

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

NITA ARYANTI<sup>1,2,\*</sup>, AWALI S. K. HARIVRAM<sup>1</sup>, DYAH H. WARDHANI<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Diponegoro University,  
Kampus Undip Tembalang, Semarang, Indonesia

<sup>2</sup>Membrane Research Centre (MeR-C), Diponegoro University,  
Kampus Undip Tembalang, Semarang, Indonesia

\*Corresponding Author: nita.aryanti@che.undip.ac.id

### 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 in 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 sought to focus on the 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: Blocking mechanism, Glycerol, Hermia, Purification, Ultrafiltration.

## 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 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, 3-5]. 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].

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 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 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. Wang et al. [13] also found a similar result. Experiments focused on glycerin purification have been performed. Dhabhai 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 the 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 the interaction of the 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 a mixture of pure glycerin with the addition of impurities as UF feed has not been investigated. The pore size of the membrane that was used in the 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 the NF membrane with rejection above 90%. However, applied operational pressure was certainly high. In addition, glycerin could not flow through the pore of the 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 the 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 the 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 a deep understanding of the fouling behaviour and blocking mechanism during the 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 was 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 glycerin was supplied from Biodiesel Plant of PT SMART Tbk., Tarjun, Indonesia was used as a raw material. The crude glycerin composed glycerin having a 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% glycerin 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, the 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.

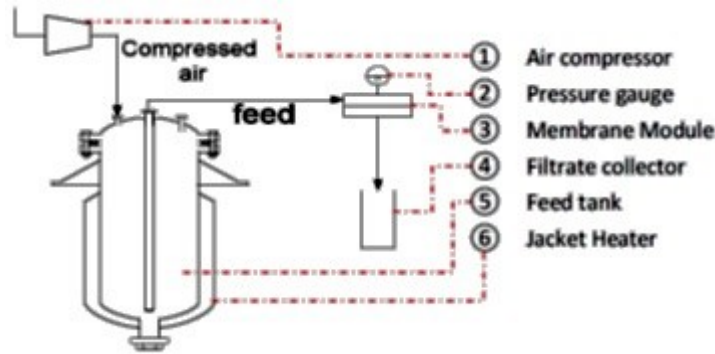


Fig. 1. Schematic illustration of UF cell with temperature control.

Experimental runs were operated at room temperature ( $25 \pm 2$  °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  $13.85 \text{ cm}^2$  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 minutes, with an interval of 5 minutes. Then, permeates were collected in a 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 ( $\text{L.m}^{-2}.\text{h}^{-1}$ ) and  $J$  or permeate flux ( $\text{L.m}^{-2}.\text{h}^{-1}$ ),  $V$  is the volume of permeate (L) and  $A$  is membrane area ( $\text{m}^2$ ).

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 the 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 minutes, with an interval of 10 minutes. 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).

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

In Eq. (2),  $R$  (%) is a rejection of FFA or impurities,  $C_f$ (mg/L) is the concentration of FFA or impurities in feed, and  $C_p$ (mg/L) is the 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 °C for 8 minutes, then the column temperature was ramped from 65 °C to 250 °C at 4 °C/minute and held for 20 minutes. Each sample (1 µL) was injected into Rxi-1ms column (30 m × 250 micrometres × 0.25 micrometres, Restek Corporations, 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/minutes and operation run time at 74 minutes.

### 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].

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

In Eq. (3),  $t$  is filtration time (minute),  $k$  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 the 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 the 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, linearization of blocking mechanism according to Eq. (3) is presented in Table 1.

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

**Table 1. Linearization 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	$\ln J = \ln J_0 - K_c t$	Formation of Surface deposit
Gel or Cake formation	0	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{cf} t$	Pore blocking

### 3. Result and Discussion

#### 3.1. Flux decline and rejection

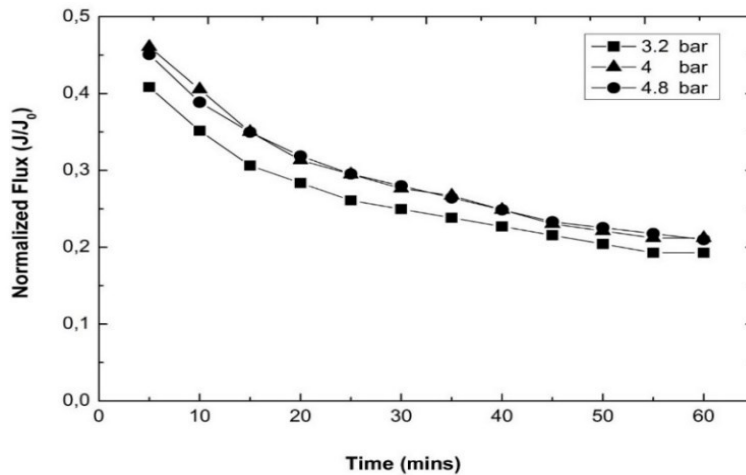
##### 3.1.1. Effect of TMP on permeate flux

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 if the resistance between the membrane and the fluid is not significant [14, 18, 23-26]. Figure 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. 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 bars. 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 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 minutes and then continued with the stationary states of flux decline at a range of 30 – 60 minutes 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 °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]. Wijewardana et al. [29] confirmed the hydrophobicity of FFA. It was found that contact angle of sands, which coated by OA reaches over 90°. The hydrophobicity of the FFA has a 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).

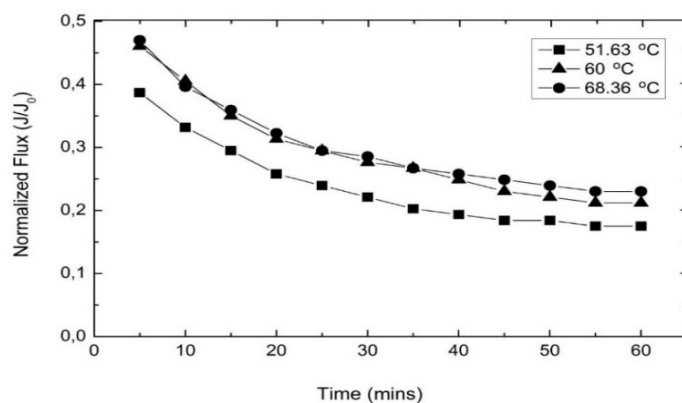


**Fig. 2. Influence of TMP on fluxes of glycerin-rich solutions at pH of 5.27 and temperature of 60 °C.**

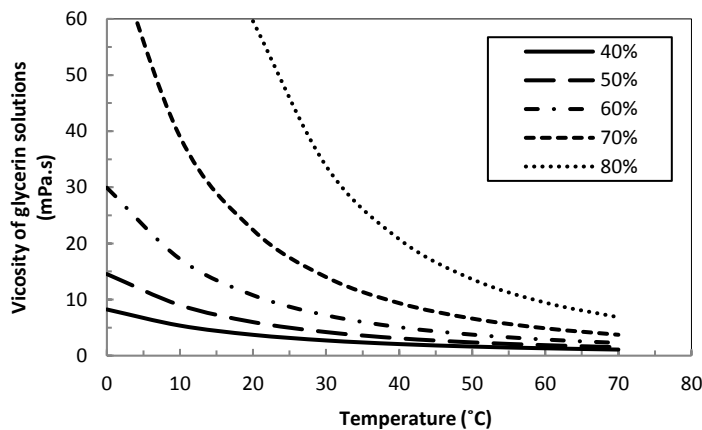
### 3.1.2. Temperature effect on permeate flux

Effect of various temperature (at a 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 in 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.

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



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

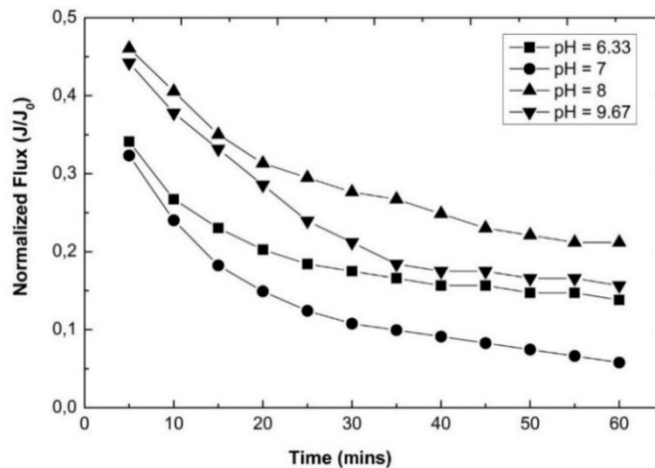


**Fig. 4. Viscosity of glycerin solution with increased temperature. Drawn from data calculation using viscosity-temperature correlation equation based on Arrhenius form [27].**



### 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 °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. A similar trend was also reported by Mah et al. [18]. According to dissociation and undissociation effect, at a 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 °C).**

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 a 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 remains inside oil phase (in the core) and a hydrophilic head (with a 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 bars 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 because of increasing temperature, which can directly affect the increase in flux and causes an increase in 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 subsection 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 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 were used in this study. The lower TMP decreased penetrating possibility by impurities to membrane pore [16, 21].

### 3.1.5. 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.**

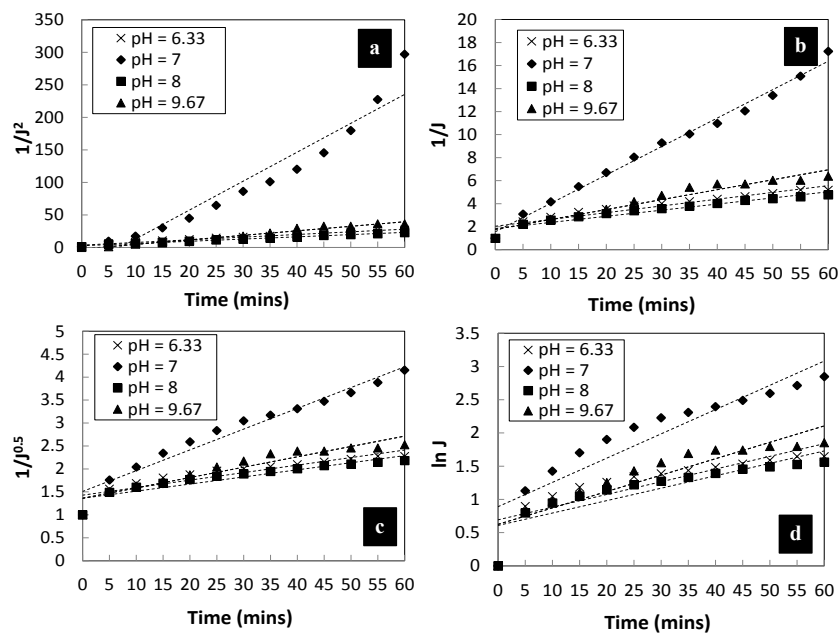
Parameter s	$n = 0$		$n = 1$		$n = 1.5$		$n = 2$	
	Cake formation		Intermediate blocking		Standard blocking		Complete blocking	
	$K_{cf}$	$R^2$	$K_i$	$R^2$	$K_s$	$R^2$	$K_c$	$R^2$
<b>Pressure</b>								
<b>3.2 bar</b>	0.4098	0.9848	0.0585	0.9031	0.0164	0.8171	0.0191	0.7051
<b>4 bar</b>	0.3508	0.9891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

Figure 6 exhibits the blocking mechanism that occurs in 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. Figures 6(b) and (c) confirm that in the initial conditions of filtration until 10 minutes, both intermediate blocking and standard blocking mechanism occurs. Then, in 15 to 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 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 piled 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 7 enter the 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].



**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.**

#### 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 was 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 glycerin. In addition, this study provides a better understanding of flux decline behaviour and blocking mechanism that occurred during the 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.

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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, $L.m^{-2}.h^{-1}$
$K_c$	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 ( $h^{-1/2} m^{-1/2}$ )
$k$	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)
$R$	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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