Flux Decline and Blocking Mechanism in Ultrafiltration of Glycerin-Rich Solution

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Abstract. In the oleochemical industry, crude glycerin is a byproduct of biodiesel production. As a byproduct, crude glycerin has a low economic value and very limited applications. To improve these limitations, the purification of glycerin is required. One method for glycerin purification is a filtration process that uses ultrafiltration (UF) membranes based on polyethersulfone (PES). However, this process has several problems, particularly the flux decline that occurs during filtration. Thus, the aim of this study was to obtain a better understanding of the flux decline and blocking mechanism that occur in the UF of glycerin. In this work, the flux decline and blocking mechanism were observed by commercializing the UF of the PES membrane with a 1-kDa molecular weight cut-off. The investigated parameters were the pressure, temperature, and pH with ranges of 2–4 bar, 40–60°C, and 4–9, respectively. The results showed that the flux decline was significant due to the relatively small size of impurities, which clog the membrane’s pores. Furthermore, the blocking mechanism was analyzed using Hermia’s model, and it was found that the blocking mechanism was mostly dominated by cake formation, except at a pH of 7.

1. Introduction

Biodiesel production is predicted to increase rapidly in the next several years. Worldwide biodiesel production is expected to reach 41.4 billion liters in 2025 at an average increase of 33% per year [1]. This increase would directly increase glycerin production since glycerin is a byproduct of the transesterification process [2-5]. In general, the transesterification reaction of biodiesel produces 10% glycerin mixed with impurities in the heavy phase [6,7] at a glycerin composition range of 30–60% [2]. The impurities in glycerin-rich solution are water, salts, matter organic non-glycerin, alcohol, and unreacted tri-, di-, and mono-glyceride [8]. Hence, glycerin purification is required to increase the economic value and application of glycerin.

Ultrafiltration (UF) is currently being developed and researched widely because it is an easy method that requires relatively little energy [9]. UF utilizes a concentration gradient, an electron potential, and hydrostatic pressure as driving forces to allow the desired fluid to flow through a membrane while restraining impurities. UF membranes are porous, allowing a desired substance to flow through. The molecular weight cut-off is defined as the capability of a membrane to retain as much as 90% of the solute and is written in Dalton (Da) units.
Glycerin/glycerol is a compound that has three alcohol functional groups and is colorless, viscous, odorless, non-toxic [10], biodegradable, and hygroscopic [8]. It has the chemical structure C$_3$H$_9$O$_3$ with propane-1,2,3-triol as its IUPAC name. Glycerin is a valuable raw material for many industries, such as the food and beverage, pharmaceutical, cosmetic, tobacco, paint, textile [11], and chemical industries, and it has the potential to be used as an additive and as an alternative fuel [8].

Several studies on the purification of crude glycerin using UF membranes have been conducted. Dhabbai et al. [8] studied the purification of crude glycerol using a sequential physicochemical treatment (saponification, acidification, and neutralization). Amin et al. [11] conducted a study on commercial UF membrane fouling characteristics in glycerin purification using Polyethersulfone (PES) membranes and Polyvinylidene Flouride (PVDF). In another study, Amin et al. [12] analyzed foulant deposition (palmitic acid, stearic acid, and oleic acid) in glycerin purification using PES membranes. Further, Mah et al. [13] identified and analyzed fouling mechanisms and the characterization of UF membranes (PVDF 30 kDa) in a mixture of palm oil, oleic acid, and glycerin. Mah et al. [14], in another study, analyzed the flux decline, fouling patterns, rejection, and characterization of UF membranes. The studies conducted by previous researchers include general descriptions of fouling mechanisms using Palmitic Acid, Oleic Acid, and free fatty acid as the main impurity compound in the form of macromolecules in glycerin-rich solution using a model based on the feed composition variation used. In a study by Dhabbai et al. [8], the purification of crude glycerin using UF membranes produced glycerin at a yield up to 90% higher. However, research on the flux decline and the analysis and identification of the fouling mechanism of PES 1-kDa membranes using crude glycerin have yet to be conducted. Therefore, this paper is focused on observing the flux decline and fouling mechanism.

2. Materials and Method

2.1. Materials

Crude glycerin as a raw material was supplied from biodiesel plant of PT SMART Tbk Tarjun. Flat sheet Polyethersulphone UF membrane having 1 kDa molecular weight cut-off was obtained from Sterlitech corp.

2.2. Ultrafiltration Procedure

Schematic illustration of Ultrafiltration Cell is depicted in Figure 1. Before used, membrane was soaked in distilled water for 12 hours. Further compacted by filtration with water for 30 minutes. The normal flux of water ($J_0$) was determined by measuring the volume of permeate within a certain time [15]. Further to observations flux and blocking mechanisms, crude glycerin was added to the feed tank for half tank capacity then passed through a membrane with a dead-end mode at the variation of the transmembrane pressure / TMP (2-4 bar), temperature (40 - 60 °C) and pH (4 - 9). pH was adjusted by adding a 0.1 N HCl or 0.1 N NaOH. Filtration was carried out for 120 minutes with sampling every 10 minutes.
2.3. Analysis of Blocking Mechanism

Hermia’s model is one of the concepts describing the fouling mechanism in the porous membrane that occurred at dead end filtration with only one of the fouling mechanism dominates the process. Based on the blocking law, Hermia’s [16] reformulated all model of blocking mechanism to a common power-law equation as written in equation (1).

\[
\frac{d^2t}{dv^2} = k \left( \frac{dt}{dv} \right)^n
\]

where \( t \) is the filtration time (h), \( V \) is permeated volume (L), \( k \) is a constant and \( n \) is a value that represents a blocking mechanism that occurs whose value ranges from 0 - 2. \( n = 0 \) represents the cake layer formation, \( n = 1 \) represents the intermediate blocking, \( n = 1.5 \) represents a standard blocking and \( n = 2 \) represents the complete blocking [13,16]. In the complete blocking model, 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 [11]. Further, linearization of blocking mechanism according to equation (1) is presented in Table 1.

| 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    | \( \frac{1}{J^2} = \frac{1}{J_{oc}^2} + K_{cf} t \) | Pore Blocking |

3. Results and Discussions

3.1. Flux Decline

3.1.1. Influence of Trans Membrane Pressure (TMP) and Temperature. Transmembrane pressure (TMP) is a driving force in the ultrafiltration process. TMP is proportional to the flux and hence increasing the TMP increase the flux directly [17]. The tendency of flux due to the effect of pressure is shown in Figure 2.a. At a pressure range of 2 - 2.5 bar, the increase in TMP shows the positive impact to flux as indicated by a higher normalized flux of 2.5 bar than 2 bar until the 80th minute. On the contrary, at a pressure range of 3 - 4 bar, the increase of TMP does not provide a positive impact on the reduction of the flux decline. This condition also occurs at 80th minute to 120th minute where for each variation of TMP does not show a positive impact on the flux decline. This condition confirms that the filtration process of glycerine-rich solution using a PES membrane UF with 1 kDa in MWCO is
controlled by the mass transfer mechanism [15]. Under these conditions, an increase in TMP which directly increase the flux leads to an increase in deposits and impurities both within the membrane pore surface that can aggravate the flux decline [11,15].

![Figure 2](image.png)

**Figure 2.** (a) Influence of TMP on Flux decline of Glycerin-rich solutions (b) Influence of Temperature on flux decline of the Glycerin-rich solution.

Figure 2 (b) shows the influence of temperature on the flux decline. An increase of temperatures slightly affects the flux decline. It is confirmed by the increase in normalizing flux at 45 °C compared to that normalized flux at 40 °C. High normalized flux is caused by the viscosity reduction of glycerin [18]; thus the fluid is easier to pass through the membrane. In addition, increasing of temperature leads to a reduction of fluid resistance-caused by viscosity-against the membrane. Moreover, the mobility of the polymer bonding in the membrane increases with increasing temperatures, and this can also reduce membrane resistance to fluid [12, 19]. Different trends are observed in the temperature range of 50-60 °C. At this condition, the temperature does not significantly affect the rate of flux decline, especially after 50 minutes. This is due to a decrease of 50% glycerin solution viscosity at temperatures above 45 °C is not significant [8]. Furthermore, decreasing in viscosity can directly increase the flux and triggers increased concentrations of impurities penetrated into the membrane and ultimately increase the deposit impurities on the membrane. This phenomenon confirms that the mass transfer is the mechanism that dominates in the glycerin-rich solution filtration using UF membrane 1 kDa.

3.1.2. *Effect of pH.* Effect of pH on the rate of flux decline is presented in Figure 3.
Observations were carried out with a pH range of 4 - 9. The results show a greater tendency of flux decreases in the acidic environment than in the alkaline environment. It is due to the nature of fatty acid that remained as an undissociated state in the presence of acidic environment and causes the fatty acid molecules to agglomerate each other and then massively form the larger molecules [13,20]. This condition leads to increasing of absorption both at the surface of the membrane and inside the membrane pores which results in increased the flux decline and fouling [14, 21-22]. Sequentially, the flux decline in various pH variations follows the order of pH 7 > pH 4 > pH 5 > pH 6 > pH 9 > pH 8. The highest flux decline for the process filtration of PES membrane UF with 1 kDa in MWCO is found at pH of 7. Based on the dissociation and undissociation effect, the pH of 7 should have lower flux decline than pH 6. The only reason for this phenomenon is presumably due to adsorption some of the fatty acids that were dissociated by the inside wall of the membrane pore and then caused blockage inside pore membrane (this is possible because the average size of the fatty acid is 1/4 part of the membrane pore size). Further research is required to examine this phenomenon. For the pH 9, even though the flux decline is greater than pH 8 but the decline is not significant. It is presented in the early stages of filtration where the rate of flux decline of glycerin at pH 9 is lower than at pH 8. Increasing flux decline of pH 9 at 30 minutes and thereafter may be due to blockage of micropores by fatty acid molecules that have dissociated almost perfectly at pH 9. This is possible considering PES-based UF membranes are one type of asymmetric porous membrane [23].

3.2. Blocking Mechanism

Table 2 shows the constant of each type of blocking mechanism along with the corresponding correlation coefficients (R²). In the case of different TMP, increasing of TMP can reduce the rate of flux decline. It was confirmed by the smaller the value of blocking constants along with increases of TMP. The smallest obstacle for the temperature variation is at 45 °C. The dominant blocking mechanism for both TMP and temperature variations is cake formation, where a deposit of impurities occurred on the membrane surface. It causes a very significant decrease in flux even from the initial conditions of filtration. The severe fouling that occurred due to a deposit of impurities may be related to the fatty acids that contained in the solution of glycerin [12]. Glycerin produced from the transesterification biodiesel fatty acids are mostly composed of palmitic acid (C16: 0), stearic acid (C18: 0) and oleic acid (C18: 1).
and oleic acid with one double bond is the major component [24]. Both palmitic acid and stearic acid have long and straight carbon chains. This causes palmitic, and stearic acids are less likely to penetrate into the pores and finally become the deposit on the surface of the membrane [12].

Table 2. Fitted Hermia’s model for various process parameters.

| Pressure | n = 0 | n = 1 | n = 1.5 | n = 2 |
|----------|-------|-------|---------|-------|
|          | Cake Formation | Intermediate Blocking | Standard Blocking | Complete Blocking |
|          | kcf | R²  | ki | R² | ki | R² | ki | R² |
| 2 bar    | 0.000403 | 0.9694 | 0.001485 | 0.8804 | 0.002224 | 0.7599 | 0.014808 | 0.5929 |
| 2.5 bar  | 0.000368 | 0.9687 | 0.001480 | 0.9371 | 0.002309 | 0.8333 | 0.014939 | 0.5853 |
| 3 bar    | 0.000227 | 0.9511 | 0.001102 | 0.8368 | 0.001907 | 0.7124 | 0.014905 | 0.5485 |
| 3.5 bar  | 0.000161 | 0.9365 | 0.000945 | 0.8327 | 0.001781 | 0.7287 | 0.016183 | 0.6452 |
| 4 bar    | 0.000137 | 0.9426 | 0.000869 | 0.8468 | 0.001702 | 0.7407 | 0.014908 | 0.5892 |

| Temperature | n = 0 | n = 1 | n = 1.5 | n = 2 |
|-------------|-------|-------|---------|-------|
|             | Cake Formation | Intermediate Blocking | Standard Blocking | Complete Blocking |
|             | kcf | R²  | ki | R² | ki | R² | ki | R² |
| 40 °C       | 0.000178 | 0.9513 | 0.000999 | 0.8564 | 0.001852 | 0.7447 | 0.015385 | 0.5876 |
| 45 °C       | 0.000075 | 0.9252 | 0.000613 | 0.8098 | 0.001348 | 0.7024 | 0.012976 | 0.5693 |
| 50 °C       | 0.000099 | 0.9778 | 0.000759 | 0.9141 | 0.001618 | 0.8252 | 0.015042 | 0.6862 |
| 55 °C       | 0.000131 | 0.9807 | 0.000901 | 0.9590 | 0.001824 | 0.8760 | 0.016239 | 0.7267 |
| 60 °C       | 0.000108 | 0.9820 | 0.000812 | 0.9432 | 0.001713 | 0.8601 | 0.015789 | 0.7210 |

| pH | n = 0 | n = 1 | n = 1.5 | n = 2 |
|----|-------|-------|---------|-------|
|    | Cake Formation | Intermediate Blocking | Standard Blocking | Complete Blocking |
|    | kcf | R²  | ki | R² | ki | R² | ki | R² |
| 4  | 0.000167 | 0.9896 | 0.000977 | 0.9123 | 0.001840 | 0.7950 | 0.015475 | 0.6238 |
| 5  | 0.000124 | 0.9770 | 0.000875 | 0.9114 | 0.001800 | 0.8286 | 0.016243 | 0.6995 |
| 6  | 0.000108 | 0.9426 | 0.000822 | 0.8985 | 0.001743 | 0.8308 | 0.016108 | 0.7135 |
| 7  | 0.000561 | 0.8649 | 0.001983 | 0.8753 | 0.002960 | 0.8181 | 0.020317 | 0.6725 |
| 8  | 0.000073 | 0.9378 | 0.000646 | 0.8905 | 0.001466 | 0.8157 | 0.014370 | 0.6933 |
| 9  | 0.000018 | 0.9301 | 0.000829 | 0.8782 | 0.001770 | 0.8153 | 0.016479 | 0.7113 |

The effect of pH toward the blocking mechanism is depicted in Figure 4. For all variables except for pH 7, the dominant blocking mechanism is the cake formation. This is consistent with the result of the flux decline observation that has shown a significant decrease in flux during the ultrafiltration process. Amin et al. [20] and Mah et al. [13] reported the same results that in pH variation the dominant blocking mechanism was cake formation. The data in Table 2 listed the value of Hermia’s model parameters (constant, k) under acidic conditions tend to be higher than the value under alkaline conditions. It presents that the severe fouling occurred in acidic condition. That condition occurred due to the nature of fatty acid which is at undissociated state in the presence of an acidic environment, and then the fatty acid would be clumping each other. In addition, Mah et al. [14] observed the droplets of a mixture of palm oil and oleic acid at pH 2, 7 and 9. It was found that at very acidic condition (pH 2) the increase in droplet size is significant, even reach 2x over the original droplet size. As a result, setting pH in acidic conditions will aggravate the occurrence of fouling.

The anomalies occurred at pH 7, where the resistance is greater than another pH. This can be seen at the value of blocking mechanism parameters that is much greater than other pH conditions. In addition,
the blocking mechanism is dominated by intermediate blocking. Fig. 4 (b) and fig. 4 (c) prove that in the initial conditions of filtration until 70 minutes, intermediate blocking mechanism occurred then in 80 minutes and afterwards the standard blocking mechanism also contributes to flux decline during the filtration process. In intermediate blocking, although there were solutes/particles accumulated on the membrane surface, the particles had the possibility to overlap another solute that has already deposited on the membrane surface [12] so that it can trigger other mechanisms during the filtration process. Because of that, another mechanism like standard blocking on fig. 4 c. can still occur. Compared to cake formation and blocking intermediates, standard blocking is serious fouling because at standard blocking there is a deposit of impurity on the inside wall of the membrane pore which causes the active area of the membrane pore to be covered and then over time all pores will be deposited by impurities [25,26]. This strengthens the evidence that fatty acids that are still dissociated enter the pore and cause blockages in the membrane pore.

![Figure 4](image-url)

**Figure 4.** Fitting of experimental data to Hermia’s model: (a) Cake formation, (b) Intermediate blocking, (c) Standard blocking, (d) Complete blocking

The fatty acids molecule is fully dissociated at high pH and become surfactants with a negative charge where the head is hydrophilic while the tail is hydrophobic. The interaction between fatty acids and membranes under that condition can induce the negative charge to the membrane; thus the repulsive force between the fatty acid and the membrane may changes. This condition resulted in a decrease in membrane resistance to permeate fluxes [11].

4. Conclusion
Flux decline and blocking mechanism that occurred during filtration process using a PES membrane UF having MWCO of 1 kDa to the glycerin-rich solution from the biodiesel industry was conducted. Flux decline is severe significantly due to a deposit of impurities especially for fatty acid which forms cake
layer formation on the membrane surface. Both pressure and temperature do not give significant effect to the flux decline due to dominating of the mass transfer mechanism. Hermia’s model that was used to predict blocking mechanism fit well to experimental data. The best-fit experiment data refers to blocking mechanism by Hermia’s is cake layer formation for all process variation except for pH 7 where the intermediate blocking take the lead and then followed by standard blocking in the final stages.

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