Effect of Acidification Mole Ratio And Solvent Volume Ratio of Glycerol Purification

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Abstract. Glycerol is the side product in producing biodiesel. Biodiesel consists of 10% glycerol in average. Methanol, water, soap, salt, catalyst, and matter organic non glycerol (MONG) are found in glycerol as impurities. These impurities effects the concentration of glycerol significantly. Therefore, some treatments are needed to eliminate the impurities. This research is done to find out the effect of acidification mole ratio and solvent volume ratio to the process of purifying glycerol using phosphoric acid in acidification at pretreatment process. This research was started by adding acid to the glycerol to neutralize the alkaline catalyst which was used to break the soap formed become salt and free fatty acid which can be removed from the glycerol easily. Ethylene glycol was used in extraction with 1:0.5; 1:1 and 1:1.5 volume ratio (v/v) and 1:0.1; 1:0.3 and 1:0.5 acidification mole ratio. The MONG contained in the purified glycerol was analyzed with the standard of ISO 2098-1972. The results obtained was the more the volume of solvent used, the less the extraction time needed to gain glycerol with high purity. The highest purity obtained in this research was 92.0382% with 60 minutes of extraction time and 1:1 ratio solvent volume ratio (v/v).

1. Introduction
Fossil fuel has decreased from year to year. Biodiesel has been an alternative source of energy to replace fossil fuel [1]. Biodiesel is one of the most used alternative energy in the world. Transesterification is one of the processes used to produce biodiesel. The raw material used is usually animal fat or vegetable oil (triglyceride). The raw material is reacted with acidic or alkaline catalyst and methanol [2]. The side product of transesterification in biodiesel production is crude glycerol. 10% weight of biodiesel produced is crude glycerol [3]. The crude glycerol purity is about 15-80%. The contaminants in the crude glycerol are salt, free fatty acid, soap, methanol, water, and residual reactant. In average, there are about 40-70% of glycerin, 10% water, 4% salt, 0.5% or less methanol and free fatty acid. Many industries have used crude glycerol in producing their products such as cosmetic, food and pharmaceutical [5]. The enhancement of biodiesel production also enhance the production of crude glycerol each year. From 2008 to 2011, the amount of crude glycerol produced has reached 2.06 million tons to 2.88 million tons [6]. The production of glycerol keep increasing and will reach 41.9 million liters by 2020. Pure glycerol price is $0.0850 to 0.0975 each pound [8]. The manufacturing process of food, medicin and cosmetic requires a high quality, odorless, low contaminant and superior physical properties of glycerol. However, the glycerol from the side product of biodiesel production is not pure enough, so that it needs a lot of treatments to remove the contaminant in the glycerol [9]. Different raw materials used in producing glycerol has different glycerol purification process [10]. Chemical processes...
and vacuum distillation, combined chemical and physical processes, extraction of ions, bipolar electrodialysis physical and chemical processes are the usual processes used to purify glycerol [11].

2. Method
2.1 Materials and Tools
The purity of crude glycerol used in this research was 74.7161%. It was the side product of biodiesel production from PT. Wilmar. Chemicals which were used in this research were ethylene glycol (C\textsubscript{2}H\textsubscript{6}O\textsubscript{2}) (p.a.) obtained from PT. Rudang Jaya, hydrochloric acid (HCl) (pa), sodium hydroxide (NaOH) (pa) 12.5 M, NaOH 0.05 N, distilled water (H\textsubscript{2}O), activated carbon, blue bromtimol, H\textsubscript{2}SO\textsubscript{4} 0.2 N and NaIO\textsubscript{4} which were obtained from chemical industry process laboratory in the department of chemical engineering, faculty of engineering, University of North Sumatera.

The tools used were whatman no. 41 filter paper, pH meter, stopwatch, pipette, funnel glass, thermometer, rod stirrer, digital scale, measuring cups, beaker glass, separating funnel, hot plate, magnetic stirrer and erlenmeyer which were obtained from chemical industry process laboratory of department of chemical engineering, faculty of engineering, University of North Sumatera.

| Run | Stirring Speed (rpm) | Temperature (°C) | Time (minutes) | Ethylene glycol:Glycerin (v/v) | H\textsubscript{3}PO\textsubscript{4} mole:glycerin mole (n/n) |
|-----|----------------------|------------------|----------------|--------------------------------|---------------------------------|
| 1   |                      |                  | 20             | 0.5:1                         | 0.1:1                           |
| 2   | 200                  | 50               | 40             | 1:1                           | 0.3:1                           |
| 3   |                      |                  | 60             | 1.5:2                         | 0.5:1                           |

2.2 Procedure
2.2.1 Raw material pretreatment. These steps were done in the pretreatment of raw materials. First, pour 30 grams of glycerol into erlenmeyer. Phosphoric acid was added into the erlenmeyer in certain ratio. This mixture stirred at 250 rpm while maintained in 70°C for an hour. The mixture is poured into a separator funnel and left out until it formed three layers then it was filtrated to eliminate the salt formed. The glycerol was taken and neutralized by NaOH. Finally, the glycerol was evaporated in order to eliminate the water content.

2.2.2 Extraction by using ethylene glycol. Glycerol and ethylene glycol was poured into erlenmeyer in certain volume ratio (v/v). This mixture was heated until 50°C by using a hot plate. During the heating process, this mixture was stirred at the speed of 200 rpm in a certain time interval and was left out until two layers was formed. The upper layer which is glycerol was taken out and evaporated at 95°C.

2.2.3 Product analysis. Some analysis were done for the purified glycerol produced. Gas chromatograph analysis was done to find out the composition of raw materials and the products. Ash content, moisture content, Matter Organic Non Glycerol (MONG) level were analyzed and compared with ISO 2098-1972 standard. pH meter was used to analyze the pH and the glycerol level by SNI titration method.

3. Results and Analysis
3.1 Characterization of gas chromatography
The result of gas chromatography analysis for purified glycerol is shown in table 1 below.
Table 2. Result of gas chromatography analysis for purified glycerol.

| Peak | Ret. Time | Area %  | Cmpnd. Name |
|------|-----------|---------|-------------|
| 1    | 2.386     | 23.4101 | Glycerol    |
| 2    | 2.697     | 4.2725  | Glycerol    |
| 3    | 2.830     | 0.6626  | Glycerol    |
| 4    | 3.734     | 28.7457 | Glycerol    |
| 5    | 3.918     | 25.2310 | Glycerol    |
| 6    | 4.883     | 10.5863 | Glycerol    |
| 7    | 8.147     | 1.4258  | Ester       |
| 8    | 26.085    | 2.3720  | Internal    |
| 9    | 30.404    | 0.6379  | Dg          |
| 10   | 35.216    | 3.0946  | Tg          |
| 11   | 35.360    | 1.5988  | Tg          |
|      | Total     | 100.000 |             |

3.2 Acidification by phosphoric acid

Phosphoric acid was used in acidification to extract crude glycerol in pretreatment [12]. The acid was also used to neutralize the alkaline catalyst used and break the soap formed into free fatty acid and salts so that it will be easier to be separated [13]. The mixture formed three layers after the phosphoric acid was added into the mixture. The upper layer was free fatty acid, the bottom layer was precipitated inorganic salts and the middle layer was glycerol [12].

The picture of the layers is shown in Figure 1 below.

![Glycerol layer formed after acidification.](image)

Figure 1. Glycerol layer formed after acidification.

The decomposition reaction of soap to form fatty acid when phosphoric acid were added is shown below.

\[
\text{RCOOK} + \text{H}_3\text{PO}_4 \rightarrow \text{RCOOH} + \text{KH}_2\text{PO}_4
\]

Beside the decomposition of acid, neutralization of alkaline catalyst is also occured because of the biodiesel reaction in the crude glycerol. The reaction is shown below.

\[
\text{NaOH} + \text{H}_3\text{PO}_4 \rightarrow \text{Na}_3(\text{PO}_4)_2 + \text{H}_2\text{O}
\]

Further filtration is done after acidification to removed the salt formed. The acidity of the glycerol after acidification is 2. It is needed to be neutralized by using NaOH 12.5 M. After it is neutralized, the glycerol was heated to evaporate the water content of the glycerol which was formed in the neutralization process and to make the salt formed quicker.

3.3 Effect of solvent volume ratio (v/v) and extraction time to the purity of glycerol produced

Relation of solvent volume ratio (v/v), extraction time and the purity of glycerol produced is shown in the figure 2 below.
Figure 2. The effect of acidification mole ratio and solvent volume ratio to the purity of glycerol

Figure 2 above shows the effect of acid added to the glycerol produced. Generally, glycerol purity decreased as the increasing of the ratio of phosphoric acid added. The best condition where the highest purity of glycerol is obtained is at the solvent volume ratio of 1:1.5 (v/v). Figure 2 also shows that the addition of the acid with mole ratio (n/n) 1:0.1 which is 58.6044%, then declined in the mole ratio (n/n) 1:0.3 into 69.6040% and decreasing the mole ratio 1:0.5 into 92.0932%.

Phosphoric acid contains H\(^+\) ion which reacts with soap and forms free fatty acid and inorganic salt. Nanda, et al (2014) stated that acidification by using phosphoric acid for 10-15 minutes caused the mixture can be separated easily. Phosphoric acid reacted and formed KH\(_2\)PO\(_4\) [14] which can be used as fertilizer [20]. Beside making the mixture easily separated, it also gives advantages by increasing crop yield and decreasing residual inorganic salt and FFA [11]. The addition of acid caused the pH of the mixture increased. The higher pH resulted KH\(_2\)PO\(_4\) was dissolved to the water and it decreases the purity of glycerol. Saddhukan, et al stated that the optimum pH of phosphoric acid is 3.26 which resulted 90.4% purity of glycerol.

3.4 Characteristic of pure glycerol

Comparison among characteristic of crude glycerol, refined glycerol and British standard 2621 : 1979 glycerol is shown in Table 2 below.

**Table 3. Physical properties of crude glycerol, British Standard 2621 : 1979 glycerol and refined glycerol.**

| Physical Properties       | Crude Glycerol | Glycerol Standard BS 2621 : 1979 [3] | Glycerol Purification Results |
|---------------------------|----------------|-------------------------------------|------------------------------|
| MONG                      | 11.3099 %      | <2.5%                               | 1.1357 %                     |
| Ash content               | 12%            | <10%                                | 8%                           |
| Glycerol content          | 74.7161 %      | >80%                                | 92.0382 %                    |
| Water content             | 1.98%          | <10%                                | 0.2183 %                     |
| Color                     | Tawny          | limpid                              | Limpid                       |
| Density                   | 1.2 gr/cm\(^3\) | 1.2671 gr/cm\(^3\)               | 1.2710 gr/cm\(^3\)          |

From the data in table 2, it can be concluded that purified glycerol obtained from this research has met the standard of commercial glycerol. It proved that the method used in this research is effective to purify crude glycerol which is a side product of biodiesel production. The result show that the purity of the glycerol has increased from 74.7161% to 92.0382%.
4. Conclusion

The highest glycerol purity obtained from this research is 92.0382% in the condition of 1:1.5 solvent volume ratio (v/v) and 60 minutes of extraction time. The physical properties such as glycerol ash content, moisture content, glycerol level, density and Matter Organic Non Glycerol (MONG) of the purified glycerol in this research has met the commercial glycerol standard, in this case British Standard 2621:1979.

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