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Glycerol from waste frying oil as sustainable fuel

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Abstract. In search of renewable and environmentally friendly fuel, transesterification of waste frying oil was an excellent method to produce biodiesel. Transesterification was not only producing biodiesel but also creating glycerol as by product. Unfortunately, transesterification of waste frying oil causes the colour of glycerol usually dark brown due to impurities, caramelization, and Millard reaction. In order to improve quality of glycerol, absorption using activated charcoal was applied. Glycerol was intended to replace diesel fuel for boiler burner. Due to high viscosity, glycerol was mixed with methanol. Mixture of glycerol and methanol in various compositions was applied on boiler burner. By analyzing the flame and flue gas, composition of 10% glycerol and 90% methanol was the best mixture.

1. Introduction

Production of renewable fuel from plants becomes more intensive since fossil fuel reserves are decreasing. In Indonesia, renewable fuel especially biodiesel is produced using palm oil. On the other hand, palm oil is also used on domestic and industrial daily purpose for frying. In fact, frying oil is one of nine basic needs for Indonesian people. Therefore, using palm oil as raw material for biodiesel production is not an excellent decision. In order to avoid conflict of interest on palm oil utilization, biodiesel can be made from waste frying oil (WFO). Frying process leaves at least 30% WFO and it is harmful to human health as well as to environment. Therefore, WFO must be converted into renewable fuel called biodiesel. Earlier experiment showed that transesterification method could reach almost 100% conversion [1]. During frying process, palm oil is usually exposed to an extreme heat to more than 200 ºC. At such temperature, most nutritious substances are destructed. Moreover, this process also causes formation of several harmful and carcinogenic molecules, such as acroleines, aldehydes, and peroxides [2]. Therefore, WFO should not be consumed and must be utilized as fuel by transesterification. Transesterification of WFO and methanol using basic catalyst producing biodiesel as main product and glycerol as by product with a chemical reaction as follows.

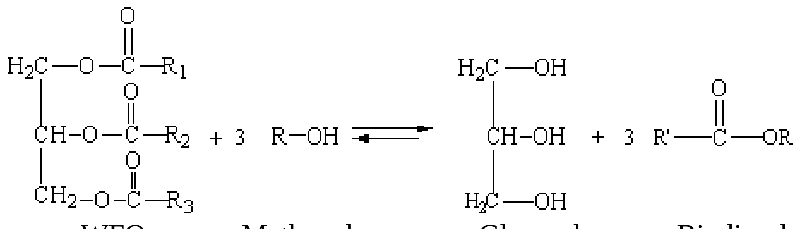

Figure 1. Transesterification of WFO.

Chemically, this biodiesel is called fatty acid methyl ester (FAME) and used as fuel to replace conventional diesel fuel that produced from fossils. Unfortunately, at this point, glycerol produced is slippery dark brown viscous liquid with strong odour. Therefore, this by product mostly discharged into environment through water system since glycerol is soluble in water (hydrophilic). Consequently, it is not in accordance with principle of environmentally friendly. Moreover, it is aginst sutainabilty development goals as stated by the UN. In order to determine renewable fuel with increase environment quality, production of biodiesel must not create waste. A biofuel production with zero waste must be taken into account. In other words, glycerol as by product must be processed to create more valuable material. Normally, standard glycerol is a colourless viscous liquid. A simple method of purification known as absorption using activated charcoal as absorbent is applied. Theoretically, absorbent can remove impurities that make glycerol has appearance as clear as the standard one.

Absorption is defined as a physical or chemical phenomenon or a process in which atoms, molecules or ions enter some phase gas, liquid, or solid material. This is a different process from adsorption, since molecules undergoing absorption are taken up by the volume, not by the surface as in the case for adsorption [3]. More general term is sorption, which covers absorption, adsorption, and ion exchange. Absorption is a condition in which something takes in another substance. In many important processes in technology, the chemical absorption is used in place of the physical process such as absorption of carbon dioxide by sodium hydroxide. Another example of this effect is liquid-liquid extraction. It is possible to extract from one liquid phase to another a solute without a chemical reaction. Examples of such solutes are noble gases and osmium tetroxide. The process of absorption means that a substance captures and transforms energy. The absorbent distributes the material it captures throughout whole and adsorbent only distributes it through the surface [4].

Activated charcoal is porous solid contains 85 to 95 carbon. It can be made by heating carbonaceous materials such as woods, coconut shell, bamboo, and etc. During heating process at a high temperature, oxygen must be prevented entering the chamber to avoid oxidation. This process is known as anaerob heating system or carbonization. Beside used as solid fuel, charcoal can also be used as excellent absorbent [3].

Capability of activated charcoal as absorbent increases by activating process, either physically or chemically. Physical activation means activated charcoal is heated at further high temperature to several minutes and then allowed to cool slowly until room temperature. Chemical activation is carried by immersing charcoal in a strong acid solution for several hours then dried. Both activation increase the size of pores and therefore increase absorption capacity. Activated charcoal is widely used as odour and colour removals [3,4]. In this experiment, activated charcoal is utilized to remove impurities in glycerol [5]. Purification of glycerol is not only increasing its economy value, but also preventing glycerol to be wasted into environment.

Glycerol is also known as glycerin, glycerol, propanetriol, 1,2,3-trihydroxypropane, and 1,2,3-propanetriol. Physical properties of pure glycerol ($C_3H_8O_3$) are molar mass 92.09 $g \cdot mol^{-1}$, density 1.261 g/cm^3, viscosity 1.412 Pa·s, refractive index 1.4746, melting point 17.8 °C (64.0 °F; 290.9 K), and boiling point 290 °C (554 °F; 563 K) [6].

Recently, glycerol is used for cosmetics, food additives, and also explosives. Glycerol is slippery viscous liquid similar to oil. However, due to –OH bond known as hydroxyl functional group, it is soluble in water. Therefore, glycerol is utilized for pharmaceutical and cosmetics industries such as skin smoothing agent. Besides that, due to similar physical properties with cooking oil in low fat content, glycerol is also utilized for food production, such as low fat foods. Glycerol also used for natural sweetener. Moreover, glycerol can preserve food excellently and hence very popular in food industries [7].

In this research, glycerol is by product of biodiesel production from WFO. It is a dark brown viscous liquid. The colour is caused by carbon formed during frying known as caramelization and impurities. In order to purify glycerol, several methods are available such as distillation and absorption. Distillation is an energy consuming process and economically unefficient [8]. On the other hand, absorption is less energy consuming and easier to carry out. Absorption is a physical and chemical reaction or process in which atoms, molecules or ions enter some bulk of liquid or solid material through their pores [9]. Glycerol is generally obtained from plant and animal sources where it occurs as triglycerides. Triglyceride is an ester of glycerol with long-chain carboxylic acids.

Glycerol is also used to power diesel generators supplying electricity for the FIA Formula E series of electric race cars. Glycerol is used to produce nitroglycerol, which is an essential ingredient of various explosives such as dynamite, gelignite, and propellants like cordite. In this research, glycerol is mixed with methanol in order to replace diesel fuel for steam generator. The purpose of this research is to find highest percentage of glycerol in the mixture.

2. Methodology

Waste frying oil was mixed with methanol containing a strong base as catalyst in a three necked round bottom flask. The flask was also equipped with an electric stirrer operated at 60 rpm to ensure the mixture reacts thoroughly. The mixture then was heated using an electric water bath with temperature was automatically kept around 65 ^oC. This process was carried out for one hour. After that, the mixture was allowed to cool until room temperature. In order to speed up cooling process, the flask was immersed in a cool water bath. Next, the mixture was transferred into a conical flask for separation. In the flask, two layers were formed naturally due to difference in density. Top layer was biodiesel and the bottom layer was glycerol [10]. The layers were separated by opening the valve near the bottom of the flask as shown on following Figure 2.

Figure 2. Layers of biodiesel and glycerol in a separating funnel.

Physical properties of separated glycerol were analysed. They were its density, viscosity, boiling point, and colour. The density was analysed using a digital densitometer while viscosity was analysed using viscometer that was in accordance with ASTM. Boiling point was analysed using a distillation apparatus. Finally, the colour was analysed using a UV-Vis spectrophotometer.

Analysis glycerol colour using UV-Vis spectrophotometer was carried out by comparing it with standard glycerol. The spectrophotometer used was made by Perkin Elmer. An amount of 10 ml glycerol and the standard were placed in two separate containers called cuvettes. A beam of light with adjusted wavelength was splitted and then pass through the cuvettes. Part of the light was absorbed by glycerol and the rest of the light was transmitted. By comparing the amount of light absorption on the glycerol and the standard, quality of the glyrerol can be determined.

Glycerol was then treated by means of absorption. An amount of activated charcoal was added as absorbent. Ratio of glycerol and activated charcoal was used as a variable in proportions of 1:1 (10 grams glycerol was mixed with 10 gram of charcoal), 1:2, 1:3, 1:4, and 1:5. This process was also carried out according to variable of time. Physical properties of the absorption product was analysed using similar previous apparatus in order to determine the quality grade of glycerol [11]. Because of its high viscosity, glycerol cannot be applied directly as boiler buner fuel. Glycerol was mixed with methanol in several proportion of 2%, 4%, 6%, 8%, 10% and 12%. The mixture was used as boiler burner fuel replacing diesel fuel. As fuel, the mixture was placed in a fuel tank. A fuel pump then pushed the fuel into a nozzle, mixed with air and changed the liquid into a small droplets that easily burned.

3. Result and discussion

According to the experiment, every litter mixture of waste frying oil and methanol produces around 260 to 280 millilitre of glycerol. Appearance of glycerol at this point was slippery and viscous with dark brown colour due to formation caramel known as Millard reaction and burnt protein during frying. A ten times dilution with distilled water as solvent was required in order to meet conditions for analysis using a UV-Vis spectrophotometer. This analysis follows Lambert Beer Law which states that concentration of substance in a solution is linear with absorbance (ABS) and also with transmittance percent (%T). The law describe how a liquid concentration using behaviour of light when passing it.

The UV-Vis spectrophotometer contains two sources of light, namely an ultraviolet and a visible light. The light was adjusted to pass a liquid that contained in a cuvette. When the source emits a light, it is considered as Io. As the light pass the cuvette, it will be separated into three ways. The first, it will be deflected and noted as Id. A special glass of the cuvette makes Id very small and neglected. Second, it will be absorbed and signed as Ia. The higher concentration of the liquid, the bigger is value of Ia. Finally, the light will pass and transmit to a sensor and noted as It. Hence, Ia + It = 100%. The equation can be deduced that when the concentration of the liquid is zero and becomes colourless, no light is absorbed by the liquid. In other words, all the light will be transmitted. Therefore, at this point the value of It is 100%. In contrary, when the liquid concentration is very high and its colour is very dark, all the light will be absorbed and none is transmitted, the value of It is 0%. This description can be used to explain the value of absorbance (ABS). When Io is 100%, the value of ABS is 0 and when Io is 0%, the value of ABS is 1.

In this experiment, ABS value of initial untreated glycerol was 0.967. Next, every 15 minutes, a sample was analysed using the spectrophotometer. This step was ended at duration of 75 minutes. Data from the spectrophotometer were plotted on following graph.

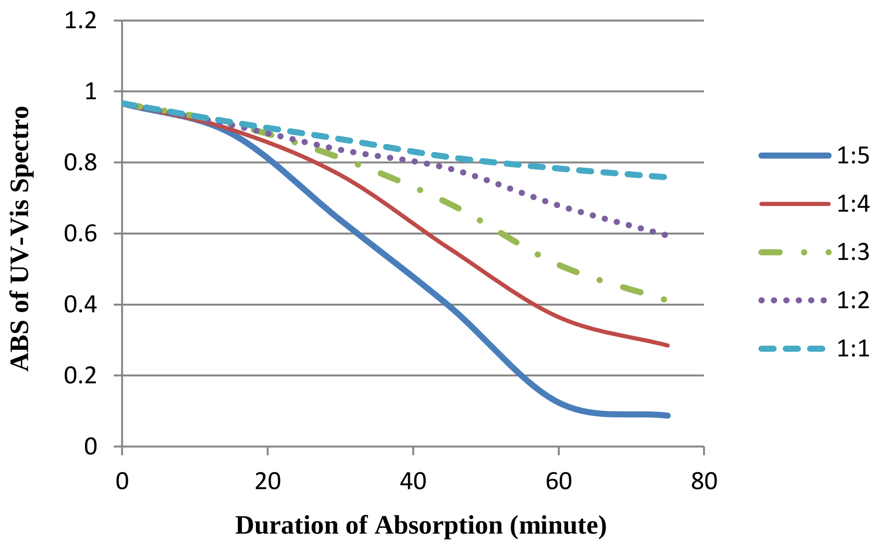

Figure 3. Graph of data from UV-Vis Spectrophotometer.

Although waste frying oil was filtered using filter paper and vacuum system, the colour of the oil for biodiesel production was still dark brown. Impurities in form of tiny particles cannot be separated. Naturally, almost all impurities gathered at the bottom layer or glycerol layer. In other words, biodiesel produced at the top layer was clear and colourless. After separated, glycerol was filtered once again. It was then diluted ten times and analysed using a UV Vis spectrophotometer.

On the spectro, the amount of light absorbed by glycerol was indicated by absorbance (ABS). The darker the colour of glycerol, the lighter was absorbed. Therefore, the value of ABS was higher. Initially, the value was around 0.900 which means 90% of light source was absorbed by dark brown glycerol and only 10% was transmitted as described by Lambert-Beer Law. Glycerol was mixed with activated charcoal for absorption process. By absorption mechanism, impurities which present in the glycerol attracted into activated charcoal pores. Graph on figure 1 shows that the higher the amount of activated charcoal, the higher was the amount impurities absorbed by activated charcoal pores. Similarly, the longer duration of absorption, the higher was the amount of impurities separated from glycerol. At weight ratio 1:5 (10 grams of activated charcoal immersed into 50 gram of glycerol), the first 15 minutes of absorption can reduce ABS from 0.967 to 0.865 or 10.55%. According to the graph, the next 15 minutes (after 30 minutes absorption), and the reduction of impurities reaching 34.64%.

Statistic analysis shows that either weight ratio of activated charcoal: glycerol, absorption duration, or their combination, significantly affecting ABS, hence appearance or colour of glycerol. Nevertheless, this process cannot make the colour of glycerol as clear as the standard one. Using this process, the best glycerol as by product of biodiesel production from waste frying oil was absorption using a ratio of 1:1 with duration of 75 minutes. At this point, the value of ABS was 0.087 while ABS of standard glycerol was 0.000. In other words, there was still 8.7% impurities in the glycerol cannot be removed using absorption methods. As shown on the following figure, the best glycerol appearance after absorption (at right most) is slightly yellowish. At this point, the boiling point of glycerol is between 280 to 283 ^oC which is slightly lower than the standard one at 290 ^oC.

After analysed using the spectrophotometer, the next physical property of glycerol was density. Analysis using a digital densitometer showed that initial glycerol before absorption process was around 1.2 gram/ml. This value was lower than the standard glycerol which is 1.261 gram/ml. The difference was caused by impurities such as tiny particles and oil which had lower densities.

Removing impurities from glycerin definitely causing its density higher. The weight ratio of glycerol and activated charcoal as absorbent obviously make the density rising. The similar effect was also shown by the absorption duration. The longer period of absorption, the higher was the density. The best result that close to the density of standard glycerol was achieved at weight ratio of 1:1 with absorption duration of 75 minutes. The best density by absorption method was 1.258. Discrepancy of density to standard was 0.24%. The next physical property of glycerol to be analysed was viscosity. Impurities tends to increase glycerol viscosity because most impurities are waterphylic with viscosity similar to water. Therefore, the more impurities, the lower is viscosity of glycerol as seen on Table 1.

Table 1. Viscosity of glycerol after absorption.

Weight Ratio Charcoal: Glycerol	**Absorption Duration (minutes)**				
	15	**30**	**45**	**60**	**75**
1 : 5	1.217	1.221	1.227	1.231	1.232
1 : 4	1.249	1.255	1.261	1.271	1.272
1 : 3	1.295	1.307	1.312	1.322	1.324
1 : 2	1.334	1.342	1.357	1.369	1.371
1 : 1	1.381	1.385	1.388	1.391	1.394

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Finally, mixture of glycerol in methanol was set for boiler burner fuel. Starting from 2%, the flame of the burner is excellent with reddish blue colour. Next, at 4%, 6%, 8%, and 10% the colour of the flame was acceptable with colour more reddish. Accidently, at 12% the burner cannot produce flame easily.

4. Conclusion

The best condition for glycerol purification was achieved on weight ratio of glycerol: charcoal at 1:1 with duration absorption for 75 minutes. At those variables, activated charcoal can reduce impurities by 91%. Glycerol at this point has physical properties of density 1.258 gram/ml, viscousity 1.394 Pa.s, and boiling point between 280 to 283 ºC. Afterwards, the appearance of glycerol cannot be as clear as the standard one. In a mixture with methanol, 10% of glycerol is the highest proportion to be applied on boiler burner replacing diesel fuel. Further experiment may be conducted by mixing glycerol with another organic liquid to create better fuel.

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