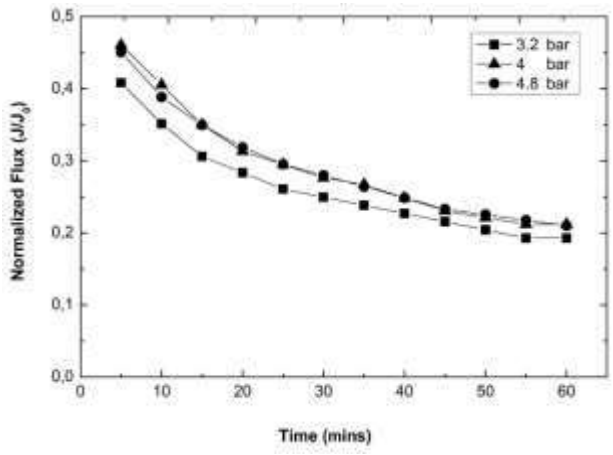

Fig. 2. Influence of TMP on fluxes of glycerin-rich solutions at pH of 5.27 and Temperature of 60 °C

Fig. 2confirms the correlation between flux and TMP, wherein increasing TMP causes an increase in the flux. The higher normalised flux at higher TMP is achieved at a pressure range of 3.2 – 4 bar. In contrast, at a range of 4 – 4.84 bar, the effect of adjustment TMP on the positive impact on the flux is not significant, indicating that the TMP has a slight impact on increasing flux. This condition reveals an increase in resistance between the membrane and the fluid that caused by polarisation of impurities on the membrane surface [16, 18]. Based on Darcy's law, flux was not only depended on TMP but also influenced by the resistance between the membrane and the fluid [26].

Adjusting TMP to a higher point lead to an increase in flux, but it still cannot affect the pattern of flux decline. This is confirmed by the flux decline pattern in Figure 2 showing similarity pattern at the variations of TMP. A significant flux decline in the early stages of the UF process a range of 0 – 25 mins and then continued with the stationary states of flux decline at a range of 30 – 60 mins are observed. This phenomenon indicates that the process more influenced by mass transfer mechanism than by TMP it's self [21]. This leads to a more severe condition of flux decline as the result of the deposits increase and impurities quantity. The impurities were carried away by the glycerin-rich solution that flows through to membrane matrix and presumably deposited both on membrane surface as well as inside the pore of the membrane [16,21].

This phenomenon is conceivable because of the nature of the raw material (glycerin) and the majority of impurity (FFA) in crudeglycerin. Glycerin has a high viscosity. The viscosity for pure glycerine was found as 1.5 Pa.s [1] and for crude glycerine containing 80% of glycerine, the viscosity was above 20 mPa.s at reference temperature [27]. The fluid characteristic is much different from Newtonian fluids such as water that only has viscosity about 1 mPa.s at 20 °C [27]. The high viscosity of glycerine indicates that the molecular spatial space of glycerin

is denser, as like as molecular space of liquid phase that is also denser than the gases phase molecular space [24]. This is due to the existence of a highly branched network of hydrogen bonds formed by three hydrophilic hydroxyl groups [28]. Besides that, the properties of FFA tend to be hydrophobic and insoluble in polar compounds [15]. The hydrophobicity of FFA was confirmed by Wijewardana et al. [29]. They found that contact angle of sands which coated by OA reaches over 90°. The hydrophobicity of the FFA has different characteristic to the hydrophilic properties of the membrane used in this study. It is accomplished that hydrophobic properties of the impurity (FFA) can increase repulsion forces on the membrane, which ultimately influences the flux trend that occurs during the filtration process (mass transfer mechanism).

3.1.2. Temperature Effect on Permeate Flux

Effect of various temperature (at pH of 8, TMP of 4 bar) on flux decline is presented in Fig. 3. Observations show the temperature has more influence than the TMP on the flux decline qualitatively. The condition occurs because the increased temperature can directly trigger the viscosity reduction. This makes the fluid more freely to flow as a result of increasing in molecular spatial space in higher temperature condition [28]. In addition, increasing the temperature can lead to an increase of the polymer bonding mobility inside the membrane matrix [16,30]. Hence, the resistance caused by both fluid and membrane against each other is reduced by the increased temperature.

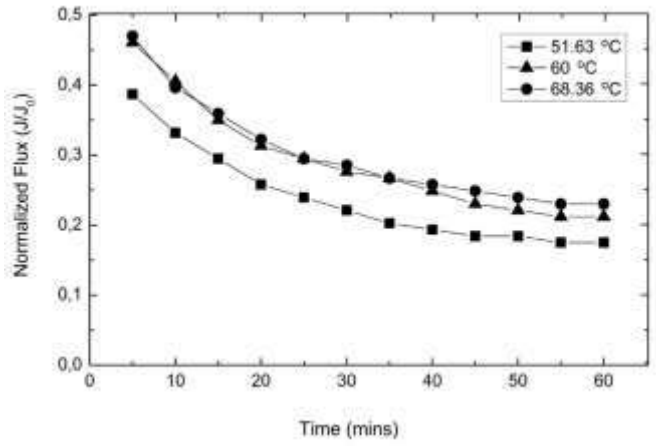

Fig. 3. Influence of temperature on flux decline of the glycerin-rich solution (pH = 8, TMP = 4 bar).

In addition, Fig. 3. shows the trend of flux response against temperature indicating that at a range of 51.63 °C – 60 °C, the increasing temperature has a

positive effect on the flux. On the contrary, in a range of 60 °C – 68.36 °C the effect of temperature is insignificant.

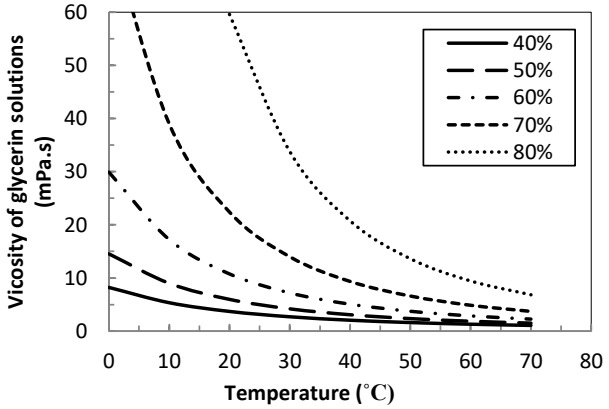

Fig.4. Viscosity of glycerin solution with increased temperature. Drawn from data calculation using viscosity-temperature correlation equation based on Arrhenius form. Source: [27]

Dhabhai et al. [3] found that the temperature did not influence the decrease of the raw glycerin viscosity at temperatures above 60 °C. It was presumably the cause of the minor effect of temperature above 60 °C.Figure 4 supports the finding confirming that the viscosity change at temperature above 60°C is insignificant. Although the viscosity of glycerin which can directly affect fluid resistance to the membrane can be reduced, it does not have a positive effect on the pattern of flux decrease as shown in TMP. This condition denotes that characteristic and properties of impurity (FFA) plays a key role in the pattern of flux decrease. Moreover, the flux can directly increase along with decreasing in viscosity which can lead to increasing of impurities concentrations both on the surface and inside pore of the membrane. This phenomenon also confirms that the process is dominated by the mass transfer mechanism.

3.1.3. Effect of pH on Permeate Flux

Fig. 5 shows the responses of flux against different pH condition at TMP of 4 and temperature of 60 °C. The pH was observed in a range of 6.33 – 9.67 where the feed sample pH was 5.27. The results show that the flux decreases the acidic state greater than those in the alkaline state. Fatty acids are impurities in a glycerin-rich solution. Based on pH condition of its environment, the fatty acid has the nature that remained as the undissociated molecule in the presence of an acidic environment and could be dissociated in an alkaline environment (below pH 9) [31-32]. A large amount of undissociated would cause severe fouling and flux decline [15, 18, 33]. Fatty acid molecules can interact with acid to form the larger molecules via an agglomeration process with another molecule of fatty acid [15,17]. The larger molecule that was formed may increase the adsorption of foulant molecule. The adsorption is formed on the membrane surface as well as on the entrance of the

membrane pore and then causes high flux decline and membrane fouling [15,33-34]. Sequentially, the flux decline follows the order of pH 7> pH 6.33> pH 9.67>pH 8 and the highest flux decline is found at pH 7. Similar trend was also reported by Mah et al. [18].According to dissociation and undissociation effect, at pH of 6.33, the flux decline should be the highest and at pH 9 the flux decline was the lowest. However, flux value at pH 7 shows higher flux decline than those at pH 6.33. This is most likely due to the fatty acid state that not fully dissociated at pH 7 [15]. In the dissociated state, fatty acid does not form clots and find as single molecule form [33]. The single molecule of fatty acid can pass through into membrane pore since the average size of the single fatty acid molecule is four times smaller than the membrane pore size [14] and then triggers the blocking inside the wall of membrane pore. The blocking at micropores is possible in PES-based UF membranes because it is an asymmetric porous membrane [35]. Adjusting the pH was performed by NaOH addition. At pH above 9, the FFA could form a soap [10] and had characteristic as surfactant with their active hydrophilic and hydrophobic sites (amphiphilic). As a surfactant, the dissociated fatty acid can form micelle where the hydrophobic tail remain inside oil phase (in the core) and hydrophilic head (with negative charge) form a layer in the surface [31-32]. Forming of the micelle is believed to be responsible for the higher flux decline at pH 9 than flux decline at pH 8.

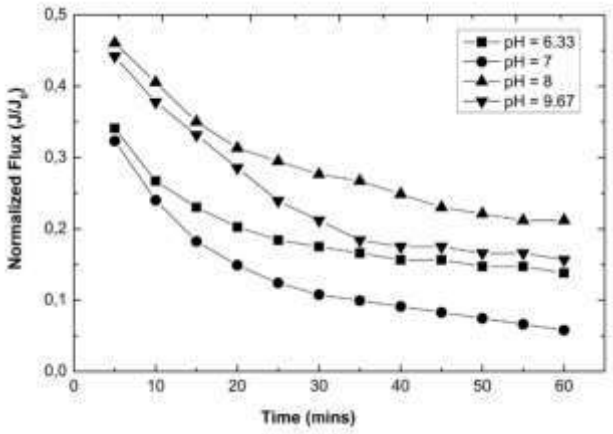

Fig. 5. Effect of pH on Flux decline of glycerin-rich solutions (TMP = 4, Temperature = 60 °C).

3.1.4. Rejection

Table 2. Summary of rejection data in various process parameters.

No.	Pressure (bar)	Temperature (°C)	pH	Rejection (%)	
				FFA	Total impurities
1.	3.2	60	8	48.10	48.50
2.	4	60	8	54.17	32.11
3.	4.8	60	8	57.63	52.86
4.	4	51.63	8	44.32	33.25
5.	4	60	8	54.17	32.11
6.	4	68.37	8	45.35	43.56
7.	4	60	6.33	30.70	21.18
8.	4	60	7	70.98	68.33
9.	4	60	8	54.17	32.11
10.	4	60	9.67	25.82	24.22

Table 2 shows a different trend in each variation of the operating condition. For TMP variation, the rejection increases with increasing on TMP. The rejection of FFA content in the filtrate at 4.8 bar and 3.2 bar are 57.63% and 48.1%, respectively. This condition takes place because in higher TMP some small foulant molecules may be penetrated the membrane pore and form a deposit, thus causing significantly reduce on the size of membrane pore which leads to an increase in rejection of impurity [18, 36]. For temperature variation, the trend of rejection tends to be similar to TMP variation where a higher temperature process has more significant rejection than lower temperature. The rejection of impurities is 33.5% at 51.63 °C while at 68.37 °C the rejection reaches 43,56%. This is likely due to the effect of increasing temperature which can directly affect the increase in flux and causes an increase the impurities that flow through the membrane pore [16]. It is similar to the condition that occurs in TMP variation. Rejection behaviour at pH variation has a different kind than the other operating parameter. The highest result is 70.98% at pH 7, and the lowest result is 25.82% at pH 9.67. This behaviour may occur due to the nature of the impurities, as described in section 3.1.3.

The result of impurities rejection at each variation in this study is higher than impurities rejection reported by Amin et al. [16]. In this study, the highest result is 70.98% rejection of FFA, whereas the most top result by Amin et al. [16] is 41.41%. It is confirmed that using smaller membrane pore size provides a positive impact on impurities rejection. In contrast, Mah et al. [18] reported higher rejection (about 97,95 at pH 2) than this study. It is presumably due to the type of impurities contained in glycerine and its operating condition. The previous researcher used PO+OA mixture as foulant that has a larger molecular and droplet size than FFA.The larger molecule and droplet size could lead to increasing the rejection of impurities [18]. Further, TMP that was also lower than those that was used in this study. The lower TMP decreased penetrating possibility by impurities to membrane pore [16,21].

3.2. Blocking Mechanism

The constant of the blocking mechanism and the corresponding correlation coefficients (R^2) during filtration is listed in Table 3. According to the Table, increasing TMP reduces the flux decline. Its condition also applies to temperature as confirmed by the smaller value of the constants along with increases of TMP and temperature. Cake formation is predicted as a dominated blocking mechanism during the filtration process for both TMP and temperature variations. In the cake formation, the foulant is firstly adsorbed on the membrane surface, penetrate the membrane pore and then form a layer that can cause a more severe decrease in flux even from the early step of filtration. The fatty acid may be the component responsible for severe fouling [14]. In biodiesel industries, glycerin was a by-product from the transesterification reaction which consists of palmitic acid (C16: 0), stearic acid (C18: 0) and most of the oleic acid that has double bond carbon chain (C18: 1) [37].

In addition, Table 3 shows the value of k (constant) at an acidic state that tends to be higher than in the alkaline state. It demonstrates that the resistance of the fluid to the membrane is larger and causing more severe fouling than in the alkaline state. The nature of fatty acids which tend to undissociated at acidic environment may be responsible for that condition. Under this environment, the fatty acid would be clumping each other [15]. Mah et al. [18] reported that the droplets of a mixture of palm oil and oleic acid at pH 2 (very acidic condition) lead to a significant increase in droplet size and even reach twice in size over the original droplet size. Therefore, setting pH under acidic conditions can lead to agglomeration of foulant molecules.

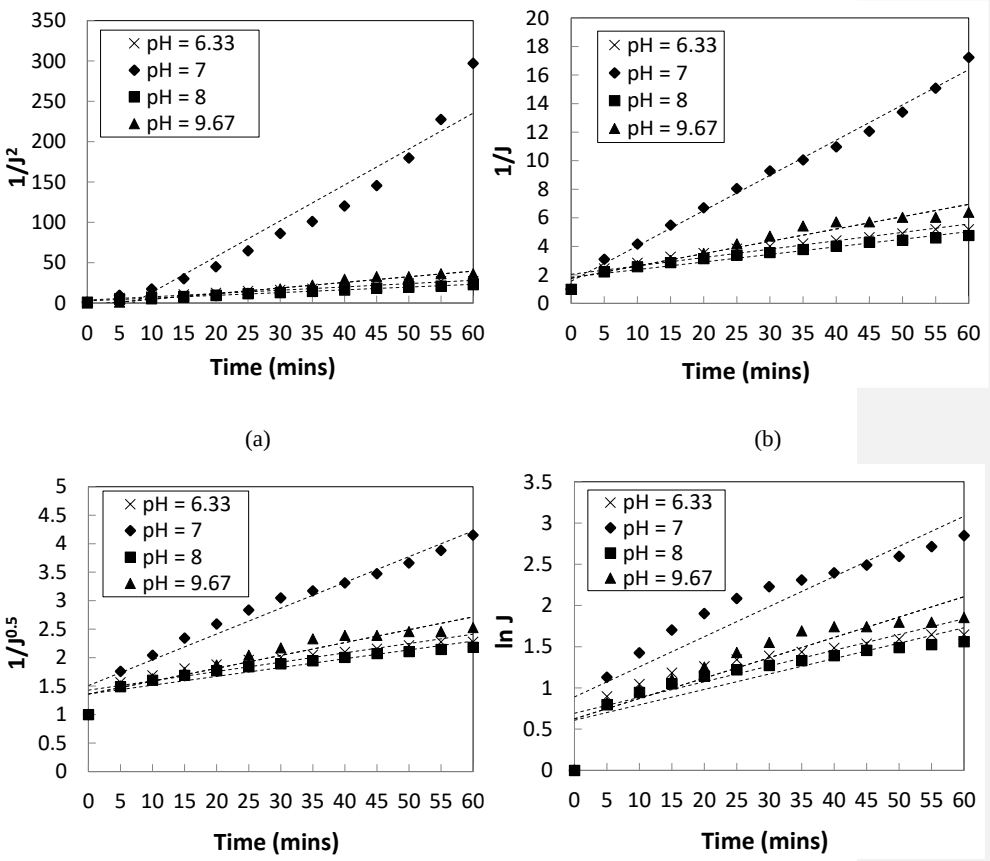

Fig. 6. Hermia's model fitting for the experimental data: (a) Cake formation (n=0), (b) Intermediate blocking (n=1), (c) Standard blocking (n=1.5), (d) Complete blocking (n=2) at TMP of 4 bar and Temperature of 60 °C

Table 3. Summary of rejection data in various process parameters.

Parameters	n=0 Cake Formation		n=1 Intermediate Blocking		n=1.5 Standard Blocking		n=2 Complete Blocking	
	K_{cf}	R^2	K_i	R^2	K_s	R^2	K_c	R^2
Pressure								
3.2 bar	0.4098	0.9848	0.0585	0.9031	0.0164	0.8171	0.0191	0.7051
4 bar	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
4.8 bar	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
Temperature								
51.63 °C	0.5329	0.9782	0.0692	0.9026	0.0185	0.8204	0.0208	0.7084
60 °C	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
68.36 °C	0.2872	0.9737	0.0476	0.8892	0.0142	0.8136	0.0176	0.7184
pH								
6.33	0.4090	0.9840	0.0580	0.9030	0.0160	0.8170	0.0190	0.7050
7	4.4480	0.9187	0.2468	0.9917	0.0453	0.9557	0.0365	0.8307
8	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
9.67	0.6982	0.9742	0.0862	0.9443	0.0225	0.8935	0.0247	0.8068

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Fig. 6. exhibits the blocking mechanism that occurs in the various pH. Generally, the mechanism is dominated by the cake formation, except for pH 7 as supported with the highest R^2 value for pH 6.33, 8 and 9.67. The similar result was reported by Amin et al. [15] and Mah et al. [18] confirming that cake formation was the dominant mechanism in pH variation. The different condition at pH 7, as seen in the value of k (constant for blocking mechanism) is much more excellent than at another pH. Moreover, the highest R^2 value in the intermediate blocking mechanism is found. Fig. 5 (b) and fig. 5 (c) confirm that in the initial conditions of filtration until 10 mins, both intermediate blocking and standard blocking mechanism occur. Then, in 15 mins until 45 mins only the intermediate blocking mechanism is observed, and for 50 mins afterwards only standard blocking contributes to the flux decline. In intermediate blocking, the solutes or particles which accumulated on the membrane surface and the entrance of membrane pore are possible to overlap another solute that has already deposited on the membrane surface. The foulant is the pilled up each other in irregular arrangement [14] and triggers other mechanisms such as standard blocking to occur during the filtration process. Standard blocking mechanism is believed to be responsible for a significant flux decline as in that condition the impurities molecule penetrates to the inside wall of the membrane pore and make a deposit which can be lead to plugging on the active area of the membrane pore [38-39]. This strengthens the previous statement that fatty acids which are not fully dissociated at pH 7enterthe pore and cause blockages in the membrane pore.

At high pH, especially for pH 9 above, the fatty acid molecule is fully dissociated and become surfactants with a hydrophilic head and hydrophobic tails which have negative charge [40]. If there was an interaction between fatty acids and membranes, it formed a negative charge induction to the membrane [15, 41]. Thus the repulsive force between the fatty acid and the membrane may change. This condition may also cause changes in the fluid resistance to the membrane [15].

4. Conclusions

The study of flux decline, rejection and blocking mechanism during UF process using 1 kDa PES membrane with various process parameters (TMP, temperature, and pH) to the glycerin-rich solution from the biodiesel industry were conducted. It was found that flux decline was severe significantly in all variation of process parameter due to a deposit of impurities. Both pressure and temperature did not give significant effect to the flux decline due to the domination of the mass transfer mechanism which is caused by the nature of impurities its self. In addition, the pressure and temperature had a similar trend of rejection that in higher process parameters the rejection becomes greater, whereas at pH variation behaviour of rejection is determined by the nature of impurities. Hermia's blocking law model found to fit well to the experimental data. The best-fit experiment data was cake layer formation mechanism for all process variation except for pH 7 where the intermediate blocking takes the lead in early stages and then followed by standard blocking. The PES UF membrane 1 kDa demonstrated to be capable of removing impurities such as FFA from industrial crude glycerine. In addition, this study provides better understanding of flux decline behaviour and blocking mechanism that occurred during UF process of industrial crude glycerin. In order to improve the UF performance, preliminary treatment of crude glycerin or modification of the membrane surface is required. This treatment is expected can reduce the membrane fouling specifically due to the FFA characteristic.

Nomenclatures

A	Membrane area, m^2
C_f	Concentration of FFA or impurities in the feed, mg/L
C_p	Concentration of FFA or impurities in the permeate, mg/L
J	Permeate Flux, $L.m^{-2}.\ h^{-1}$
J_0	Initial Flux, $L.m^{-2}.\ h^{-1}$
k	Constantofblocking mechanism
K_c	constants of complete blocking (h^{-1})
K_{cf}	constants of gel or cake formation (h/m^2)
K_i	constants of intermediate blocking (m^{-1})
K_s	constants of standard blocking ($h^{-1/2}\ m^{-1/2}$)
n	Value that represents a blocking mechanism, n = 0 (cake layer formation), n = 1 (intermediate blocking), n = 1.5 (standard blocking), and n = 2 (complete blocking)
R	Rejection, %
R^2	The corresponding correlation coefficients
t	Filtration time (h)
V	Permeated volume (L)
W	Weight of permeate (g)

Abbreviations

ASTM	American Society for Testing and Materials
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
NGOM	Non-Glycerol Organic Matter
OA	Oleic Acid
PO	Palm Oil
TMP	Trans Membrane Pressure
UF	Ultrafiltration

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OUTLINING HOW THE ISSUES ARE ADDRESSED

Title of paper: PURIFICATION OF GLYCERIN-RICH SOLUTION FROM PALM OIL BASED PRODUCTION BIODIESEL BY ULTRAFILTRATION MEMBRANE

1. Address all the concerns/recommendations of the reviewers.
2. All amendments made are to be highlighted in red color in the revised paper.

Reviewer # 1

Final Recommendation	Accepted without modification	Accepted with minor corrections	Accepted with major modification	Rejected
Please tick	☐	☐	☐	☑

Comments	Addressed (Y/N)	Reply/Action taken
1. The title is not reflecting the content of the manuscript, if not misleading. No purification is achieved, as no results obtain >95% pure concentration (maximum rejection around 70%). Therefore, the TITLE MUST BE CHANGED to: "Fouling behavior of polyethersulphone ultrafiltration membrane in the separation of glycerin-rich solution as byproduct of palm-oil-based biodiesel production".	Y	Thank you for your suggestion. The title is changed.
2. Abstract: The current range of TMP, temperature, and pH is too shallow. It might be widened but it was argued that those parameters were the result of optimization from previous research. Where is the reference?	Y/N	Our previous study was presented in an international conference and it would be published in IOP Conference proceeding. However, it had not publishet yet so we can not add this in the referrence section. Is it okey if we add an article that has not published yet?
3. Section 1, paragraph 1: How come reference #10 jumps up, and bypassing references number 6, 7, 8 and 9? Fix the sequence of the references!	Y	It has been modified
4. Section 1, paragraph 1: The word “matter organic non-gycerol” is not appropriate. Change it to “non-glycerol organic matter (NGOM)”.	Y	It has been changed
5. Section 1, paragraph 2: Beside those aforementioned processes, there is also an emerging process to remove impurities (i.e. water) from viscous glycerin-like product is pervaporation. Cite Y. Wang et al, J. Membr. Sci. 363 (2010) 149-159 and Y. Wang et al, J. Membr. Sci. 378 (2011) 339-350. It was previously argued that the suggested reference are "not similar to our process", yet you cite processes having no membrane at all, e.g. adsorption, ion exchange,	Y	The suggestion articles have been cited

saponification, acidification, neutralization, extraction, and drying!! Pervaporation is a membrane-based process, and it is more similar to membrane ultrafiltration process, than those non-membrane processes. How absurd. Reference #23 is about pervaporation. If pervaporation is not similar to your process, then remove the reference #23.		
6. Section 1, paragraph 4: What do you mean by "To the best of our knowledge, the applications of PES UF for separation or of glycerin used pure glycerin or mixture of pure glycerin with impurities as UF feed". Very confusing!	Y	The paragraph has been modified
7. Section 1, paragraph 4: Similar works have been done before. Cite Bellona et al., Sep. Purif. Technol. 74 (2010) 44-54, "The effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes" https://dx.doi.org/10.1016/j.seppur.2010.05.005 that employed GE/Osmonics SEPA membrane (now Suez (GE) Sepa CF, http://www.sterlitech.com/ultrafiltration-uf-membrane-ympwsp1905.html) to separated several organic compounds (including glycerin). Cite Arenillas et al., J. Membr. Sci. Res. 3 (2017) 102-108 "Glycerin removal from ultrafiltration flat sheet membranes by filtration and soaking" https://dx.doi.org/10.22079/jmsr.2016.23080 that employed ultrafiltration membrane for removing glycerin.	Y	The suggestion articles have been cited
8. Section 1, paragraph 4: Write reasons/justifications on why no pretreatment was taken, in order to obtain >95% pure concentration. Moreover, the title of this manuscript must be change. The word "purification" in the old title (and in Section 1, paragraph 4, the last three lines) must be removed, since the product is not really pure.	Y/N	The title has been changed. Since at that time we were not focused on modification of material. We add the suggestion of pretreatment in the conclusion. We also consider to do pretreatment in our future research. Thank you for your suggestion.
9. Section 2.1: You use a membrane with 1000 Da molecular weight cut-off, to separate glycerin (92 Da) from impurities. However you missed to write what are the impurities and their molecular weight. If the impurites are free fatty acids, most fatty acids such as lauric acid, stearic acid, cerotic acid, even docosahexaenoic acid with 22 carbons are around 300 Da only. This is the fundamental on why the	Y	At the time of research we were focused on using very low MWCO to follow and compare with previous research in the literature. We add the suggestion of pretreatment in the conclusion. We also consider to do pretreatment in our future

ultrafiltration experiments in this study (without any initiative for modification taken) shall give rejection only 70%, since the permeate streams contains not just glycerin, but also 300 Da fatty acids, also water (highly likely). It is better to use UF with 200 Da MWCO, or employ some pretreatments. Write reasons/justifications on why no pretreatment was taken.		research. Thank you for your suggestion.
10. Section 2.4: Add the parameter "n" to the Table 1, and the caption of Figure 6. The Table 3 has the "n" parameter written in it.	Y	They have been modified
11. Table 1: in the column of "Physical Concept", use uppercase S and D for the 3rd line (Formation of Surface Deposit).	Y	It has been corrected
12. Section 3.1.1, paragraph 4: Any data for contact angle of free fatty acids that reflect their hydrophobic properties?	Y	The data from literature has been added
13. Figure 4, Y-axis: "glycerin", not "glycerinE"	Y	It has been corrected
14. Figure 5: The irregular sequence of normalized flux (fluctuating trend of flux vs. pH 6.33, 7.00, 8.00, and 9.67) was attempted to be justified by reference #11 (J. Food Eng. 101 (2010) 264-272), and #13 (Sep. Purif. Technol. 98 (2012) 419-431), with the theory of dissociation/undissociation of fatty acid. The discussion related to the irregularities for pH 6.33 and 7.00 has been written. However, the irregularities for pH 8.00 and 9.67 have not been discussed. Add the related discussion! What are the causes or reasons behind the imperfection of dissociation of fatty acids? Add the related discussion!	Y	We add related discussion
15. Section 3.1.3: Edit the excess square bracket	Y	It has been corrected
16. Abbreviation: add PO, OA, NGOM, FAME into the list	Y	The list in abbreviation has been added
17. Reference #3: add a space to separate "andReaney" to be "and Reaney"	Y	It has been changed
18. Reference #5: Be consistent! Remove the DOI in order to make the format of this reference is in unison with other references.	Y	It has been changed
19. Reference #6: Be consistent! Remove the DOI in order to make the format of this reference is in unison with other references.	Y	It has been changed
20. Reference #8: Be consistent! Remove the DOI in order to make the format of this reference is in unison with other references.	Y	It has been changed
21. Reference #18: …2nd ed.	Y	It has been correcetd

22. Reference #19: Be consistent! Remove the DOI, and also the "p" in "p.42-69", as this format is not in unison with other items in the list of references.	Y	It has been changed
23. Reference #20: The name of the first author must be "van den Berg, G.B."	Y	It has been corrected
24. Reference #27: Be consistent! Check the manuscript preparation guide for writing the format of the reference. Is the requirement stated to use the abbreviated name of the journal, or to use the full name of the journal? Reference #27 is much different with references #1 to #32. Or, maybe reference #27 is the right one (using abbreviated name), and the format of other references must be changed. Check and recheck it.	Y	It has been corrected
25. Reference #31: …6th ed	Y	It has been changed
26. Reference #31: Use uppercase M and uppercase S for "Journal of Membrane Science". Or, for "J. Membr. Sci.".	Y	It has been corrected

(Please add more rows if needed)

Reviewer # 2

Final Recommendation	**Accepted without modification**	**Accepted with minor corrections**	**Accepted with major modification**	**Rejected**
Please tick	☑	☐	☐	☐

Comments	**Addressed (Y/N)**	**Reply/Action taken**
•		
•		
•		

(Please add more rows if needed)

Reviewer # 3

Final Recommendation	**Accepted without modification**	**Accepted with minor corrections**	**Accepted with major modification**	**Rejected**
Please tick	☐	☑	☐	☐

Comments	**Addressed (Y/N)**	**Reply/Action taken**
• Sentence not clear For the research gap, what are the different on the current study with other/previous studies?	Y	We modified the paragraph
• Density is used to convert from mass to volume? How do you get the density value?	Y	We add an sentence to make it clear

• Add citation/ref	N	Our previous study was presented in an international conference and it would be published in IOP Conference proceeding. However, it had not publishet yet so we can not add this in the referrence section. Is it okey if we add an article that has not published yet?

(Please add more rows if needed)

Reviewer # 4

Final Recommendation Please tick	Accepted without modification	Accepted with minor corrections	Accepted with major modification	Rejected
	☑	☐	☐	☐

Comments	Addressed (Y/N)	Reply/Action taken
•		
•		
•		
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•		

(Please add more rows if needed)

Reviewer # 5

Final Recommendation Please tick	Accepted without modification	Accepted with minor corrections	Accepted with major modification	Rejected
	☐	☐	☑	☐

Comments	Addressed (Y/N)	Reply/Action taken
• Various is an adjective of variation. So please choose one, not 'various variation'.	Y	The word has been changed as "various"

(Please add more rows if needed)

Reviewer # 6

Final Recommendation Please tick	Accepted without modification	Accepted with minor corrections	Accepted with major modification	Rejected
	☐	☐	☐	☐

Comments	Addressed (Y/N)	Reply/Action taken
•		

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FOULING BEHAVIOR OF POLYETHERSULPHONE ULTRAFILTRATION MEMBRANE IN THE SEPARATION OF GLYCERIN-RICH SOLUTION AS BYPRODUCT OF PALM-OIL-BASED BIODIESEL PRODUCTION

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Abstract

Crude glycerin, as a by-product of the transesterification process, has low economic value and limited applications. Membrane process using ultrafiltration membrane is an alternative to purify the glycerin. However, flux decline behaviour during the ultrafiltration process is a major limitation. Since specific information of blocking information in ultrafiltration of glycerin rich solution was not found, this research seek to focus on separation of glycerin rich solution from its impurities. In this research, flux decline, rejection, and blocking mechanism at various Trans Membrane Pressure (TMP), temperature, and pH were observed. Experiments were carried out at the variation of the TMP (3.2 – 4.8 bar), temperature (51.63 – 68.36 °C), and pH (6.32 – 9.67). The research showed that the flux decline was significant at all variations of the process parameter. Both TMP and temperature had no significant effect on flux decline. Rejection value was proportional to TMP and temperature while at pH variation, the rejection was determined by the characteristic of impurities. Hermia's model was selected to analyse the blocking mechanism during filtration. It was confirmed that the mechanism was dominated by cake formation for all process parameters except for pH 7. At pH 7, the mechanism was controlled by intermediate blocking at an early stage and then followed by standard blocking. This research demonstrated that the ultrafiltration process was capable of removing some impurities of crude glycerin up to 68.33% and 70.98% for total impurities and FFA, respectively. However, process development such as feed pretreatment or membrane modification is suggested to improve rejection and reduce the membrane fouling.

Keywords: Glycerol, Purification, Ultrafiltration, Blocking Mechanism, Hermia.

1. Introduction

Production of biodiesel generates crude glycerin as a by-product. It was reported that the production of 10 kg biodiesel produced 1 kg of crude glycerin [1]. Crude glycerin from biodiesel production has low economic value since the glycerin product is mixed with impurities in its heavy phase. On the other hand, glycerin is the raw material for many industries such as pharmacy, food, cosmetic, cigarette, automotive, textile or chemical industry. In addition, pure glycerin is potential for bio-lubricant, additive and an alternative fuel by adjusting the combustion cycle [2]. As a by-product, glycerin is found in its crude form (crude glycerine or raw glycerin) which contain many impurities and non-glycerol organic matter (NGOM) at various concentrations. The NGOM found in crude glycerin is fatty acid methyl esters (FAME), fatty acid ethyl esters, free fatty acids (FFA) and glycerides. Application of crude glycerin has many disadvantages such as low fuel value, require purification to increase its fuel value and high cost [1,3,4,5]. Crude glycerine contains many contaminants such as water, inorganic salts and other organic materials (FFA, FAME or biodiesel, alcohol (methanol), unreacted palm oil and triglyceride, diglyceride, monoglyceride) [3].

In general, crude glycerin is purified by distillation. However, the low vapour pressure of glycerin and its temperature sensitivity causes degradation or polymerisation of glycerin, and hence, vacuum distillation is applied more frequently than the normal distillation [4]. As a consequence, application of vacuum distillation was expensive due to the high energy required to create vacuum condition and evaporate glycerin [3, 4]. Other purification processes such as ion exchange [6], acidification, neutralisation (pre-treatment) [7], extraction [8], pervaporation [9, 10] adsorption, saponification, and drying [4] have been implemented to obtain high purity glycerine. Nevertheless, the usage of chemicals and energy requirement has a consequence of high cost.

Purification of glycerin by membrane technology has been developed and studied due to its process simplicity and can minimise energy requirement by utilising concentration difference, electron potential and hydroscopic pressure [4, 11]. One type of the membrane for purification or separation glycerin is Ultrafiltration (UF). Separation of glycerin from FAME by UF and microfiltration ceramic membrane was studied [12]. The research confirmed that the biodiesel met the American Society for Testing and Materials (ASTM D6751-09) standard for glycerin content. A similar result was also found by Wang et al. [13]. Experiments focused on glycerin purification have been performed. Dhabbai et al. [3] investigated purification of crude glycerol using a sequential physicochemical treatment, membrane filtration, and activated charcoal adsorption. It was reported that the result of maximum glycerol content was 97.5 wt% with acid value and FFA content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Other studies focused on the application of UF for glycerin model of glycerin separation. Amin et al. [14] evaluated UF fouling characteristic for filtration of pure mixture glycerin having 15% w/w and found that the flux decline involved cake layer model as well as pore blocking model. In addition, the separation of glycerin mixed with fatty acids (palmitic, stearic, and oleic acids) by polyethersulphone (PES) UF membrane was also studied [15]. It was reported that the PES membrane exhibited severe fouling for all types of fatty acids in solution with glycerol–water. A similar study by Amin et al. [16] investigated glycerin-rich fatty acid solutions confirming that the addition of fatty acid affected

significant flux decline. Mah et al [17, 18] studied on UF of palm oil-oleic acid-glycerin mixture and performance. It was found that cake formation was the blocking mechanism that occurs during UF process based on prediction using Hermia's model and the smallest flux decline occurred at palm oil (PO) and oleic acid (OA) mixtures. Blocking behaviour between PO and OA was different, where for PO blocking was occurred only at the surface while for OA blocking reached inside the pore of the membrane. Observation of the influence of pH was also carried out. It presented that flux decline was getting worse in the presence of the acidic environment. This study using hydrophilic PES membrane to minimize fouling which is caused by interaction of hydrophobic site of FFA towards membrane material (surface and inner pore surface).

To the best of our knowledge, the applications of PES UF for separation impurities from glycerin used glycerin-rich solution from mixture of pure glycerin with addition of impurities as UF feed has not been investigated. The pore size of the membrane that was used in previous study also extremely larger (around 5 – 30 kDa) than the size of impurities [14, 17]. Bellona et al. [19] investigated the effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes. It was found that organic foulant such as glycerin could be removed by NF membrane with rejection above 90%. However, applied operational pressure was certainly high. In addition, glycerin could not flow through the pore of NF membrane and caused the glycerin still mixed with the impurities. Arenillas et al. [20] studied removal glycerin from UF flat sheet membrane via filtration and soaking process. Their study was only focused on removal of glycerin contain in membrane matrix as the preservative.

This research emphasised the use of crude glycerin from biodiesel plant as UF feed to study the possibility and performance of UF membrane 1 kDa in separation of impurities from industrial crude glycerin. The objectives of the research were to study the effect of process parameter (TMP, temperature and pH) on membrane performance (flux and rejection) for purification of crude glycerin. In more specific, this study was to gain deep understanding about the fouling behavior and blocking mechanism during UF process of industrial crude glycerin with 1 kDa UF membrane. The crude glycerin contains many impurities consist of water inorganic salt from catalyst residue, methanol, unreacted palm oil (mono-, di- and triglycerides), free fatty acids, lipids, methyl esters, as well as a various other NGOM. By using the PES UF membrane, compound shaving high molecular weight were separated and retained in retentate and glycerin permeated to the membrane. In addition, investigation of the blocking mechanism of the UF membrane in crude glycerin purification was addressed.

2. Materials and Methods

2.1. Materials

Crude glycerine was supplied from Biodiesel Plant of PT SMART Tbk., Tarjun, Indonesia was used as a raw material. The crude glycerin composed glycerin having concentration of 82.17 %, 10.56% FFA and NGOM other than FFA of 7.27%. The crude glycerin was then mixed with demineralised water at ratio 1:1 to form 50% glycerine solution. In this research, PES flat sheet UF membrane (Synder Filtration XV) having 1 kDa molecular weight cut-off was purchased from Sterlitech Corp,

USA. It was reported that UF membrane having 30 kDa pore size was able to separate oleic acid (as a model of fatty acid) in a mixture of pure glycerin, oleic acid and palm oil [17, 18]. In this research, UF membrane having 1 kDa pore size which was smaller than 30 kDa was selected to increase the UF performance in separating impurities such as FFA and palm oil.

2.2. UF Membrane

Experiments were carried out by a laboratory-scale UF Cell equipped with compressor and instrumentation control, as illustrated in Fig. 1.

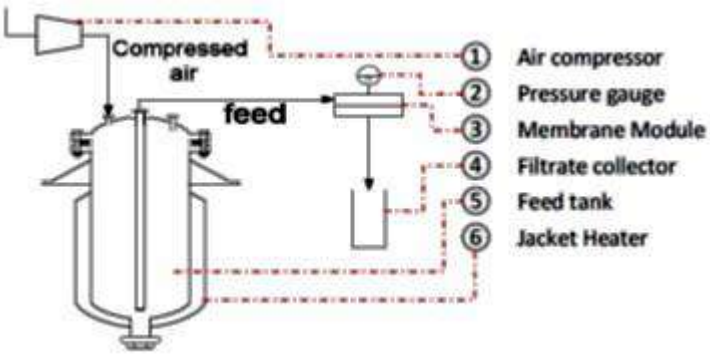

Fig. 1. Schematic illustration of UF cell with temperature control.

Experimental runs were operated at room temperature (25 ± 2 °C). Before each run, membranes were first compacted by filtering distilled water through the membrane at a pressure of 1 bar for 60 mins. For each experimental work, a new circular membrane sheet having area of 13.85 cm^2 was placed inside the UF cell. Pure water flux (J_0) was determined for initial water characteristic. The pure water flux was evaluated by weighing permeate collected at a specific time. The permeate flux (J) was determined by collecting permeate for 120 mins, with interval of 5 mins. Then, permeates were collected in glass graduated cylinder Pyrex™ 10 mL to measure the volume (V). Both pure water flux and permeate flux were calculated according to (Eq. 1).

$$J = \frac{V}{A \cdot t} \tag{1}$$

In eq. (1), J can be represented as J_0 or water flux ($L.m^{-2}.h^{-1}$) and J or permeate flux ($L.m^{-2}.h^{-1}$), V is volume of permeate (L) and A ismembrane area (m^{-2}).

Permeate fluxes, and blocking mechanisms were observed by adding crude glycerin to the feed tank for half tank capacity. Further, the UF cell was operated at a dead-end mode at the variation of the transmembrane pressure (TMP) at 3.2 – 4.8 bar, temperature (51.63 – 68.36 °C) and pH (6.32 – 9.67). The value of process parameters was selected according to optimisation of each process parameters in our previous study. The pH adjustment was conducted by adding a 0.1 N HCl or

0.1 N NaOH. Sampling for permeate flux determination was carried out for 60 mins, with an interval of 10 mins. Flux decline, rejection, and the blocking mechanism were observed in various of the process parameters.

2.3. Analysis

UF performance for glycerin purification from the feed solution was evaluated through the rejection of FFA and impurities. The rejection (R) was calculated by using eq. (2).

$$R = \frac{C_f - C_p}{C_f} \tag{2}$$

In equation (2), R (%) is rejection of FFA or impurities, C_f (mg/L) is concentration of FFA or impurities in feed, and C_p(mg/L)is concentration of FFA or impurities in the permeate. The composition of permeate was analysed by using gas chromatography and mass spectrometry (GCMS, Shimadzu TQ8030). Column oven temperature is 65 ºC for 8 min, then the column temperature was ramped from 65 ºC to 250 ºC at 4 ºC/min and held for 20 min. Each sample (1 µL) was injected into Rxi-1ms column (30m × 250 micrometres × 0.25 micrometres, Restek Corp, USA) with linear velocity as flow control mode and injection that was used is split injection with ratio 20:1. The injection temperature is 250 °C where the operating pressure is 75.5 kPa with detector temperature held constant at 300 °C. Helium was used as the carrier gas at a flow rate of 1.2 mL/min and operation run time at 74 min.

2.4. Model of Blocking Mechanism

Hermia's model defines the fouling mechanism, especially in the porous membrane with dead-end system filtration. In more specific, the model highlighted the fouling mechanism which dominates in the entire of the process. This model applied a common power-law equation to describe the blocking mechanism and written in Eq. (3) [17, 21].

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{3}$$

In eq. (3), t is filtration time (min), k is filtration constant, and V is filtrate volume (L). Complete pore blocking illustrates that each solute is assumed to participate in blocking the entrance of the membrane pores completely. With the assumption that every solute stays on previously deposited solute, it is represented of intermediate pore blocking. Standard pore blocking describes that each solute is deposited to the internal pore wall. Determination based on the accumulation of the solute on the membrane surface is representative of cake or gel formation [14]. Mah et al. [17] and Amin et al. [14] concluded that Hermia's model was fit well with the experimental data for predicting the blocking mechanism during UF. It was confirmed by the value of R^2 which is mostly above 0.9 for appropriate model. In addition, optimising process parameters, analysing the transition of each fouling

mechanism and predict cleaning or replacing membrane during operation can be predicted based on Hermia's model [17]. Further, linearisation of blocking mechanism according to equation (3) is presented in Table 1.

Table 1. Linearisation equation of blocking models based on Hermia's model [22]

Pore Blocking Models	n	Linearisation Equation	Physical Concept
Standard Blocking	1.5	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore Blocking + Surface Deposit
Intermediate Blocking	1	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore Constriction
Complete Blocking	2	$\ln J = \ln J_o - K_c t$	Formation of Surface Deposit
Gel or Cake Formation	0	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore Blocking

In Table 1, K_s, K_i, K_c and K_{cf} are constants of standard blocking ($h^{-1/2}$ $m^{-1/2}$), intermediate blocking (m^{-1}), complete blocking (h^{-1}) and gel or cake formation (h/m^2), respectively.

3. Result and Discussion

3.1. Flux decline and rejection

3.1.1. Effect of TMP on Permeate Flux

UF process is one method to separate substances which have different molecular size using TMP as a driving force. The fluxes increase along with the increase on TMP, indicating that the flux is proportional to TMP as long as the resistance between the membrane and the fluid are not significant [14, 18, 23-26]. Fig. 2 shows the flux response against the TMP at pH 5.27 and temperature 60 ^oC. Generally, the flux decline over time is caused by the impurities deposited on the surface and inside the membrane pores. The figure confirms the correlation between flux and TMP, wherein increasing TMP causes an increase in the flux. The higher normalised flux at higher TMP is achieved at a pressure range of 3.2 – 4 bar. In contrast, at a range of 4 – 4.84 bar, the effect of adjustment TMP on the positive impact on the flux is not significant, indicating that the TMP has a slight impact on increasing flux. This condition reveals an increase in resistance between the membrane and the fluid that caused by polarisation of impurities on the membrane surface [16, 18]. Based on Darcy's law, flux was not only depended on TMP but also influenced by the resistance between the membrane and the fluid [26].

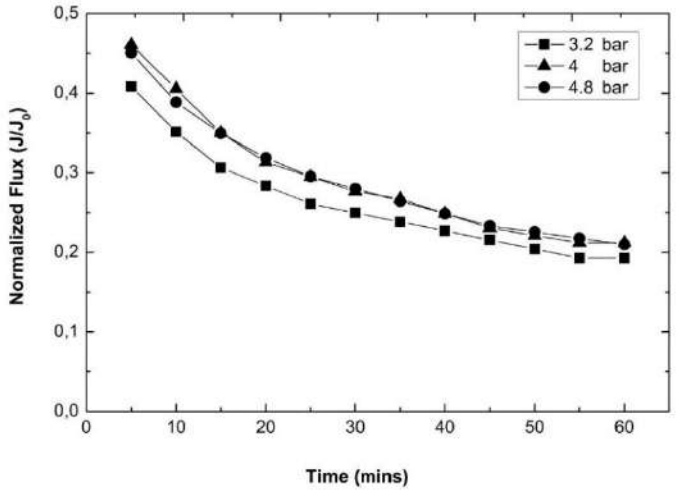

Fig. 2. Influence of TMP on fluxes of glycerin-rich solutions at pH of 5.27 and Temperature of 60 ºC.

Adjusting TMP to a higher point lead to an increase in flux, but it still cannot affect the pattern of flux decline. This is confirmed by the flux decline pattern in Fig. 2 showing similarity pattern at the variations of TMP. A significant flux decline in the early stages of the UF process a range of 0 – 25 mins and then continued with the stationary states of flux decline at a range of 30 – 60 mins are observed. This phenomenon indicates that the process more influenced by mass transfer mechanism than by TMP it's self [21]. This leads to a more severe condition of flux decline as the result of the deposits increase and impurities quantity. The impurities were carried away by the glycerin-rich solution that flows through to membrane matrix and presumably deposited both on membrane surface as well as inside the pore of the membrane [16, 21].

This phenomenon is conceivable because of the nature of the raw material (glycerin) and the majority of impurity (FFA) in crude glycerin. Glycerin has a high viscosity. The viscosity for pure glycerine was found as 1.5 Pa.s [1] and for crude glycerine containing 80% of glycerine, the viscosity was above 20 mPa.s at reference temperature [27]. The fluid characteristic is much different from Newtonian fluids such as water that only has viscosity about 1 mPa.s at 20 ºC [27]. The high viscosity of glycerine indicates that the molecular spatial space of glycerin is denser, as like as molecular space of liquid phase that is also denser than the gases phase molecular space [24]. This is due to the existence of a highly branched network of hydrogen bonds formed by three hydrophilic hydroxyl groups [28]. Besides that, the properties of FFA tend to be hydrophobic and insoluble in polar compounds [15]. The hydrophobicity of FFA was confirmed by Wijewardana et al. [29]. It was found that contact angle of sands which coated by OA reaches over 90º. The hydrophobicity of the FFA has different characteristic to the hydrophilic properties of the membrane used in this study. It is accomplished that hydrophobic properties of the impurity (FFA) can increase repulsion forces on the membrane, which ultimately influences the flux trend that occurs during the filtration process (mass transfer mechanism).

3.1.2. Temperature Effect on Permeate Flux

Effect of various temperature (at pH of 8, TMP of 4 bar) on flux decline is presented in Fig. 3. Observations show the temperature has more influence than the TMP on the flux decline qualitatively. The condition occurs because the increased temperature can directly trigger the viscosity reduction. This makes the fluid more freely to flow as a result of increasing in molecular spatial space in higher temperature condition [28]. In addition, increasing the temperature can lead to an increase of the polymer bonding mobility inside the membrane matrix [16, 30]. Hence, the resistance caused by both fluid and membrane against each other is reduced by the increased temperature.

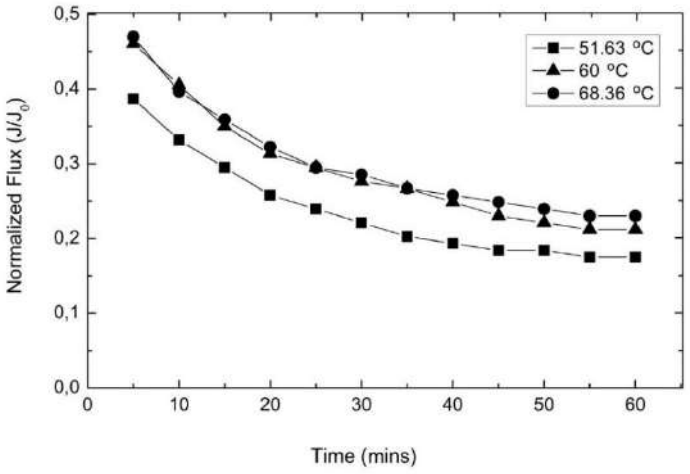

Fig. 3. Influence of temperature on flux decline of the glycerin-rich solution (pH = 8, TMP = 4 bar).

In addition, Fig. 3 shows the trend of flux response against temperature indicating that at a range of 51.63 °C – 60 °C, the increasing temperature has a positive effect on the flux. On the contrary, in a range of 60 °C – 68.36 °C the effect of temperature is insignificant.

Dhabhai et al. [3] found that the temperature did not influence the decrease of the raw glycerin viscosity at temperatures above 60 °C. It was presumably the cause of the minor effect of temperature above 60 °C. Figure 4 supports the finding, confirming that the viscosity change at temperature above 60°C is insignificant. Although the viscosity of glycerin which can directly affect fluid resistance to the membrane can be reduced, it does not have a positive effect on the pattern of flux decrease as shown in TMP. This condition denotes that characteristic and properties of impurity (FFA) plays a key role in the pattern of flux decrease. Moreover, the flux can directly increase along with decreasing in viscosity which can lead to increasing of impurities concentrations both on the surface and inside pore of the

membrane. This phenomenon also confirms that the process is dominated by the mass transfer mechanism.

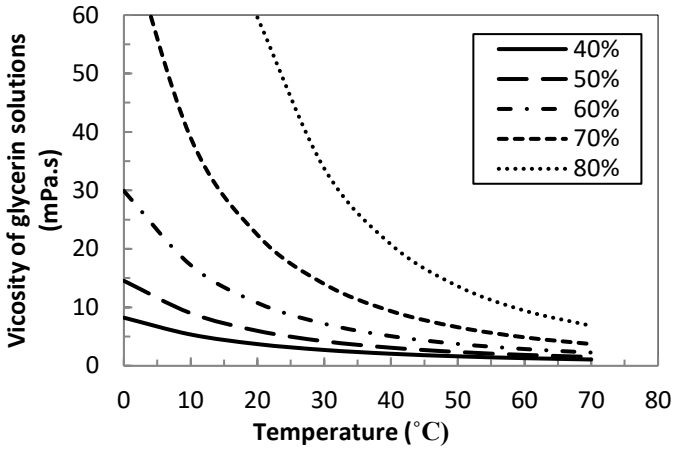

Fig. 4. Viscosity of glycerin solution with increased temperature. Drawn from data calculation using viscosity-temperature correlation equation based on Arrhenius form. Source: [27]

3.1.3. Effect of pH on Permeate Flux

Figure 5 shows the responses of flux against different pH condition at TMP of 4 and temperature of 60 ºC. The pH was observed in a range of 6.33 – 9.67 where the feed sample pH was 5.27. The results show that the flux decreases the acidic state greater than those in the alkaline state. Fatty acids are impurities in a glycerin-rich solution. Based on pH condition of its environment, the fatty acid has the nature that remained as the undissociated molecule in the presence of an acidic environment and could be dissociated in an alkaline environment (below pH 9) [31-32]. A large amount of undissociated would cause severe fouling and flux decline [15, 18, 33]. Fatty acid molecules can interact with acid to form the larger molecules via an agglomeration process with another molecule of fatty acid [15, 17]. The larger molecule that was formed may increase the adsorption of foulant molecule. The adsorption is formed on the membrane surface as well as on the entrance of the membrane pore and then causes high flux decline and membrane fouling [15, 33-34]. Sequentially, the flux decline follows the order of pH 7> pH 6.33> pH 9.67>pH 8 and the highest flux decline is found at pH 7. Similar trend was also reported by Mah et al. [18].According to dissociation and undissociation effect, at pH of 6.33, the flux decline should be the highest and at pH 9 the flux decline was the lowest.

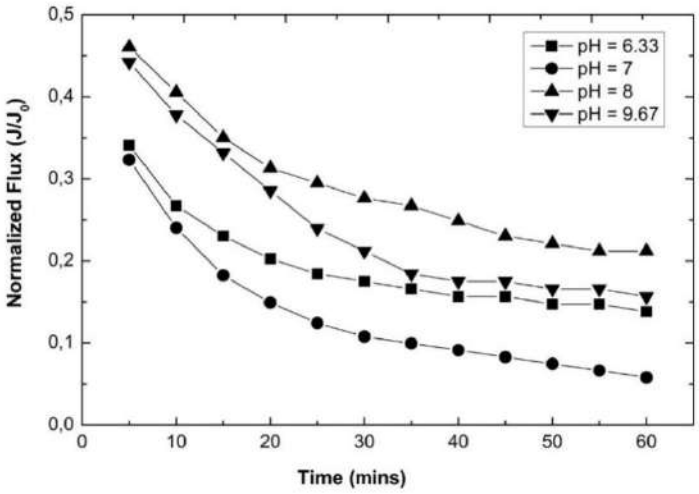

Fig. 5. Effect of pH on Flux decline of glycerin-rich solutions (TMP = 4, Temperature = 60 ºC).

However, flux value at pH 7 shows higher flux decline than those at pH 6.33. This is most likely due to the fatty acid state that not fully dissociated at pH 7 [15]. In the dissociated state, fatty acid does not form clots and find as single molecule form [33]. The single molecule of fatty acid can pass through into membrane pore since the average size of the single fatty acid molecule is four times smaller than the membrane pore size [14] and then triggers the blocking inside the wall of membrane pore. The blocking at micropores is possible in PES-based UF membranes because it is an asymmetric porous membrane [35]. Adjusting the pH was performed by NaOH addition. At pH above 9, the FFA could form a soap [10] and had characteristic as surfactant with their active hydrophilic and hydrophobic sites (amphiphilic). As a surfactant, the dissociated fatty acid can form micelle where the hydrophobic tail remain inside oil phase (in the core) and hydrophilic head (with negative charge) form a layer in the surface [31-32]. Forming of the micelle is believed to be responsible for the higher flux decline at pH 9 than flux decline at pH 8.

3.1.4. Rejection

Table 2 shows a different trend in each variation of the operating condition. For TMP variation, the rejection increases with increasing on TMP. The rejection of FFA content in the filtrate at 4.8 bar and 3.2 bar are 57.63% and 48.1%, respectively. This condition takes place because in higher TMP some small foulant molecules may be penetrated the membrane pore and form a deposit, thus causing significantly reduce on the size of membrane pore which leads to an increase in rejection of impurity [18, 36]. For temperature variation, the trend of rejection tends to be similar to TMP variation where a higher temperature process has more significant rejection than lower temperature. The rejection of impurities is 33.5% at 51.63 °C while at 68.37 °C the rejection reaches 43.56%. This is likely due to

the effect of increasing temperature which can directly affect the increase in flux and causes an increase the impurities that flow through the membrane pore [16]. It is similar to the condition that occurs in TMP variation. Rejection behaviour at pH variation has a different kind than the other operating parameter. The highest result is 70.98% at pH 7, and the lowest result is 25.82% at pH 9.67. This behaviour may occur due to the nature of the impurities, as described in section 3.1.3.

Table 2. Summary of rejection data in various process parameters.

No.	Pressure (bar)	Temperature (°C)	pH	Rejection (%)	
				FFA	Total impurities
1.	3.2	60	8	48.10	48.50
2.	4	60	8	54.17	32.11
3.	4.8	60	8	57.63	52.86
4.	4	51.63	8	44.32	33.25
5.	4	60	8	54.17	32.11
6.	4	68.37	8	45.35	43.56
7.	4	60	6.33	30.70	21.18
8.	4	60	7	70.98	68.33
9.	4	60	8	54.17	32.11
10.	4	60	9.67	25.82	24.22

Impurities rejection at each variation is higher than impurities rejection reported by Amin et al. [16]. In this study, the highest result is 70.98% rejection of FFA, whereas the most top result by Amin et al. [16] is 41.41%. It is confirmed that using smaller membrane pore size provides a positive impact on impurities rejection. In contrast, Mah et al. [18] reported higher rejection (about 97.95 at pH 2) than this study. It is presumably due to the type of impurities contained in glycerine and its operating condition. The previous researcher used PO+OA mixture as foulant that has a larger molecular and droplet size than FFA. The larger molecule and droplet size could lead to increasing the rejection of impurities [18]. Further, TMP that was also lower than those that was used in this study. The lower TMP decreased penetrating possibility by impurities to membrane pore [16, 21].

3.2. Blocking Mechanism

The constant of the blocking mechanism and the corresponding correlation coefficients (R^2) during filtration is listed in Table 3.

Table 3. Summary of rejection data in various process parameters.

Parameters	n=0 Cake Formation		n=1 Intermediate Blocking		n=1.5 Standard Blocking		n=2 Complete Blocking	
	K_{cf}	R^2	K_i	R^2	K_s	R^2	K_c	R^2
Pressure								
3.2 bar	0.4098	0.9848	0.0585	0.9031	0.0164	0.8171	0.0191	0.7051
4 bar	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
4.8 bar	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
Temperature								
51.63 °C	0.5329	0.9782	0.0692	0.9026	0.0185	0.8204	0.0208	0.7084
60 °C	0.3508	0.9891	0.0546	0.9291	0.0159	0.8588	0.0192	0.7613
68.36 °C	0.2872	0.9737	0.0476	0.8892	0.0142	0.8136	0.0176	0.7184
pH								
6.33	0.4090	0.9840	0.0580	0.9030	0.0160	0.8170	0.0190	0.7050
7	4.4480	0.9187	0.2468	0.9917	0.0453	0.9557	0.0365	0.8307
8	0.3400	0.9920	0.0532	0.9249	0.0155	0.8499	0.0187	0.7483
9.67	0.6982	0.9742	0.0862	0.9443	0.0225	0.8935	0.0247	0.8068

According to the Table, increasing TMP reduces the flux decline. Its condition also applies to temperature as confirmed by the smaller value of the constants along with increases of TMP and temperature. Cake formation is predicted as a dominated blocking mechanism during the filtration process for both TMP and temperature variations. In the cake formation, the foulant is firstly adsorbed on the membrane surface, penetrate the membrane pore and then form a layer that can cause a more severe decrease in flux even from the early step of filtration. The fatty acid may be the component responsible for severe fouling [14]. In biodiesel industries, glycerin was a by-product from the transesterification reaction which consists of palmitic acid (C16: 0), stearic acid (C18: 0) and most of the oleic acid that has double bond carbon chain (C18: 1) [37].

In addition, Table 3 shows the value of k (constant) at an acidic state that tends to be higher than in the alkaline state. It demonstrates that the resistance of the fluid to the membrane is larger and causing more severe fouling than in the alkaline state. The nature of fatty acids which tend to undissociated at acidic environment may be responsible for that condition. Under this environment, the fatty acid would be clumping each other [15]. Mah et al. [18] reported that the droplets of a mixture of palm oil and oleic acid at pH 2 (very acidic condition) lead to a significant increase in droplet size and even reach twice in size over the original droplet size. Therefore, setting pH under acidic conditions can lead to agglomeration of foulant molecules.

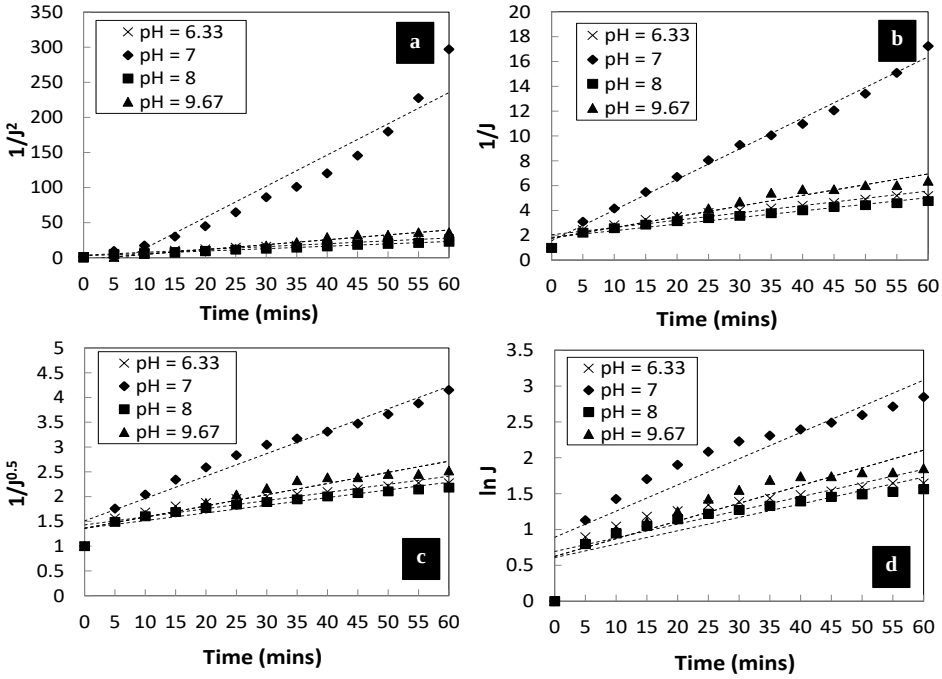

Fig. 6. Hermia's model fitting for the experimental data: (a) Cake formation (n=0), (b) Intermediate blocking (n=1), (c) Standard blocking (n=1.5), (d) Complete blocking (n=2) at TMP of 4 bar and Temperature of 60 °C

Figure 6 exhibits the blocking mechanism that occurs in the various pH. Generally, the mechanism is dominated by the cake formation, except for pH 7 as supported with the highest R^2 value for pH 6.33, 8 and 9.67. The similar result was reported by Amin et al. [15] and Mah et al. [18] confirming that cake formation was the dominant mechanism in pH variation. The different condition at pH 7, as seen in the value of k (constant for blocking mechanism) is much more excellent than at another pH. Moreover, the highest R^2 value in the intermediate blocking mechanism is found. Fig. 6 (b) and Fig. 6 (c) confirm that in the initial conditions of filtration until 10 mins, both intermediate blocking and standard blocking mechanism occur. Then, in 15 mins until 45 mins only the intermediate blocking mechanism is observed, and for 50 mins afterwards only standard blocking contributes to the flux decline. In intermediate blocking, the solutes or particles which accumulated on the membrane surface and the entrance of membrane pore are possible to overlap another solute that has already deposited on the membrane surface. The foulant is the pilled up each other in irregular arrangement [14] and triggers other mechanisms such as standard blocking to occur during the filtration process. Standard blocking mechanism is believed to be responsible for a significant flux decline as in that condition the impurities molecule penetrates to the inside wall of the membrane pore and make a deposit which can be lead to plugging on the active area of the membrane pore [38-39]. This strengthens the previous statement that fatty acids which are not fully dissociated at pH 7enterthe pore and cause blockages in the membrane pore.

At high pH, especially for pH 9 above, the fatty acid molecule is fully dissociated and become surfactants with a hydrophilic head and hydrophobic tails which have negative charge [40]. If there was an interaction between fatty acids and membranes, it formed a negative charge induction to the membrane [15, 41]. Thus the repulsive force between the fatty acid and the membrane may change. This condition may also cause changes in the fluid resistance to the membrane [15].

4. Conclusions

The study of flux decline, rejection and blocking mechanism during UF process using 1 kDa PES membrane with various process parameters (TMP, temperature, and pH) to the glycerin-rich solution from the biodiesel industry were conducted. It was found that flux decline was severe significantly in all variation of process parameter due to a deposit of impurities. Both pressure and temperature did not give significant effect to the flux decline due to the domination of the mass transfer mechanism which is caused by the nature of impurities its self. In addition, the pressure and temperature had a similar trend of rejection that in higher process parameters the rejection becomes greater, whereas at pH variation behaviour of rejection is determined by the nature of impurities. Hermia's blocking law model found to fit well to the experimental data. The best-fit experiment data was cake layer formation mechanism for all process variation except for pH 7 where the intermediate blocking takes the lead in early stages and then followed by standard blocking. The PES UF membrane 1 kDa demonstrated to be capable of removing impurities such as FFA from industrial crude glycerine. In addition, this study provides better understanding of flux decline behaviour and blocking mechanism that occurred during UF process of industrial crude glycerin. In order to improve the UF performance, preliminary treatment of

crude glycerin or modification of the membrane surface is required. This treatment is expected can reduce the membrane fouling specifically due to the FFA characteristic.

Acknowledgment

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Nomenclatures

A	Membrane area, m^2
C_f	Concentration of FFA or impurities in the feed, mg/L
C_p	Concentration of FFA or impurities in the permeate, mg/L
J	Permeate Flux, $L.m^{-2}. h^{-1}$
J_0	Initial Flux, $L.m^{-2}. h^{-1}$
k	Constant of blocking mechanism
K_c	Constant of complete blocking (h^{-1})
K_{cf}	Constant of gel or cake formation (h/m^2)
K_i	Constant of intermediate blocking (m^{-1})
K_s	Constant of standard blocking ($h^{-1/2}\ m^{-1/2}$)
n	Value that represents a blocking mechanism, n = 0 (cake layer formation), n = 1 (intermediate blocking), n = 1.5 (standard blocking), and n = 2 (complete blocking)
R	Rejection, %
R^2	The corresponding correlation coefficients
t	Filtration time (h)
V	Permeated volume (L)
W	Weight of permeate (g)

Abbreviations

ASTM	American Society for Testing and Materials
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
NGOM	Non-Glycerol Organic Matter
OA	Oleic Acid
PO	Palm Oil
TMP	Trans Membrane Pressure
UF	Ultrafiltration

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