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Biodiesel Production From High Free Fatty Acid Of Sludge Palm Oil

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Abstract: Biodiesel is a promising alternative to fossil fuel as it is renewable, environmentally-friendly and has various advantages. However, the major limitation of the application of biodiesel is due to the high cost that is mainly sourced from its raw material. Using edible vegetable oils consumed 80% of the cost and also unethical. Sludge palm oil on the other hand is cheap and low in quality but has the potential as biodiesel feedstock. The high free fatty acid in sludge palm oil is necessarily to reduce to at least 3% of free fatty acid prior to produce biodiesel due to the undesirable presence of soap. Glycerolysis is performed by using 100% excess of glycerol and 1 wt% of zinc oxide as catalyst at 220°C to reduce 59% of high free fatty acid in sludge palm oil. The result shows the effectiveness of the method to reduce the free fatty acid to as low as 0.4% within 4 hours of reaction time. Biodiesel is then produced by undergo transesterification using 12:1 methanol to oil ratio, 2 wt% of potassium hydroxide as catalyst. The experiment was carried out for 3 hours at a constant temperature of 70°C and speed of 300rpm. The FTIR analysis then verifies the production of biodiesel. This paper proves the feasibility of sludge palm oil to transform into biodiesel and demonstrates the waste-to-wealth concept.

Keywords: *Biodiesel, Sludge palm oil, Free fatty acid, Glycerolysis*

1. Introduction

The development of modern civilization has risen the dependance of fossil fuel as the main source of energy that has caused harmful effects to the environment for decades. The supply and demand market also has contradicted as there is high demand, due to variety of applications, but lower in supply, as it has come to depletion because of its non-renewable factor [1]. Transportation sector includes 28% in application of fossil fuel and more than three quarters of the sectors' users utilize diesel [2]. The dependance of this resource should be replaced with another alternative that should be renewable and environmentally friendly.

Studies for biodiesel have caught many researchers' attention as it gives solemn promise and possibility as the alternative due to its characteristics and advantages. Biodiesel is a bio-based fuel that mainly produced from the presence of fats in vegetable oils such as sunflower, soybean and palm oil through transesterification process to produce fatty acid alkyl esters (which is the biodiesel) [3]. It has higher biodegradability, lower toxicity, lower carbon emissions and higher flash point compared to the common diesel [4]. However, the common feedstock for biodiesel which is the vegetable oil has brought issues to the development of biodiesel due to several factors. The main factor is because, 80% of total cost for biodiesel production is originated from the feedstock [5]. Considering these vegetable oils are edible, the high demand competition with the food industry has risen the price. Also, using edible materials as the raw material might be observed as unethical. Thus, exploring the ideal raw materials that can tackle both issues is carried out tremendously.

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Sludge palm oil (SPO) which is the residual oil that is collected from the upper layer surface from Palm Oil Milling Effluent (POME) [6]. SPO is used for production of animal feed and soap while the latter is disposed as waste. It is brown in colour and has bad odour which implied the low quality of oil [7]. Although the quality is low, it has similar attributes and constituents with crude oil which deduced the potential feasibility of SPO to produce biodiesel [8]. By utilizing this oil, the production cost can be reduced, there will be worry-free of the availability due to the high abundance and sustainability of biodiesel can be promoted broadly.

The major drawback for SPO as the raw material for biodiesel production is the presence of high amount of free fatty acid (FFA). FFA is one of the crucial elements in quality of palm oil as it indicates the level of deterioration of oil. High FFA of oil as biodiesel feedstock is unfavorable due to the soap formation from the saponification reaction that is hard to separate at the end product [9]. This factor will lead to low yield of biodiesel [10]. Therefore, a pre-treatment process is essential to lower down the amount of FFA in SPO hence, improve the quality of the oil. The content of FFA that can be tolerated without affecting the process negatively is at or lower than 3% [11].

Glycerolysis process is an ideal strategy to resolve this issue effectively. The significant of this method is the relevance in the reaction as shown in Figure 1. Glycerol is added with the aid of catalyst to form bonds with the free fatty acid present in the oil and transformed into respective glycerides which include monoglycerides (MG), diglycerides (DG) and triglycerides (TG) – important component to produce biodiesel [12]. Consequently, these formations resulting to an acceptable low amount of FFA. Another value added to this method is, glycerol is a by-product produced in the biodiesel production. This implied the high accessibility of glycerol to carry out this process.

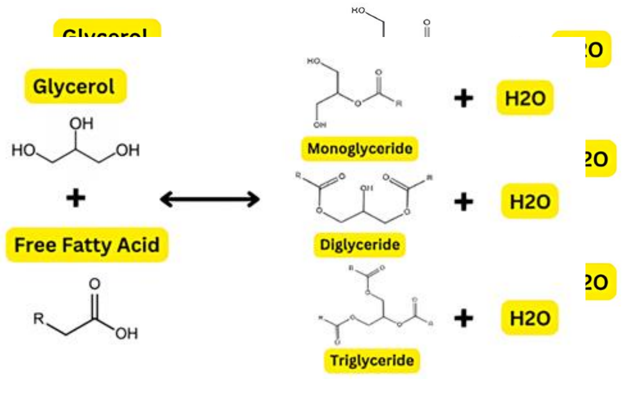

Figure 1: Glycerolysis reaction with FFA to form monoglyceride, diglyceride and triglyceride with water [13].

2. Materials and Methods

2.1 Raw materials and chemicals

SPO collected from cooling pond to obtain the maximum FFA, >99% Pure glycerol (Sigma-Aldrich), 0.1M NaOH Sodium hydroxide, >99% Phenolphthalein indicator (Sigma-Aldrich), >99% Isopropyl Alcohol (Systerm), >99% powder Zinc Oxide (Systerm), >99% Methanol (Systerm), and >99% pallet Potassium hydroxide (Systerm).

2.2 Collection of sludge palm oil

SPO is collected from cooling pond which is the first stage of waste water treatment plant for palm oil mill effluent in Bukit Bandi Palm Oil Mill, Kemaman, Terengganu. The FFA of SPO is recorded by using titration method with the aid of phenolphthalein as indicator. Approximate of 0.5g of SPO is titrated with NaOH until the mixture turns into light pink [14]. The amount of NaOH is recorded and FFA is calculated using Equation 1[15]. The procedure is repeated three times.

$$\text{FFA (\%) as palmitic acid} = (25.6 \times N \times a) / b \quad (1)$$

where; N = normality of NaOH
a = volume of NaOH, mL
b = weight of oil sample, g

2.3 Pre-treatment of SPO

SPO is first heated at 65°C as it is in semi-solid state in room temperature. The liquid state of SPO is then filtered using cotton cloth to remove solid elements (i.e., debris) [16].

2.4 Glycerolysis of SPO

Glycerolysis is performed by heating the mixture of SPO, glycerol and zinc oxide on a hot plate at 220°C and 300rpm in an Erlenmeyer flask. The amount of each compound is measured by following the parameter of 100% excess glycerol and 1 wt% of zinc oxide [13].

Upon reached the desired temperature, the mixture is heated at constant temperature for 4 hours. Glass pipette is used to collect the oil sample hourly. An approximate of 0.5 to 0.6g of collected sample is measured and then tested for FFA value. In order to inhibit the reaction to hydrolysis, condenser is installed and cold water is supplied to cool down the hot steam [10]. The procedure is then repeated for three times.

2.5 Production of biodiesel

Transesterification method is performed with the aid of methanol to produce biodiesel. The treated SPO with low value of FFA is first heated inside Erlenmeyer flask on a heat plate. A value of methanol with a ratio of 12:1 of methanol to oil is added inside the flask. Upon heating at temperature of 70°C, 2wt% of KOH is added as catalyst to increase the rate of reaction. The mixture is stirred at 300rpm to allow proper mixing.

After 3 hours, the mixture is allowed to cool down before being transferred into a separating funnel. The mixture is then left for 30 hours inside the separating funnel to separate biodiesel with other constituents by gravity allowance. The lower part is removed while the upper part is taken out as biodiesel. The product is then washed by distilled water to eliminate other elements. The procedure is repeated three times [17].

The functional group and chemical structure presented within the oil is planned to be analysed to verify the presence of biodiesel. This analysis is carried out by using Perkin-Elmer model Fourier transform infrared spectroscopy (FT-IR) spectrometer equipped with attenuated total reflectance (ATR). The model capable of covering the spectral range of 4000–400 cm^{-1}. This method needs the absorption of infrared light wavelength from the oil. A drop of 2 μL of sample is first spotted on the plate. The IR spectra of the sample was recorded on spectrophotometer using KBr disc by pressing the mixture into the form of a pellet at 134 MPa for 2–3 min to obtain transparent pellets. The functional group as well as bond types will then be obtained [15, 18].

3. Results and Discussion

SPO collected is observed to be in brown colour, high viscosity, bad odour and in semi-solid state at room temperature as shown in Figure 2, as mentioned similarly by Škrbic [19]. The FFA of SPO is recorded at 59% by performing titration method. The result hinted that the value is considered very high compared to other waste oil that has been used in previous studies. Waste cooking oil or used frying oil usually consist a maximum of 15% of FFA [20]. This is relatively lower than the tested SPO, implying SPO has lower quality compared to the latter.

Figure 2: Collected SPO

While performing glycerolysis, SPO is mixed with glycerol to initiate the reaction. The FFA is recorded hourly as depicted in Figure 3. It can be seen that the value of FFA is dropped drastically from 59% to 1.2% within an hour. According to comprehensive review by Oyekunle, heterogenous catalyst is more favourable compared to homogenous catalyst. This is due to its robustness, easy to separate, lower reaction time, higher reaction rate and lower operational cost [21]. Using zinc oxide as catalyst promotes the rate of reaction while increase the speed of reaction simultaneously. Applying 2wt% of catalyst is more than sufficient to assist in the reaction. Furthermore, running the reaction at 220°C also contribute a big factor to the glycerolysis efficiency. The range of temperature that is ideal for glycerolysis is within 180°C to 220°C [22]. It is established that glycerolysis method require high temperature which is one of its drawbacks. High kinetic energy is required to ensure the effective reaction of glycerolysis [13]. In addition, the reaction also needs excess glycerol in order to react with the FFA present in the oil and promotes forward rection [10]. At 3rd and 4th hour, it is observed that the values are slightly constant. This implied the completion of reaction. The final FFA is recorded at 0.4%. The acceptable amount of FFA to produce biodiesel is at least 3% of below, but the ideal would be below 1% [23].

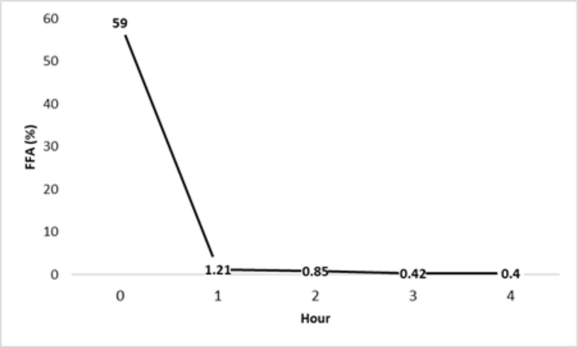

Figure 3: Reduction of FFA result through glycerolysis

Produced biodiesel from treated SPO is performed for 3 hours at low temperature in accordance to study by Agarwal *et al.* [24]. Excess amount of reactant which is methanol is needed to maintain the reaction in forward direction in transesterification. Some studies applied up to 30:1 methanol to oil ratio to effectively execute the transesterification process [25, 26]. However, over excessive amount of methanol may possibly decrease the yield of biodiesel. This is due to the unreacted amount of methanol that interferes the separation of glycerol [27]. Hence, optimum value of methanol to oil ratio is necessary to analyze beforehand to obtain the maximum yield of biodiesel. Micro-emulsification and pyrolysis are examples of methods to produce biodiesel other than transesterification. However, transesterification method is more preferrable due to its economical and efficient factor [28].

Figure 4 displayed the FTIR analysis upon biodiesel production. Basically, the presence of biodiesel is displayed at the sharp peak observed around $1735cm^{-1}$. It was interpreted as carbonyl stretch of the ester group. Meanwhile, the peak at around $2920cm^{-1}$ was detected which implied the symmetric and asymmetric C-H stretching [29]. The peaks exhibit the presence of biodiesel which deduce the successful of transformation of biodiesel from the glycerides present in the oil.

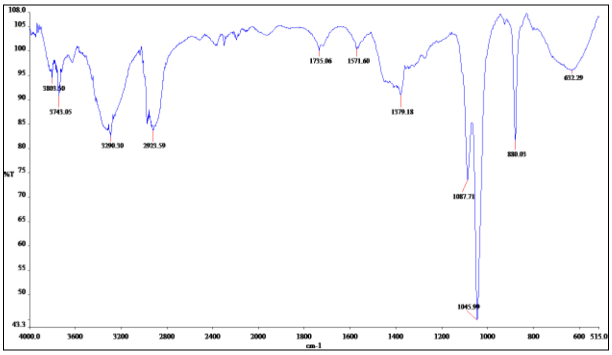

Figure 4: FTIR analysis of produced biodiesel

4. Conclusion

In order to promote the reliance on biodiesel for conventional diesel fuel, the primary aspect that is required to regard is the feedstock. This is because, the current raw materials used for production of biodiesel demonstrates an inferior comparison with petroleum fuel. SPO is a promising candidate to apply widely as biodiesel feedstock due to its high availability and accessibility along with the renewable factor. Glycerolysis is capable to reduce high FFA of SPO to the acceptable value in order to improve its quality. The presence of glycerol allows the reduction of FFA by transforming the FFA to glycerides. By promoting glycerides, transesterification is performed with the aid of methanol to produce biodiesel. For future perspective, further research in implementing and promoting waste to produce biodiesel is highly suggested.

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