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RESEARCH ARTICLE

Effect of Free Fatty Acid on Transesterification of Waste Cooking Oil

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ABSTRACT - The presence of high free fatty acids (FFA) in the feedstock is a primary concern in biodiesel production. Waste cooking oil (WCO) is a potential environmentally friendly source, but further research is needed to fully characterize its properties. This study successfully explored the effect of FFA on the transesterification reaction and achieved the conversion of triglycerides in WCO to biodiesel under optimal conditions (molar ratio of oil to methanol 1:9, 2 hours, 65°C, catalyst loading 2.0 wt.% of WCO). The results show that for feedstocks with 0-3% FFA content, methyl ester conversion exceeds 90%, while for feedstocks containing 4-6% FFA, the conversion rate is less than 50%. Biodiesel containing 4–6% FFA undergoes saponification reaction during washing, highlighting the need for pretreatment prior to transesterification. In contrast, 0-3% FFA showed no saponification effect. The physicochemical properties of biodiesel from each FFA% feedstock, including acid value, degree of saponification, viscosity, density, and moisture content, were observed and compared with the ASTM D6751 standard. The results show that the acid value is directly proportional to FFA%, while the saponification value is inversely proportional. This study found that other properties such as viscosity, density, and moisture content were not related to biodiesel quality. In contrast, saponification value testing and GC analysis highlighted the impact of FFA percentage in the feedstock on biodiesel production.

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1.0 INTRODUCTION

Petro-diesel is the primary source of fuel used around the world. Nowadays, the prices of petro-based diesel are increasing rapidly because the demand for petroleum for running engines has been rising. U.S. Environmental Protection Agency stated that petro-based diesel emissions would contribute to air pollution and has serious human health and environmental effects. Soot or particulate matter (PM) and nitrogen oxide (NOx), which will cause the production of ground-level ozone (smog) and acid rain, hydrocarbon (HC), and carbon monoxide (CO) are the main pollutant emissions from diesel engines [2] and these gases that will cause the greenhouse effect [1]. When burning petro-based fuel in engines, greenhouse gases can be released and trapped inside the earth's ozone layer, thus increasing the earth's temperature. Lindsey and Dahlman [3] stated the global surface temperature increased from around 1978 to 2020. They also mentioned that year 2022 was the sixth-warmest year compared to the 20th century and the pre-industrial period (1880 – 1990). Emissions of these gases also can cause heart and lung disease as well as damage plants, animals, crops, and water resources. From this side effect, much research was conducted to find another alternative energy source that is more environmentally friendly, renewable and has a considerable cost. Many kinds of alternative energy, such as wind, geothermal, solar, and biomass, are sustainable, but only a few are feasible.

Biodiesel has achieved global consideration to replace petro-based diesel due to its biodegradability, low toxic emission, carbon neutral, sulphur-free, and environmentally friendly [4]. Biodiesel is a type of diesel fuel that is made from vegetable oil and animal fats. It is created by converting the long-chain fatty acids found in these oils and fats into mono-alkyl esters, which can be used as a substitute for traditional diesel fuel. One of the biggest benefits of using biodiesel as a fuel source is its renewable nature. Compared to petro-based diesel, biodiesel can be reused and unlimited. According to a recent study by Jahnke [5], converting to biodiesel has various significant health benefits, including a lower risk of developing cancer, fewer early deaths, and fewer asthma problems. Switching to 100% biodiesel in the transportation and home heating sectors would significantly improve community health and have a positive impact on health outcomes and medical expenses.

Many Malaysians frequently use cooking oil, especially for food producers, restaurateurs, and households. Cooking oil plays a vital role in Malaysia, especially since fried food is widely cherished in Malaysian cuisine. According to a study conducted by Daud [6], most respondents from Pasir Gudang who took part in their survey reported cooking on a daily basis. Most did not know that used cooking oil could be recycled. The waste cooking oil also could be repurposed to household products such as soap [7] and candles [8]. The waste cooking oil also can be recycled and reused in biodiesel and biofuel production. In addition to its use in soap production, cooking oil can be broken down into glycerine and biodiesel through a chemical process called 'transesterification'. Using waste as feedstock for biodiesel production helps

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reduce costs by utilizing materials that are readily available or even obtained for free. Waste feedstock, such as used cooking oil or animal fats, not only lowers raw material expenses but also promotes waste management and environmental sustainability. Challenges include ensuring consistent quality and addressing logistics for waste collection and transportation. Despite these challenges, the cost-saving potential and environmental benefits make using waste feedstock an attractive option for biodiesel production.

Free fatty acids (FFA) are one of the factors affecting the efficiency of biodiesel transesterification reactions. Different raw materials have different FFA contents, and waste cooking oil has high FFA contents due to repeated heating and exposure to air [9]. However, when waste cooking oil contains inconsistent levels of water, free fatty acids (FFA), and food residues, its suitability as a biodiesel feedstock diminishes, thereby reducing its value in the process. According to a study by Mićić [10], elevated levels of free fatty acids (FFA) in waste cooking oil (WCO) can result in saponification reactions, leading to the formation of soap. This can make it more challenging to separate biodiesel from the mixture and prolong the decantation process, ultimately reducing the yield and efficiency of biodiesel production. Additionally, it can decrease the effectiveness of the catalyst and contribute to the formation of emulsions. These challenges increase the difficulty of converting WCO into biodiesel, requiring additional processing steps and increasing production costs. Therefore, understanding the effects of FFA on transesterification reactions is of great significance for realizing the economic and environmental benefits of using waste cooking oil to produce biodiesel. Biodiesel is experiencing a growing global trend, particularly in developing country like Malaysia. This research aims to promote the widespread adoption of waste cooking oil as a valuable resource for biodiesel synthesis by analyzing the effects of FFA on transesterification reactions. This will ultimately help advance sustainable energy and waste management technologies. Additionally, the study's findings could have a significant impact on industry and government guidelines regarding biodiesel production, which could expand the market for alternative fuels and support the development of a more environmentally friendly and sustainable energy sector.

2.0 METHODS AND MATERIAL

Waste cooking oil (WCO) was obtained from a household, where it had been used for frying food. The characteristics of both WCO and biodiesel were tested. Six parameters were utilized to determine the characteristics of WCO. Meanwhile, for the biodiesel samples produced from each percentage of free fatty acid (FFA) in the feedstock, five parameters were assessed. The six parameters for WCO included acid value, saponification, peroxide, moisture content, density, and viscosity.

2.1 Determination of Acid Value and FFA

Determination of acid value using the AOCS official method Cd 3a–63. The oil sample (5 g) was mixed with 50 mL isopropanol and added with 2 mL phenolphthalein in a 250 mL Erlenmeyer flask. The mixture was titrated with 0.01 M of KOH and shaken vigorously until the colour was changed (from white to pink). The result was expressed as the number of milligrams of KOH required to neutralize the free fatty acid in 1 g of the sample. The test was repeated by replaced oil sample to biodiesel sample.

2.2 Analysis of Methyl Ester

Thin Layer Chromatography (TLC) and Gas-Chromatography Mass-Spectroscopy (GC-MS) were used as instruments to test the methyl ester content. TLC had been carried out to analyse the methyl ester qualitatively. TLC plate had been cut into a dimension of 6 cm long and 3 cm wide. Then, a straight line had been drawn near the bottom and the top of the TLC plate. A small volume of sample and methyl heptadecanoate had been deposited on the bottom line of the TLC plate as small spots. The developing solvent used in TLC analysis is a mixture of petroleum ether and chloroform in the 2:3 ratio, while iodine vapor had been used to visualize the spots. The TLC plate had been removed when the solvent reached the line on top of the TLC plate. The completion of the transesterification reaction had been indicated by the formation of methyl ester spot and the disappearance of triglyceride spot. GC-MS had been used to identify the fatty acid methyl ester of WCO. GC-MS analysis was performed using GC-MS (Agilent 5973 Network MSD) with a capillary column (DB Wax - MS, 30 m length x 0.25 mm internal diameter x 0.25 μm film thickness) and C_{17} methyl heptadecanoate as an internal standard. Helium gas was used as carrier gas. The initial temperature is 150 °C for 5 min and had been raised 12 °C per minute until 200 °C for 17 minutes. The temperature of both the injector and detector was 260 °C. The injection volume was 1 μL. The fatty acid compositions had been determined from Mass Spectral Library.

2.3 Saponification Reaction (Washing Process)

Wet washing removes polar contaminants such as alcohol and catalyst residue. The volume of hot distilled water (70°C) used in the washing process is the same as the volume of biodiesel that needs to be treated. After vigorous shaking, the mixture was distributed by gravity in a separatory funnel. The higher the FFA% of oil, the higher the possibility of saponification. Observe the reaction of the emulsion whether if it is partially saponified or fully saponified.

3.0 RESULTS AND DISCUSSION

3.1 Characteristic of WCO

This experiment investigates the characteristics of WCO in comparison with ASTM D 6751 standard. The experimental parameters used in this experiment are shown in Table 1. For WCO, the acid value and FFA% were tested as 13.37 mg KOH/g with 6.10% FFA, while the ASTM are 0.5 mg KOH/g with <0.45% FFA. For peroxide value, it was tested as 17.22 meq/kg, indicating a relatively high level of peroxides present in the oil. The saponification value of WCO was tested as 205.326 mg KOH/g, which in the range of ASTM, less than 500 mg KOH/g. Lastly, for moisture content, density and viscosity, it was tested as 0.25%, 0.9091 g/cm^3, 648.9 mm^2/s, respectively.

Table 1. The characteristics of waste cooking oil.

Parameters	Value	ASTM D 6751
Acid Value of WCO (mg KOH/g)	13.37	0.5
FFA of WCO (%)	6.10	<0.45
Peroxide Value (meq/kg)	17.22	-
Saponification Value (mg KOH/g)	205.326	<500
Moisture content (%)	0.25	0.05
Density (g/cm^3)	0.9091	0.86-0.89
Viscosity (mm^2/s)	648.9	1.9-6.0

3.2 Analysis of Methyl Ester

TLC was the simplest, fastest, cheapest, and easiest method to determine the presence of methyl ester before GC-MS analysis. In the experiment, the biodiesel that produced from various FFA% had tested a methyl ester spot. So, its means that the biodiesel can produced from high FFA% of feedstock but in low yield or low methyl ester content. Figure 1 shows the result of TLC of methyl ester from 0% and 6% FFA of feedstock.

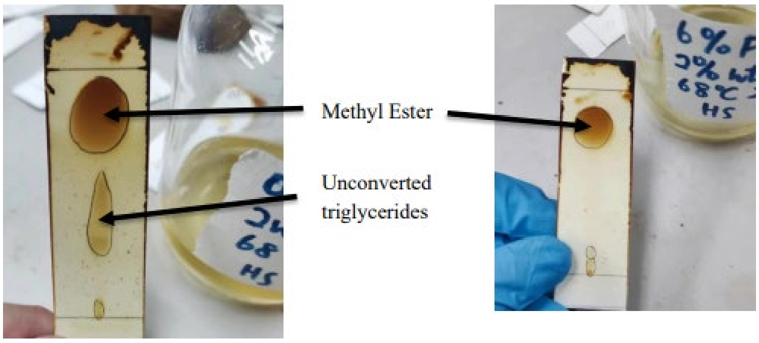

Figure 1. Result of TLC of methyl ester from 0% and 6% FFA of feedstock.

For GC-MS analysis, there is a decreasing trend in the methyl ester content from 0% FFA to 6% FFA in the feedstock as shown in Table 2. Biodiesel produced from 0% FFA feedstock exhibited the highest methyl ester content at 95.87%, while the 6% FFA feedstock resulted in the lowest methyl ester content, measuring 42.12%. These findings proven that there has a significant influence of FFA on the methyl ester content (%) since lower FFA content in the feedstock corresponds to higher conversion rates.

Table 2. The methyl ester content of each FFA%.

FFA (%)	Methyl ester content (%)
0	95.87
1	94.44
2	92.59
3	90.63
4	50.12
5	46.51
6	42.12

3.3 Characteristic of FAME

In this study investigated the impact of varying FFA% (0% to 6%) in waste cooking oil on biodiesel production. The colour of biodiesel produced serves as an indicator of its stability, with darkening or discoloration over time potentially signalling oxidation or degradation. In this experiment, there were illustrates a noticeable darkening trend as the FFA% increases from 0% to 6% as shown in Figure 2. This darkening is attributed to higher levels of FFAs, which can contribute to increased oxidation and polymerization reactions in biodiesel.

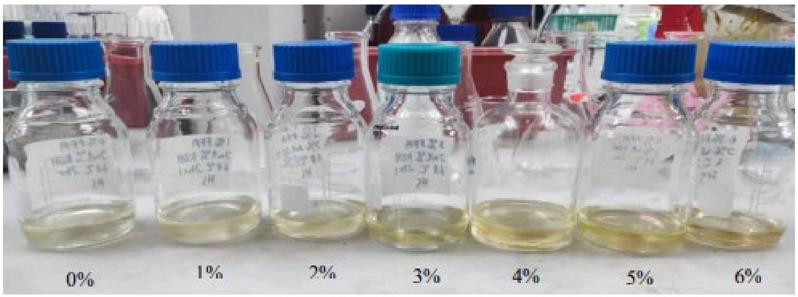

Figure 2. A comparison of the biodiesel colours produced from different free fatty acid percentages (FFA%) of feedstock

Table 3. The acid value of biodiesel that produced by different %FFA of feedstock.

FFA (%)	Acid Value (mg KOH/g)
0	0.2356
1	0.2592
2	0.9063
3	0.3299
4	0.3535
5	0.4001
6	0.4241

In this experiment, there are focus on the effect of acid value on different FFA% of feedstock. Table 3 presents the acid value and free fatty acid percentage (FFA%) of biodiesel produced from varying FFA% levels in the oil. From the table, there are a notifiable increase trend in acid value when the FFA% increase. A discernible trend emerges as the concentration of free fatty acids in the feedstock used for biodiesel production increases, there is a corresponding rise in the acid value. A high acid value can lead to increased corrosion in engines and fuel systems. The acidic components can react with metal surfaces, causing damage and reducing the lifespan of engine components.

Table 4. The saponification value of biodiesel that produced by different %FFA of feedstock

FFA (%)	Acid Value (mg KOH/g)
0	196.94
1	196.42
2	194.93
3	192.67
4	191.87
5	190.79
6	190.26

In this experiment, there are focus on the effect of saponification value on different FFA% of feedstock. Table 4 shows the saponification value of biodiesel produced from varying FFA% levels in the oil. From the table, a noticeable trend emerges where the saponification value decreases with an increase in FFA%. This trend can be attributed to the fact that FFAs consume some of the alkali during acid-base neutralization reactions, reducing the available amount for the saponification of triglycerides. Consequently, a decrease in the saponification value can impact the quality of biodiesel in various ways. The saponification value is inversely proportional to the FAME content in biodiesel. A decrease in the saponification value indicates a higher FAME content, which is desirable for biodiesel quality.

The viscosity and density of biodiesel play a important role in engine performance, as proper combustion is essential for optimal efficiency and reduced emissions. The density and viscosity of the tested biodiesel in this experiment were 0.8656 g/cm³ and 43.28 mm^2/s, respectively. According to ASTM D6751, which outlines requirements for 100% biodiesel (B100), the range of kinematic viscosity in 1.9 - 6.0 mm^2 /s while for density is 0.86 - 0.89 g/cm³. The density of biodiesel is in the range of ASTM D6751 but viscosity no. Higher viscosity in biodiesel tends to result in a longer ignition delay and slower combustion rate, impacting engine efficiency and emissions. High moisture content in biodiesel can give rise to various issues, such as microbial growth, corrosion in fuel components, and the formation of biofilm in fuel lines. In this experiment, y, the measured moisture content was 0.13%. According to ASTM D6751, which outlines requirements for 100% biodiesel (B100), the maximum allowable moisture content is 0.050% by volume. Therefore, the moisture content of biodiesel in this study exceeds the requirement set by ASTM D6751. The moisture content in biodiesel significantly affects its combustion characteristics. Excessive moisture may lead to incomplete combustion and reduced energy output.

3.4 Saponification Reaction

It has been observed that biodiesel with 0 - 3% FFA does not undergo saponification, which indicates that feedstock with less than 3% FFA does not need to undergo an esterification process to remove or reduce the acid value. For biodiesel containing 4% FFA, it undergoes "partial" saponification. Although it did not exhibit two visible layers of biodiesel and water, no soap bubbles were observed after vigorous mixing. In contrast, biodiesel containing 5-6% FFA undergoes complete "saponification" after washing with hot water. Soap lather develops after vigorous shaking and no visible two layers form in the mixture. Therefore, it can be concluded that raw materials with FFA content exceeding 4% require pretreatment before transesterification.

4.0 CONCLUSION

The work has successfully achieved the influence of free fatty acid (FFA) on the transesterification process of waste cooking oil (WCO). Varying FFA percentages in the feedstock revealed that 0-3% FFA did not lead to saponification, while 4-6% FFA triggered the saponification reaction. This implies that feedstock with more than 4% FFA should undergo pre-treatment, also known as esterification, before being used in biodiesel production through transesterification. Additionally, the study addressed the physicochemical properties of biodiesel produced from feedstocks with varying FFA percentages. The acid value demonstrated a direct proportionality to the FFA percentage of the feedstock, while the saponification value showed an inverse relationship. The other physicochemical properties such as viscosity, density, and moisture content were found to be unrelated to the quality of biodiesel in this study. Instead, the saponification value test and Gas Chromatography (GC) analysis indicated the influence of the FFA percentage in the feedstock on the production of biodiesel. The study can be further extended to use waste composite as a catalyst, making both the oil and catalyst from waste materials.

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6.0 CONFLICT OF INTEREST

The authors declare no conflicts of interest.

7.0 AUTHORS CONTRIBUTION

G.P. Maniam (Conceptualization; Visualisation; Supervision; Funding acquisition)

H.S. Lim (Writing – Original draft; Methodology; Formal analysis; Investigation)

N.M. Hussin (Conceptualization; Visualisation; Supervision)

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