

Effect of solvent volume ratio and time extraction of glycerol purification

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Abstract. Glycerol as a byproduct of biodiesel production about 10% of the biodiesel weight. Impurities which contained in the glycerol such as catalyst, soap, methanol, water, salt, and matter organic nonglycerol (MONG) on have a significant effect on the glycerol concentration. So, it is necessary to treat the impurities. The purpose of this study is to know the effect of ethylene glycol to glycerol purification process with acidification method using phosphoric acid as pretreatment process. This research was begun with an acid addition to the glycerol to neutralize the base content and to split the soap content into free fatty acid and salt, which easier separated from glycerol. Then the process was continued with extraction by the solvent ethylene glycol using the variable of test volume ratio (v/v) (1:0,5, 1:1, 1:1,5) and the extraction time (20, 40, and 60 minutes). The results showed that the more volume of solvent used, gave less extraction time to produce high purity of glycerol. The highest purity produced in this study amounted to 90.646% is obtained at the ratio of the volume solvent (v/v) 1:1 with extraction time 60 minutes.

1. Introduction

Biodiesel has emerged as an alternative fuel to replace fossil fuels is continually dwindling. Biodiesel is non-toxic, renewable and environmentally friendly. Biodiesel also has low emissions renewable and also an excellent lubricant [1]. Therefore, biodiesel has become one of the most common biofuels in the world. Biodiesel is the most widely produced by transesterification of vegetable oils or animal fats (triglycerides) with methanol using alkaline or acidic catalysts [2]. During the process of transesterification in biodiesel plant produces crude glycerol as a by-product accounting for about 10% by weight of biodiesel products [3]. Crude glycerol has a purity of 15-80% and contains amounts of contaminants such as water, methanol, soap, free fatty acid (FFA), salt, and reactant [4]. Average - Average crude glycerol composition oscillates between 40-70% glycerin, 10% water, 4% salt, 0.5% less than about 0.5% methanol and free fatty acids. Many applications for crude glycerol are used in the pharmaceutical, food, industrial and cosmetic products [5]. Production of crude glycerol from biodiesel conversion increases every year. From 2008 – 2011 the conversion is 2.06 to 2.88 million tonnes [6]. It is estimated that in 2020 global production of glycerol would reach 41.9 million liters [7]. Current market value is \$.0850 to .0975 per pound of pure glycerol [8]. However, glycerol is produced as a product of biodiesel transesterification process is not pure enough to be used directly in the form of food, medicine, and cosmetics. To solve this problem, there are solution to remove impurities. Also, manufacturing and pharmaceutical and food industries are increasingly demanding high quality and superior physical properties and low contamination and odorless [9]. Crude glycerol



produced from various raw materials have different compositions, the process of purification also is different [10]. In general, the methods used to improve the purity glycerol such as by extraction of ions, the combined chemical and physical processes, chemical processes and vacuum distillation, bipolar electrodialysis chemical and physical processes [11]. According Singhabandhu and Tetsuo purification process begin with chemical pre-treatments that neutralization with acid, to remove water and alcohol in this process to produce 80-88% pure glycerin that is ready to be sold as crude glycerin. In a further process, refined glycerin is produced back to the purity to 99% or higher. Glycerin with a purity of 99% can be sel to cosmetic and pharmaceutical markets.

2. Method

2.1 Raw Material

The materials used in this study:Crude glycerol byproduct of biodiesel production with a purity of 74.7161% of PT. Wilmar, ethylene glycol ($C_2H_6O_2$) from PT. Rudang Jaya, sodium hydroxide (NaOH) 12.5 M, Hydrochloric Acid (HCl) acid, Aquadest (H_2O), Activated Carbon, blue bromthymol, H_2SO_4 0.2 N NaOH 0.05 N, $NaIO_4$ obtained from the Laboratory of Chemical process Industry Department of Chemical Engineering Faculty of Engineering, University of North Sumatra. The equipment used in this study is Erlenmeyer, magnetic stirrer, hot plate, separating funnel, glass beakers, measuring cups, digital balance, rod stirrer, thermometer, funnel glass, pipette, stopwatch, pH meter, Whatman no.41. It was obtained from the Laboratory of Chemical Process Industry Department of Chemical Engineering Faculty of Engineering, University of North Sumatra.

Table.1 The Structure of variable research

Run	StirringSpeed (Rpm)	Temperature (°C)	Time (minutes)	Etylene Glicol:Gliseryn (v/v)	Mol H_3PO_4 : Gliceryn (n/n)
1	200	50	20	0.5:1.0	0.1:1.0
2			40	1.0:1.0	0.3:1.0
3			60	1.5:2.0	0.5:1.0

2.2 Pretreatment Raw Materials

As a pretreatment step, put glycerol weighing 30 grams into Erlenmeyer, then added phosphoric acid with the ratio determined. The mixture was heated up to 70°C and stirring with a speed of 250 rpm for 1 hour, then fed into a separator funnel and allowed to stand to form three layers. A layer of glycerol taken and neutralization with NaOH, and after that glycerol is evaporated to remove the water contents.

2.3 Extraction with Ethylene Glycol

Entered ethylene glycol is glycerol with the volume ratio (v / v). The mixture was heated on a hot plate until the temperature reaches 50 ° C with stirring 200 rpm during a specified time interval, then allowed to stand to separate into two phases. Glycerol is evaporated at a temperature of 95 °C.

2.4 Characterization

Analysis of the purified glycerol produced include the analysis of the composition of raw materials and products using GC 2010, moisture content, ash content, levels MONG (Matter Organic Non-Glycerol) with Test Method Standard Method ISO 2098-1972, pH by using a pH meter, and glycerol levels SNI Titration method.

3. Results and Discussion

3.1 Characterization of Gas Chromatography

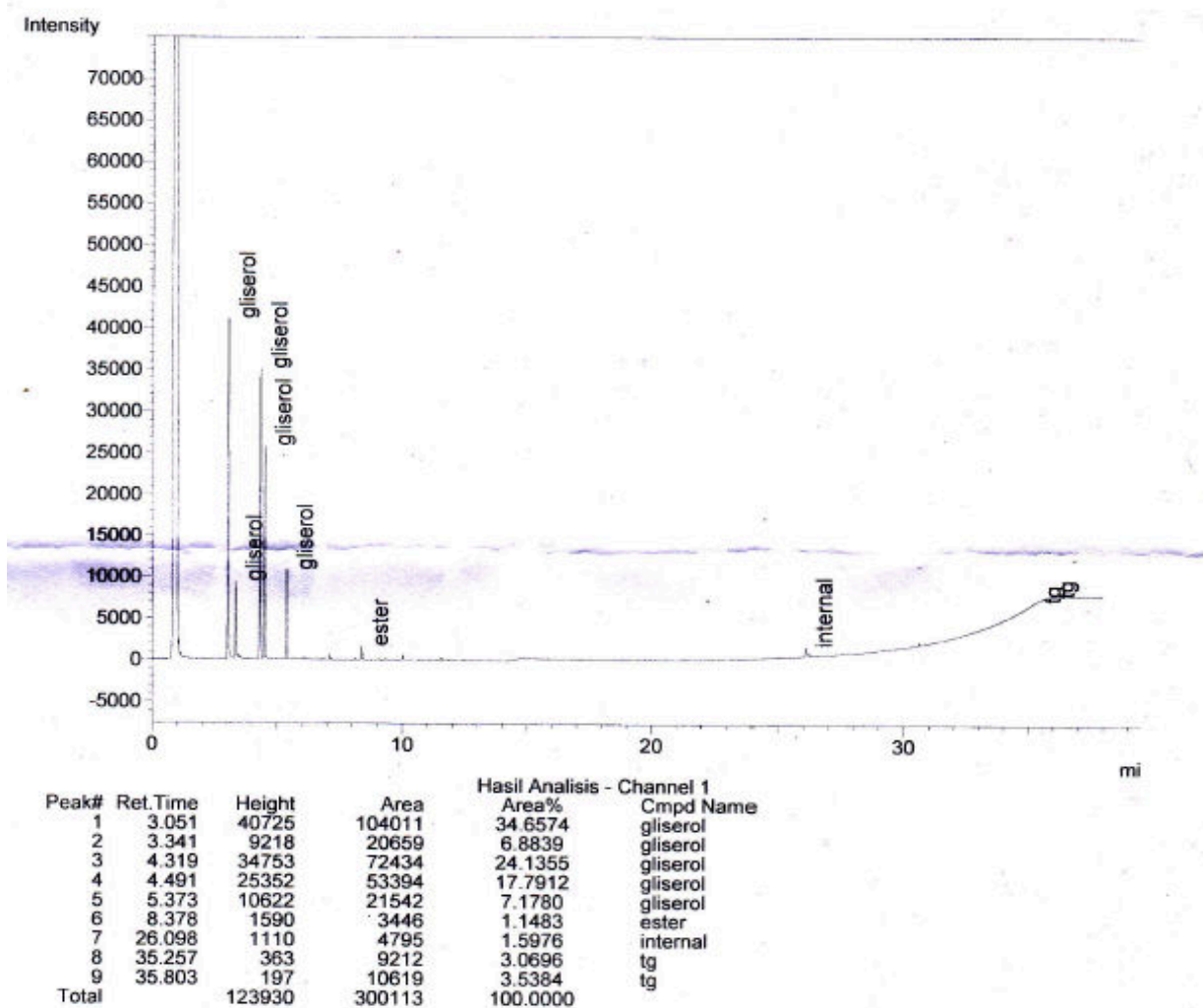


Figure 1. The Analysis of Glycerol Using GC 2010

3.2 Acidification Phosphoric Acid

Acidification performed as a pretreatment step before extraction of crude glycerol. In this study, the acid used is phosphoric acid. When acid is add to glycerol, is formed of three layers, wherein the top layer is a layer that contains free fatty acids, the next layer is a layer rich in glycerol, and the bottom layer is the inorganic salts precipitated [4].

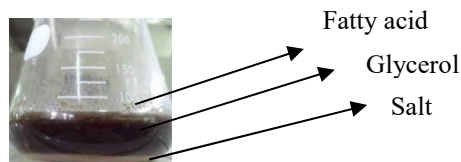
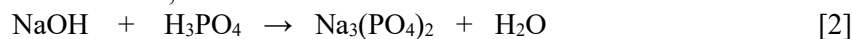


Figure 2. Glycerol layer is formed after the acidification process

The experiment begins with the addition of acid to glycerol to neutralize the alkaline catalyst used and broke the soap formed, into free fatty acids and salts are more easily separated from the glycerol. Decomposition reaction of the soap with the aid of hydrochloric acid into fatty acids can be seen as follows:



In addition to the acid decomposition, occurs neutralizing the base catalyst derived from the reaction of biodiesel contained in crude glycerol. The catalyst reacts with hydrochloric acid to form chloride salts, can be see as follows:



After acidification, further filtration to filter out the salt buildup. pH glycerol acidification is currently under acidic conditions, namely 2. It is necessary for neutralization with NaOH 12.5 M. After the neutralization, heating is done to remove the water formed from the neutralization reaction, and also to accelerate the formation of salt deposits.

3.3 Effect of Solvent Volume Ratio (v / v) Extraction And Time Of Purity Glycerol

Relationships amount of solvent volume ratio (v / v) the length of time the extraction of the purity of the resulting glycerol can be see in the graph below. The extraction is finish at 70 ° C and stirring conditions of 200 rpm with variations in time and also the ratio of solvent volume (v / v) were use.

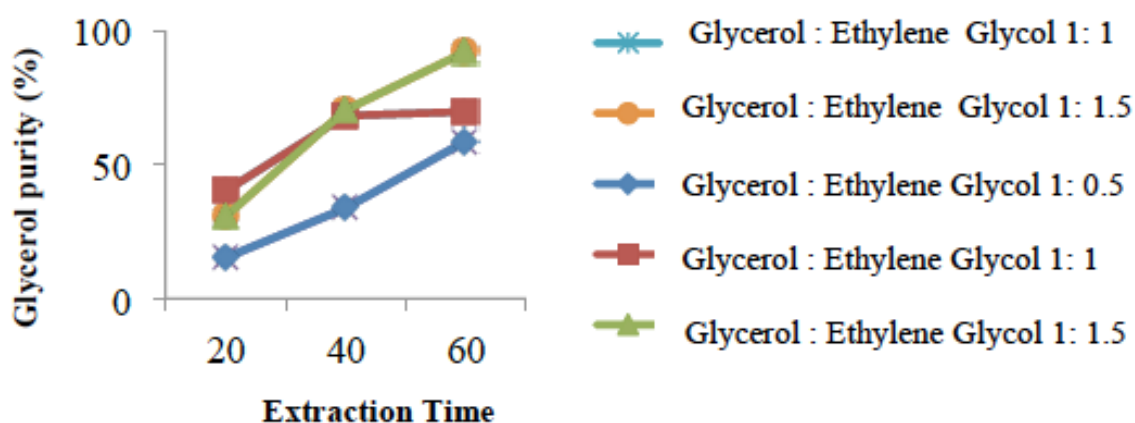


Figure 3. Effect of Solvent Volume Ratio (v / v) Extraction and Time of Glycerol Purification

From Figure 3 can be see that, volume ratio of 1: 0.5, the glycerol concentration when the extraction time 20 minutes is 15.3214%, then increased at 40 minutes to 33.7381% and increased again at 60 minutes to 58.6044 %. For solvent volume ratio of 1: 1, the glycerol concentration when the extraction time 20 minutes is 40.2715% and then increased at 40 minutes to 68.1732% and at 60 minutes increased very little to 69.6040%. For solvent volume ratio of 1: 1.5, the glycerol concentration when the extraction time 20 minutes is 30.7321% and then increased at 40 minutes into 70.2515% and increased again on 60 minutes to 90.6466%. To increase levels of glycerol, it is necessary to solvent extraction after acidification stage. From the chart above, we can conclude that the use of ethylene glycol as a solvent in the extraction of glycerol, with a low solvent ratio, it takes a longer time to get the best levels of glycerol. And for ratio higher, it takes only a short extraction. However, for the ratio of solvent volume (v / v) 1: 1.5, the extraction solvent glycerol with ethylene is effective.

On the use of a polar solvent, i.e., methanol, found that the best conditions for the extraction solvent is to volume ratio (v / v) 1: 2 with the same extraction time [13]. Hunsom et al. (2013) in his study found that using the solvent hexane and diethyl ether, increased levels of glycerol with increasing the ratio of solvent, even though only a small increase. The best ratio obtained difference due to treatment conditions, and the type of solvent that is different from that used by researchers and ratio of solvents used are very influential in glycerol purification to increase levels of glycerol.

3.4 Characteristics of Pure Glycerol

From table 2 below can be see a comparison between the characteristics of the crude glycerol and glycerol is refine, as well as glycerol standard set by British Standard 2621: 1979.

Table 2. Physical properties of Crude Glycerol, Glycerol Purification results, and Glycerol Standard

Physical Properties	CrudeGlycerol	Glycerol Standard BS 2621 : 1979 [3]	GlycerolPurificationRe sults
Color	tawny	limpid	limpid
Glycerol content	74.7161 %	>80%	90.646 %
Density	1.2 gr/cm ³	1.2671gr/ cm ³	1.2710gr/ cm ³
Ash content	12%	<10%	8%
Water content	1.98%	<10%	0.2183 %
MONG	11.3099 %	<2.5%	1.1357 %

It can be shown from the table above, that glycerol purification results in this study have met the standards set for commercial glycerol. Then the method has been effective enough to purify crude glycerol rest of the manufacture of biodiesel, where the crude glycerol is a product with a purity of 74.7161% increase to 90.646%.

4. Conclusion

The highest purity results generated in this study is 90.646% were obtained at a ratio of solvent volume (v / v) 1: 1.5 with the old extraction 60 minutes. The results of the analysis that has been purified either glycerol density, moisture content, ash content, thecontent of glycerol and also MONG (Matter Organic Non-Glycerol) meets the standards of commercial glycerol by British Standard 2621: 1979.

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