Density, flash point, viscosity, and heating value of waste cooking biodiesel (B20) with bioadditive essential oil (lemon, lemongrass, eucalyptus)

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Abstract. This research is motivated by the decreasing of fossil fuels in the earth while the level of consumption of fossil fuels is getting higher from year to year, so the need for alternative fuels increases, one of which is biodiesel. The existence of studies in preparing biodiesel as an alternative fuel is essential. This study aimed to determine the effect of bioadditive essential oils (lemon, lemongrass, and eucalyptus) on biodiesel fuels' thermophysical properties. The method used in this study is using esterification and transesterification step for making biodiesel. The character of biodiesel can be recognized by testing the physicochemical properties which consist of kinematic viscosity, density, flash point, and low heating value tests. The results show that the density of all samples is not significantly different in value. Increased density occurs in each sample due to the higher concentration of essential oils. As the concentration of essential oil increases, flashpoint tends to decrease. Low heating value tends to decrease with the increase concentration of essential oil. Kinematic viscosity has a value that tends to decrease with the addition of essential oil concentrations.

1. Introduction
Consumption of fuel oil in Indonesia has continuously been increasing since 2017, where Fuel consumption reached 55.400.604.901 liter when compared to 2016. There was an increase of about 13.8 percent [1]. The increase in fuel consumption is not compensated with the availability of natural resources which has continued to decline. During the last ten years, oil production tends to decrease. Production in 2009 was 346 million barrels, while in 2018, it became 283 million barrels [2]. The use of fuel is not reduced, then will be more critical. Fuel consumption percentage breakdown by sector is as follows: transportation (40%), industry (36%), households (16%), commercial (6%) and others (2%) [3]. The availability of fossil fuels in the oil sector can only support energy for the next nine years [3], if within the next nine years, new sources of fuel are not found.

Biodiesel is one of the most promising alternatives. Biodiesel is defined as a long chain fatty acid mono-alkyl ester, usually produced from plant oils, animal fat or other lipids [4]. Advantages of biodiesel over fossil diesel is biodegradability, reduced toxicity, higher flash point, improved cetane number, and improved lubricity [5]. The biodiesel parts can be made from waste cooking oil using the transesterification method [6]. The transesterification reaction is the reaction of the production of
Fatty Acids Methyl Ester (FAME) or biodiesel and glycerol by reacting triglycerides with alcohol and producing side products in the form of glycerol [7]. Biodiesel quality must comply with the specified fuel standards. The quality of biodiesel can be improved by adding additives. Additives can contribute to improving performance and reducing exhaust emissions from the engine [8]. Among several types of biodiesel, bioadditive was chosen because of the weaknesses of biodiesel fuels for the fuel mixing process: density, toxicity, viscosity, energy content, economic viability, additive solubility, automatic ignition temperature, flash point, and cetane number [8].

The solution to reduce biodiesel resistance to lower energy content and oxidation is addition of bioadditive essential oil. Bioadditive essential oil is an additional substance that has an oxygen content that can improve thermophysical properties. This study analyzes density, kinematic viscosity, flash point, and low heating value of biodiesel from waste cooking oil with the addition of bioadditive essential oil. The essential oils used are lemon, lemongrass, and eucalyptus with variations of B20 + 0.1% lemon oil; B20 + 0.15% lemon oil; B20 + 0.2% lemon oil; B20 + 0.1% lemongrass oil; B20 + 0.15% lemongrass oil; B20 + 0.2% lemongrass oil; B20 + 0.1% eucalyptus oil; B20 + 0.15% eucalyptus oil; B20 + 0.2% eucalyptus oil; B20 (pure biodiesel-diesel), essential oil is used for additive because essential oil can improve density, decrease viscosity, flash point, and heating value, other advantages is essential oil can decrease emission and improve oxidation stability [8]. Differences in the amount of variation are used to determine the effect of the quality of biodiesel with bioadditive additions.

2. Methods
This study uses 10 types of fuel variations, including B20 (20% biodiesel mixed with 80% pure diesel oil), B20 + 0.1% lemon oil; B20 + 0.15% lemon oil; B20 + 0.2% lemon oil; B20 + 0.1% lemongrass oil; B20 + 0.15% lemongrass oil; B20 + 0.2% lemongrass oil; B20 + 0.1% eucalyptus oil; B20 + 0.15% eucalyptus oil; B20 + 0.2% eucalyptus oil. Figure 1 shows the fuel that has been mixed with bioadditive essential oil.

![Figure 1. Biodiesel B20 with the addition of bioadditive essential oil.](image)

2.1. Sample Preparation
The processes of making biodiesel uses two chemical reactions, namely esterification, and transesterification [9]. Esterification is used to reduce levels of FFA contained in waste cooking oil. The esterification process in waste cooking oil reacts with methanol in a ratio of 1:6 using a 1% wt H₂SO₄ catalyst at 60 °C, then stirred for 120 minutes. After the FFA level has decreased to less than 2%, it is continued with the transesterification process for making biodiesel. The transesterification process occurs between the used cooking oil and methanol (1: 6) with the help of the KOH catalyst at 60 °C for 120 minutes. A 24-hour precipitation process is carried out to separate biodiesel and glycerol, which is the result of the transesterification reaction. Furthermore, biodiesel is washed with distilled water three
times or more until it is clear, then it is heated at temperatures above 100 °C to remove its water content [9, 10].

The next step is mixing biodiesel and diesel fuel with a comparison of 20% waste cooking oil biodiesel and 80% diesel fuel mixed using a magnetic stirrer for 30 minutes. The finished B20 is added with bioadditive essential oil. The process of mixing B20 with essential oil is carried out using an ultrasonic homogenizer (KG-MT-UPDHM-3N) set at an amplitude of 50% for 2 minutes to prevent the danger of chemical properties of the fuel and the fuel element. The mixing process must take no more than 2 minutes to avoid dangerous chemical properties and the element itself. The temperature is maintained between 30 – 32 °C to maintain chemical properties [4].

2.2. Density Test
Tests are carried out by weighing as much as 50 ml of biodiesel at a temperature of 40 °C in analytical balance. The mass that has been obtained is substituted into Equation 1 [11].

\[ \rho = \frac{m}{V} \left( \frac{kg}{L} \right) \]  (1)

2.3. Kinematic Viscosity Test
The NDJ-8S viscometer is used in this test by inserting biodiesel samples into a 300 ml beaker glass with a temperature of 40 °C. The data obtained in the form of dynamic viscosity are then converted to kinematic viscosity using Equation 2 [12].

\[ \text{Kinematic Viscosity (cSt)} = \frac{\text{Dynamic Viscosity (cP)}}{\rho} \left( \frac{cP}{kg/L} \right) \]  (2)

2.4. Flash Point Test
Flash point test uses the Flash Point Tester SYD - 3536 with the process of taking data using standardization ASTM D 93, IP 34 or ISO 2719.

2.5. Heating Value Test
The HHV value must be obtained by using the XRY-1A Bomb Calorimeter. After the HHV value is obtained, it is substituted in Equation 3 with the latent heat of water vaporization value of 3.052 MJ / kg [13].

\[ LHV = HHV - 3.052 \left( \frac{MJ}{kg} \right) \]  (3)

3. Results and Discussion
Figure 2 shows biodiesel density with bioadditive essential oil. The highest density is biodiesel B20 mixed with lemon oil with a concentration of 0.2% with a value of 0.8405 kg / L. The lowest density is on biodiesel B20 without mixture which is 0.8363 kg / L. Essential oil has a higher density than biodiesel B20, so the density value increases after mixing [14]. The density value of eucalyptus oil is 0.914 kg / L [8], the density value of lemongrass oil is 0.891 kg / L [15], and the density value of lemon oil is 0.853 kg / L [16]. The density value increase with the increase in additive concentration.

Figure 3 shows that the highest kinematic viscosity is in biodiesel without mixture with a value of 5.5 cSt while the lowest viscosity is in biodiesel B20 + 0.2% Eucalyptus Oil at 5.36 cSt. Essential oil has a lower viscosity than biodiesel B20, so that the viscosity value decreases after mixing. The viscosity of eucalyptus oil is 1.66 cSt [8], the viscosity of lemongrass oil is 4.45 cSt [15], and the viscosity of lemon oil is 1.06 cSt [16]. Kinematic viscosity value decreases with increasing concentration of essential oil.
Table 1. Thermophysical properties biodiesel B20 with bioadditive essential oil.

| Sample                     | Density (kg/L) | Flash Point (°C) | High Heating Value (HHV) (MJ/kg) | Low Heating Value (LHV) (MJ/kg) | Dynamic Viscosity (cP) | Kinematic Viscosity (cSt) |
|----------------------------|----------------|------------------|----------------------------------|---------------------------------|------------------------|--------------------------|
| B20                        | 0.8363         | 104              | 43.70                            | 40.64                           | 4.6                    | 5.500                    |
| B20 + 0.1% Eucalyptus Oil  | 0.8366         | 96               | 43.59                            | 40.53                           | 4.6                    | 5.498                    |
| B20 + 0.1% Lemongrass Oil  | 0.8377         | 104              | 43.02                            | 39.97                           | 4.6                    | 5.491                    |
| B20 + 0.1% Lemon Oil       | 0.8365         | 104              | 43.94                            | 40.89                           | 4.6                    | 5.499                    |
| B20 + 0.15% Eucalyptus Oil | 0.8374         | 96               | 43.33                            | 40.28                           | 4.53                   | 5.414                    |
| B20 + 0.15% Lemongrass Oil | 0.8386         | 104              | 42.15                            | 39.10                           | 4.6                    | 5.485                    |
| B20 + 0.15% Lemon Oil      | 0.8379         | 102              | 43.62                            | 40.57                           | 4.6                    | 5.490                    |
| B20 + 0.2% Eucalyptus Oil  | 0.8395         | 94               | 42.91                            | 39.86                           | 4.5                    | 5.360                    |
| B20 + 0.2% Lemongrass Oil  | 0.8392         | 102              | 41.34                            | 38.29                           | 4.57                   | 5.442                    |
| B20 + 0.2% Lemon Oil       | 0.8405         | 98               | 43.47                            | 40.42                           | 4.57                   | 5.437                    |

Figure 2. Biodiesel density with bioadditive essential oil.

Figure 3. Biodiesel viscosity with bioadditive essential oil.
Figure 4 shows that the highest flash point is in B20 biodiesel without mixture, B20 + 0.1% Lemongrass Oil, and B20 + 0.1% Lemon oil biodiesel at 104 °C. The lowest flash point is on biodiesel B20 + 0.2% Eucalyptus Oil by 94 °C. Flash points decrease with increasing concentrations of essential oils because essential oils have lower flash points compared to biodiesel B20. Flash point eucalyptus oil is 55 °C [8], lemongrass oil is 50 °C [18], and lemon oil is 54 °C [15]. Flash points decrease with increasing concentrations of essential oils.

Figure 5 shows that the highest LHV is in biodiesel B20 + 0.1% lemon oil with a value of 40.89 MJ / kg and the lowest LHV is biodiesel B20 + 0.2% Lemongrass Oil with a value of 37.99 MJ / kg. LHV tends to decrease with increasing levels of essential oil. The LHV value comes from the conversion of the HHV value, the HHV value is strongly influenced by oxygen, carbon, and hydrogen content [17] [16]. The higher oxygen content, the HHV will be decrease. The higher carbon and hydrogen content, the HHV will be increase. Eucalyptus oil has a carbon content of 79.94%, hydrogen 11.63%, and oxygen 8.44% [8]. Lemon oil has a carbon content of 89.93%, hydrogen 9.25%, and oxygen 0.81% [16]. Heating value decrease with increasing concentrations of essential oils.
4. Conclusion
The density of all samples is not significantly different. Each sample experienced an increase in density due to higher concentrations of essential oils. Kinematic viscosity decreases with increasing concentrations of essential oils. Essential oil has a lower viscosity than B20 biodiesel so that the viscosity value decreases after mixing. Flash point decreases with increasing concentration of essential oil because essential oil has a lower flash point than biodiesel B20. Lower heating value (LHV) has decreased with increasing concentrations of essential oils. The LHV value is related to the HHV value which is strongly influenced by oxygen, carbon, and hydrogen content. The higher oxygen content, the HHV will decrease. The higher carbon and hydrogen content, the HHV will increase.

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