Synthesis of Biodiesel from Waste Cooking Oil by Alkali Catalyzed Transesterification

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Abstract. Biodiesel is an alternative fuel to petroleum diesel because it is renewable sources and considered to be smart waste management solution for used cooking oil since plenty amount of waste cooking oil is being produced from households and restaurants. Irresponsible practice to get rid of this waste is by pouring it down the sink or drain. However, this practice causes damage mainly to the ecosystem (water pollution). In this study, biodiesel was synthesized from waste cooking oil by alkali catalyzed transesterification method. Alkali transesterification is a reaction between oil and alcohol in presence of alkali catalyst. Methanol and sodium hydroxide were used in this transesterification. Treated oil and sodium methoxide mix at constant temperature for certain period to yield methyl ester and glycerin. Characterization was carried out by using thermal gravimetric analysis, differential scanning calorimetry, and normal analytical methods mainly for density and viscosity. This study shows that biodiesel was successfully synthesized from waste cooking oil and characterization of the synthesized biodiesel was almost similar to the conventional diesel. From this, it can be concluded that pollution caused by disposal of waste cooking oil can be turned into value-added product.

Keywords: Biodiesel, Waste Cooking Oil, Alkali Transesterification, Alternative fuel

1. Introduction

Zero emission concept could be defined as using resources effectively and prevent resources depletion, or activities that are being carried out to curb waste generation, reduce emissions, in order to achieve the maximum usage of wastes through loop recycling[1]. This research goes online with this concept in which waste cooking oil was utilized to synthesize biodiesel. Currently, fossil fuel is depleting as a matter of fact this resource is non-renewable thus there will be time where no more or limited amount of fossil fuel available.

Biodiesel is a non-petroleum based fuel and also renewable fuel that consists of alkyl esters derived from either the transesterification of triglycerides with low molecular weight alcohol, such as methanol or ethanol. Problems encountered in replacing triglycerides for diesel fuels are mostly related with their high viscosity, low volatility, and polyunsaturated character [2]. The flow and combustion properties of biodiesel are similar to petroleum based diesel and, therefore, can be used as a substitute for diesel fuel or more commonly in fuel blends. Another significant advantage of biodiesel is its low emission profile and its oxygen content of 10-11%. Biodiesel is called the
environmentally friendly bio-fuel since it provides a means to recycle carbon dioxide. In other words, biodiesel does not contribute to global warming. Biofuels are less pollutant than fossil fuels because they emit less harmful chemical substances during combustion and their production processes tend to be cleaner[3]. Biodiesel is an alternative liquid fuel that can substantially replace diesel and reduce exhaust pollution and engine maintenance costs. Biodiesel can be also used alone, or blended with diesel in any proportions. The use of alkaline catalysts in the transesterification of waste cooking oil is the most commonly used technique by the industry; however, it has several limitations. The most commonly used catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH) which are high sensitive to the purity of the reaction being affected by the water and free fatty acids content [4].

The vegetable oil, animal fat and waste oils can produce water pollution if the waste oil pours into sink or drains which cause waste to coagulate and block public drains. Vegetable oil, animal fat and waste oils insoluble with water and become lump at low temperature. Untreated sewage mixture with vegetable oil, animal fat and waste oils in the water causes oxygen levels to drop drastically, sewage fungus covers the bed of the drains like a blanket and in more severe cases the river can no longer support fish, insects and animals that live in and around the water.

Biodiesel can be blended and used in many different concentrations, including B100 is pure biodiesel, B20 is combination between 20% biodiesel and 80% petroleum diesel, B5 is combination between 5% biodiesel and 95% petroleum diesel and B2 is combination between 2% biodiesel and 98% petroleum diesel.

Diesel engines with vegetable oil, animal fat or waste oils, suffer from operational and durability problems for long-term operation as vegetable oils are much more viscous, relatively more reactive to oxygen, and have higher cloud point and pour point temperatures than conventional diesel. These problems can be solved if the vegetable oil, animal fat and waste oils are chemically modified to biodiesel, which is similar in characteristics to diesel. Engines functioning on B20 show similar fuel consumption, horsepower, and torque to engines running on conventional diesel. Biodiesel has a higher cetane number which is a measurement of the ignition value of diesel fuel and higher lubricity which is the ability to lubricate fuel pumps and fuel injectors. Therefore, biodiesel production is a very attracted topic within researchers, politicians and investors worldwide.

Main objective of this research is to use filtered waste cooking oil that is free from food particles to produce biodiesel by using alkali transesterification. Meanwhile characterize the produced biodiesel and compare it with the conventional diesel.

2. Methodology

The most practical and common way of producing biodiesel is by transesterification. This reaction of oil in the presence of alcohol and catalyst to yield biodiesel and glycerol. Waste cooking oil was collected from local restaurants around Teluk Kalong, Kemaman, Malaysia. Sodium hydroxide in powder form, methanol, and isopropanol were purchased from Permula Saintifik Sdn Bhd, Kemaman, Terengganu. The waste cooking oil was filtered to remove food particles. To make it filter smoothly, the oil was heated around 35°C. After the waste cooking oil was filtered it was heated to remove water at 100°C.

To determine the correct amount of NaOH required, a titration was performed on the oil being transesterified. Titration procedure was carried out by mixing 10 ml of isopropyl alcohol, 1 ml sample of waste cooking oil and 2 drops of phenolphthalein in a small beaker to perform titration.

Normally, the amount of methanol needed is 20% from the volume of waste cooking oil. Different waste cooking oil can have different densities depending on what type of oil it originally was and how long it was used in the deep fryer.

Temperature applied for treatment waste cooking oil between 48 and 54°C. Heating was carried out by using hot plate that capable of using magnetic stirrer. Excessive speed stir may cause splashing and bubbles through vortexing and reduces mixing efficiency. Sodium methoxide was poured into the waste cooking oil while stirring. The mixture was stirred for one hour. The transesterification process separates into methyl esters and glycerin.
Solution was allowed to cool for at least eight hours. The methyl esters or biodiesel floats on the top while the denser glycerin congeals on the bottom and forming a hard-gelatinous. The obtained pH of treated biodiesel between 8 and 9. This pH indicates that the biodiesel is alkaline because of sodium hydroxide used as catalyst. Therefore the water washing step is necessary to get rid of any remaining catalyst, soap, methanol, or free glycerol from the biodiesel. To remove water, equal amount of distilled water was added into biodiesel in a separatory funnel. After shaking aggressively two layers will be formed. Removes the bottom layer (water) and repeat the same till pH reaches 6 or 7. Since micro particle of water in biodiesel make the colour of biodiesel like orange juice. The presence of water in fuel can damage the diesel engine. Therefore water must be removed from fuel by keeping the sample at temp 50 oC for a few day until it become to yellow or orange clear color to ensure all water evaporated.

Characterization was carried out by using Thermal Gravimetric Analysis as one of the suitable method for quantitative analysis for the produced biodiesel due to the high temperature difference between the weight loss temperatures of biodiesel and conventional diesel and by this method we can determine the conversion. Analysis was carried out by using Mettler Toledo TGA/SDTA 851 E. Temperature was in the range between 25°C and 350°C, heating rate 10°C per minute and 100ml per minute of air flow was used.

Energy and temperature related to transitional materials changes were characterized by using Differential Scanning Calorimetry (DSC). Under isothermal conditions DSC can detect the difference in energy required for the substance and known reference material that inert thermally, while both are controlled difference temperature so that the sample and reference are sustained. Analysis was carried out by using Mettler Toledo DSC 822 E with temperature range between 25to 500°C, heating rate 10°C per minute and 100ml per minute of air flow was used. Other parameters such as; density, viscosity & others were evaluated by conventional methods.

3. Results and discussion

3.1 Thermal gravimetric analysis

From the experiments conducted, the transesterification of waste cooking with sodium methoxide obtained was 65% of biodiesel and 35% of glycerin. There are many factors presumably affect the yield of methyl ester and glycerin such as; method used, type and concentration of alcohol and catalyst, temperature, pressure and other factors.

Thermal gravimetric analysis relates the difference in weight of sample caused by physical changes. Parameters either physical such as; sublimation, evaporation and condensation or chemical such as; degradation, decomposition, oxidation could be plotted versus time or temperature. Or could be defined as determination of material thermal performance. Idea lies on how the thermal gravimetric curve obtained either by illustrating mass (mg) or percentage of weight loss against temperature or time. On degradation process, the sample loses the mass because the sample volatiles and the sensor detect the consistent mass loss.
Figure 1: Thermal gravimetric curve for biodiesel.

The first derivative of the thermal gravimetric curve (DTG) can be identified by knowing the beginning and the end of weight loss phase displaying range of temperature where specific decomposition reaction occurs, at the same time recognize the composition of the residue after combustion.

As shown in Figure 1, the biodiesel starts to thermally decompose at and continues its thermal degradation at 170.37°C and the mass start decrease until it is completely degrade at 218.21°C. The weight loss was recorded as 16.5906 mg and overall weight loss percentage was around 91.66% on degradation temperature range. After degradation at 218.21°C, 1.5094 mg of residue obtained which represents approximate 8.34% from the total weight.

Figure 2: Thermal gravimetric curve for conventional diesel.

At the same time the conventional diesel starts to thermally decompose at and continues its thermal degradation at 155.19°C and the mass start decrease until it is completely degrade at 220.85°C. The weight loss was recorded 14.7706 mg and overall weight loss percentage was around 84% on degradation temperature range. After degradation at 220.85°C, 2.8294 mg of residue obtained was approximate 16% as shown in Figure (2).
Figure 3: Thermal gravimetric curve for B5.

B5 diesel starts thermally to decompose at 155.81°C and the mass start decrease until it is completely degrade at 219.55°C. The weight loss was recorded 15.9361 mg and overall weight percentage lost was around 87.56% on the degradation temperature range. After degradation at 220.65°C, 2.2634 mg of residue was obtained which represents approximately 12.44% as shown in Figure 3.

Figure 4: Thermal gravimetric curve for B10.

For B10 diesel the thermal decomposition was started at 168.09°C and the mass start decreasing until it is completely degrade at 221.57°C. This is clearly illustrated in Figure 4. The weight loss was recorded 16.1033 mg and overall weight loss percentage was around 84% on the degradation temperature range. After degradation at 221.57°C, 2.8294 mg of residue was obtained which form approximately 16%. Summary of the all above mentioned cases depicted in Figure 5.
3.2 Thermal stability

Based on Figure 6 the biodiesel showed higher thermal stability compared to the conventional diesel, B5 and B10. Non–isothermal TGA is more suitable for analyzing thermal stability characteristics of biodiesel rather than its relative oxidative stability [5]. The thermal gravimetric curves of the samples were similar to conventional fuel, but the different is the weight loss. The difference is in the temperature range in which vaporization of biodiesel, and conventional diesel, B5 diesel and B10 diesel occurs, were around 170.37°C, 155.19°C, 155.9°C and 168.09°C respectively.

It is clear that molecules of biodiesel are larger than conventional biodiesel due to its chemical composition (mainly fatty acid methyl esters). Due to his fact significant difference in the thermal stability occurred.
Similarity was found between vaporization curve profiles of all mixture ratios with the curve profile of fossil diesel. Increasing concentration causes curves displacement toward higher temperatures as a result relatively higher stability of the mixtures compared to the pure fossil diesel.

Clear idea about the merits from preference of using biodiesel is related to the environmental issues as shown in Figure 7. Biodiesel forms less residue compared to the conventional diesel. Low residue is preferable as obtained from this work where blending of biodiesel gives noticeable reduction in the carbon residue and enhances the fuel engine combustion.

![Figure 7: Residue & overall weight loss for different biodiesel compositions.](image)

As shown in Figure 7, conventional diesel formed more residue compared to biodiesel and diesel blend with biodiesel. Formation of residue could be attributed to the incomplete burning of impurities, catalysts, additives and ash in fuel [6]. Aromatic compounds also considered to be another source to form residue and soot after fuel burning [7]. The effect of accumulated residue inside the combustion chamber of piston ring can damage the engine cylinder liner due to formation of more soot. The main reason for formation of residue in biodiesel is the composition of fatty acid methyl ester that forms few impurities and nearly no aromatic compounds [8]. Oxygen exists in biodiesel is high compared to conventional one which leads to complete combustion, hence less carbon residue formation after the burning process. A lower carbon residue indicates that complete combustion, and thus is better for liquid fuel [9]. The most common mix or biodiesel fuel blends is referred to as “B20” containing 20% biodiesel by volume, and 80% conventional diesel can usually be used in unmodified diesel engines. Biodiesel can be used in its pure form (B100) however, certain engine modifications may be necessary to avoid maintenance and performance problems. The greater the percentage of biodiesel fuel in its blend, the more ecology-friendly is the fuel. Table 1 shows comparison between pure biodiesel and blended diesel in term of degradation temperature, overall weight loss and residue.

| Table 1: Comparison the biodiesel, conventional diesel, B5 and B10 diesel. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Biodiesel       | Conventional    | B5 Diesel       | B10 Diesel      |
| Degradation     | Start           | 170.37          | 155.19          | 155.81          | 168.09          |
| Temperature (°C)| End             | 218.21          | 220.85          | 219.55          | 221.57          |
| Overall Weight Loss (%) | 91.66          | 83.92           | 87.56           | 88.48           |
| Residue (%)     | 8.34            | 16.08           | 12.43           | 11.52           |
3.3 Differential scanning calorimetry

According to Figure 8, biodiesel melting point starts at 15.48°C. Since the curve in moving downward, it can be classified as exothermic (a transition that releases energy). The specific energy for biodiesel was -50.97 J/g. At second transition, the peak was at 249°C and the specific energy was -364.63 J/g.

As expected for conventional diesel there is no melting point as shown in Figure 9. Reason behind this could be related to the set temperature which is below 0 °C (temperature where diesel become solid). On the other hand exothermic transition occurred on 199°C and the specific energy was -436.25 J/g.
Figure 10 shows that B5 diesel melting point started at -25.01°C and the maximum melting point was -3.23°C. Therefore it can be classified as exothermic. The specific energy for biodiesel was -41.75 J/g. At second transition, the peak was at 203°C and the specific energy was -410.39 J/g.

Figure 11 shows that, B10 diesel starts melting at -25.01°C and the maximum melting point was -2.07°C. Similarly it can be classified as exothermic. The specific energy for biodiesel was -39.85 J/g. At second transition, the peak was at 202°C and the specific energy was -384.65 J/g.

3.4 Other characterization parameters

3.4.1 Density
One of the most important characteristics for the biodiesel fuel is density since the fuel injection mechanism solely depends on the volumetric system. Based on that if the density of biodiesels is high, mass delivery of fuel into the combustion chamber will be high also. In other words more particulate matter will be formed due to the low efficiency for fuel atomization [10].
Typical density of biodiesel is 0.8729 kg/L at 27°C while conventional diesel is 0.8248 kg/L. Based on Table 2, the density for biodiesel is 0.8729 kg/L indicating that higher than conventional diesel. Reason for that could be attributed to the saturation fatty acids which can increase the density. Density can be changed if we change either pressure or temperature. Increasing pressure always increases the density of materials. At the same time increasing temperature generally decreases the density. Oxidation of fuel also affects the density. The molecular weight and oxidation of fuels produce by-products and sediment that increase the mass of fuel consequently increment in the density [11].

Table 2: Comparison density between biodiesel & conventional diesel.

| Biodiesel  | Conventional Diesel | Unit |
|------------|---------------------|------|
| 0.872904   | 0.8248              | g/ml |
| 0.872904   | 0.8248              | kg/l |
| 872.904    | 824.8               | kg/m³|

3.4.2 Viscosity

Another important property of biodiesel is the viscosity which affects the process of fuel injection equipment mainly under low temperatures. Increasing viscosity makes fluid thicker, hence affects the fluidity of the fuel. High viscosity causes gentle flow of the fluid, while low viscosity causes rapid flow. Biodiesel has viscosity almost similar to diesel fuels because the transesterification of oils is the process to decrease the viscosity of the oil and make it similar to the conventional diesel. High viscosity drives to worse atomization of the fuel spray and less precise function of the fuel injectors. Soot deposit on injectors, certain components deposit of piston, inlet and outlet valves and fuel filter plugging can be caused by high viscous fuel [12]. Viscosity influences the fuel atomization and volatility. Higher viscosity cause inefficient of fuel atomization as consequence deterioration in the combustion efficiency [13]. Flow at low temperature can cause delay in ignition during start up due to high viscosity [14].

Table 3: Comparison viscosity between biodiesel conventional diesel.

| Biodiesel  | Conventional Diesel | Unit    |
|------------|---------------------|---------|
| 4.0627     | 3.2569              | Pa . S  |
| 4062.7498  | 3256.8979           | cP      |
| 4.6543     | 3.9487              | cSt     |
| 4.6543     | 3.9487              | mm²/s   |
The viscosity obtained for biodiesel and conventional biodiesel were 4.6543 mm$^2$/s and 3.9487 mm$^2$/s respectively as shown in Table 3. It is worthy to mention here usually viscosity of pure biodiesel is higher than blended and commercial biodiesel.

### 3.4.3 Cold flow properties

Figure 12 shows sample of synthesized biodiesel that left in the freezer for few days. Biodiesel became solid when the temperature was below 15℃. This can also determine that the biodiesel not suitable for extremely low temperature because the biodiesel become more viscous and can damage the engine due to incomplete combustion compare to conventional one. The conclusion from the fact that biodiesel needs to be heated or to be used under moderate weather like in Malaysia and other tropical countries where temperature always higher that 10 ℃. In order to prevent solidification engine must be modified so that burning of biodiesel in the combustion chamber can be performed efficiently or by adding additives that can be able to change the fuel structure.

### 3.4.4 Specific energy

![Specific energy comparison for different biodiesel compositions.](image)
Calorific value is an important parameter in the selection of a fuel therefore the energy contained in the fuel could be defined as the specific energy and can be evaluated by measurement of heat that produced during complete combustion when specified quantity used.

Figure 13 shows that, conventional diesel (B0) has higher specific energy compared to conventional diesel. This means conventional diesel releases more energy compared to biodiesel. Energy increase depends on the blending ratio. The main elements of conventional diesel during combustion are; carbon, hydrogen, oxygen, and sulphur and the calorific value of a fuel is directly related to its elemental composition and increases with the chain length of molecules. [15 &16].

Chemical composition is the main reason for producing high calorific value. Conventional diesel however have low oxygen content and higher amount of carbon compared with biodiesel[17]. It is well known that when the value of oxygen in fuel structure is high, carbon and hydrogen will be low as a result low energy will be produced. Oxygen works as stabilizer in fuel at the same time carbon and hydrogen are foundation of thermal energy [18].

4. Conclusion
It is estimated that conventional diesel will be in high demand in the future since conventional diesel is produce from distillation of crude oil and one day the fossil fuel will be depleted. Biodiesel was successfully synthesized using alkali catalyzed transesterification method from waste cooking oil. This study showed that characterization of the biodiesel was almost similar to conventional diesel. Nevertheless, most countries use biodiesel blend with conventional diesel. Even though, The B10 policy in Malaysia effectively mandates the use of palm oil in diesel andis one ofthe measures the government has initiated to support the palm oil industry. At the moment diesel sold has 7% biodiesel content and is called B7.

At present the cost for synthesizing biodiesel is high compared to conventional diesel due to pure and high grade chemical use. Cost can be reduced if we use commercial chemicals at the same time blending biodiesel with conventional diesel.

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