Biodiesel from Palm Fatty Acid Distillate (PFAD) and its nature of oxidative stability

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Abstract. Palm Fatty Acid Distillate (PFAD) is relatively cheap and its utilization does not compete with food needs. The availability of PFAD in Indonesia is considered sufficient as a supply of raw material for making biodiesel. This study aims to make biodiesel from PFAD in accordance with SNI 7182-2015 and to determine the best concentration of antioxidant additions. The research stage begins from making biodiesel through esterification reaction at 60 °C for 1 hour and continues with determination of each biodiesel Induction Period (IP) using a modified Rancimat device. PFAD used consisted of 99.85% mole total free fatty acids, consisting of 88.35% mole of saturated fatty acids and 11.5% mole of unsaturated fatty acids. Based on the research results, biodiesel produced meets SNI 7182-2015 from parameters of density, viscosity, alkyl ester content, and oxidative stability but does not fulfil the requirement of water content and value of acid numbers. The average IP in pure biodiesel has reached the minimum standard of 6 hours, which is 6.15 hours. Additions of six antioxidant Z concentrations (0.1, 0.3, 0.4, 0.5, 0.7, and 0.9 ppm) resulted in 0.1 ppm as the best antioxidant concentration in increasing IP to become 11.05 hours.

1. Introduction
Biodiesel is a renewable energy made from vegetable oil, animal fat, and cooking oil. Biodiesel is used as alternative fuel for diesel engines. The availability of PFAD in Indonesia is considered sufficient as a supply of raw material for making biodiesel. The use of biodiesel in Indonesia has increased along with the enactment Minister of Energy and Mineral Resources Regulation No. 12 of 2015 which requires usage biodiesel by 20% (B20) in motor vehicles in 2016 [1]. Moreover, B30 road test has been conducted and resulted in the use of the B30 giving increased engine power; reducing emissions; and giving no negative impact on the engine [2].

On the other hand, biodiesel has shortcomings, especially in terms of storage and distribution. During storage and distribution, biodiesel undergoes oxidation which is marked by a decrease in the value of oxidative stability. This happens because biodiesel has a double bond derived from unsaturated fatty acids that causes easy oxidation [3]. Based on this, most of the stability oxidative properties of biodiesel do not meet established standards. Therefore, antioxidants need to be used to increase oxidative stability on biodiesel [4]. Antioxidants often used are usually synthetic antioxidants because of antioxidants higher efficiency than natural antioxidants. The synthetic antioxidants most commonly used are propyl gallate (PG), pyrogallol (PY), butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT) [5].
Some of the studies that have been carried out up to 2019 and that are used as the basis for this research are a study by Diana and Holik [6] stating that PFAD is not permitted to be used as raw material for cooking oil because it is toxic, research by Ki vivele et all. [3] finding that PY antioxidant is more effective than PG and BHA antioxidants in preventing oxidation of biodiesel with Jatropha Oil as raw material. Xiong et al. [7] also found that PY is the appropriate antioxidant to obtain the best efficiency of biodiesel produced from waste cooking oil. The biodiesel efficiency decreases with increasing operating temperature. Budiastuti et al. [8] and Widarti et al. [9] investigate that addition of different types of antioxidant results in different values of oxidation stability.

Based on those studies, this study utilizes the same source of PFAD [10], as a raw material for making biodiesel and continues by adding higher concentrations of antioxidant to obtain the best antioxidant concentration to meet Indonesia’s standard biodiesel requirements (SNI 7182-2015). The physical and chemical properties of PFAD are also conducted to determine the right reaction to produce high-quality biodiesel.

2. Research methodology

2.1. Raw materials, operating conditions, antioxidant, and analyzed parameters
PFAD as a raw material for making biodiesel was obtained from Research Center of Palm Oil Plantation, North Sumatra. The operating conditions were maintained at temperature of 60 °C, molar ratio of PFAD:methanol = 1:9, H₂SO₄ catalyst loading of 0.5% (v/v), and operation time of 1 hour [10]. PFAD composition analysis was carried out by Chromatography method using Gas Chromatography Mass Spectroscopy (GCMS).

The set-up of the reactor was a three neck rounded flask, completed with reflux condenser, thermometer, and magnetic stirrer. The oil bath heated by an automatic temperature heater was used to maintain the constant operating temperature. The antioxidants added were symbolized as antioxidants Z. Variations in the concentration of antioxidant used were 0.1, 0.3, 0.4, 0.5, 0.7, and 0.9 ppm. Several parameters analyzed to measure the quality of biodiesel were density, viscosity, water content, flash point, acid value, and oxidative stability measure by induction period (IP).

2.2. Induction Period (IP) measuring kit
The IP measuring kit was set up based on principle of Rancimat equipment, which is applied to measure the IP of biodiesel without and with addition of antioxidants. The kit is equipped with air pressure at 25 kPa/hour and heating at 110 °C. The biodiesel sample in this kit is oxidized and its conductivity is measured during operating time with time interval of 15 minutes. Each sample was measured in duplicate (duplo).

3. Results and discussion

3.1. Determination of PFAD composition
The composition of PFAD analyzed using GCMS is presented in Table 1 there are 88.35% mole saturated fatty acids and 11.5% mole unsaturated fatty acids, so that the total free fatty acids in PFAD is 99.85% mole. It justifies that the right reaction to produce biodiesel is the esterification reaction. From Table 1, it can be concluded that PFAD does not contain natural antioxidants, which are usually represented by tetracosapentaen compounds [9,10]. The tetracosapentaen compounds are phenolic compounds having various biological effects such as antioxidant activity through mechanisms as reducing agents, free radical scavengers, metal chelating, dampening of the formation of oxygen singlets, and electron donors [11].
Table 1. Composition of PFAD.

| No | PFAD Composition       | % mole | Chemical Formulae | Notes         |
|----|------------------------|--------|-------------------|---------------|
| 1  | Acetyl Glutamate       | 0.04   | C₇H₁₁NO₅         | Amino acids   |
| 2  | Hexane                 | 0.10   | C₆H₁₄             | Hidrocarbon   |
| 3  | Dodecanoic Acid        | 0.09   | C₁₂H₂₄O₂          | Saturated FFA |
| 4  | Tetradecanoic Acid     | 0.73   | C₁₄H₂₈O₂          | Saturated FFA |
| 5  | Hexadecanoic Acid      | 33.74  | C₁₇H₃₄O₂          | Saturated FFA |
| 6  | Heptadecanoic Acid     | 0.13   | C₁₇H₃₂O₂          | Saturated FFA |
| 7  | Octadecadienoic Acid   | 8.54   | C₁₈H₃₂O₂          | Unsaturated FFA |
| 8  | Octadecenoic Acid      | 39.61  | C₁₉H₃₆O₂          | Saturated FFA |
| 9  | Octadecadienoic Acid   | 2.80   | C₁₈H₃₂O₂          | Unsaturated FFA |
| 10 | Stearic Acid           | 12.34  | C₁₈H₃₆O₂          | Saturated FFA |
| 11 | Oleic Acid             | 0.13   | C₁₈H₃₄O₂          | Unsaturated FFA |
| 12 | Octadecatrienoic Acid  | 0.03   | C₁₈H₃₀O₂          | Unsaturated FFA |
| 13 | Octadecenoic Acid      | 0.28   | C₁₉H₃₆O₂          | Saturated FFA |
| 14 | Octadecenoic Acid      | 0.53   | C₁₉H₃₆O₂          | Saturated FFA |
| 15 | Eicosanoic Acid        | 0.91   | C₂₀H₄₀O₂          | Saturated FFA |

FFA = Free Fatty Acid

3.2. Biodiesel production

Based on the amount of FFA contained in the PFAD, making of biodiesel was conducted through an esterification process. The esterification reaction conversion resulted in 99.85%. Amelia et al. obtained the esterification reaction conversion of 97.8%, with the same operating conditions, namely the esterification reaction time for 1 hour at 60°C using the same reactor set up [10]. A difference of only about 2% can justify the PFAD raw material used is the same but becomes a little bit different, may be due to the storage factor of the PFAD.

Table 2. Characteristics of pure biodiesel.

| No | Parameter                             | Test Results | SNI 7182-2015 | Notes       |
|----|---------------------------------------|--------------|---------------|-------------|
| 1  | Density at 40°C (kg/m³)               | 861.044      | 850-890       | fulfil      |
| 2  | Viscosity at 40°C (cst)               | 2.5526       | 2.3-6.0       | fulfil      |
| 3  | Water content (%)                     | 0.09 %       | Max, 0.04     | not fulfil  |
| 4  | Acid value (mg KOH/g)                 | 7.8321       | Max, 0.6      | not fulfil  |
| 5  | Alkyl Ester (% mass)                  | 97.8         | Min, 96.5     | fulfil      |
| 6  | Oxidative Stability (hours)           | 6.1 6        |               | fulfil      |

Table 2 shows the results of analysis of density, viscosity, alkyl ester content, and oxidation stability in the biodiesel produced, which are in accordance with Indonesian Standard, SNI 7182-2015. The water content and acid value, however, do not comply with SNI 7182-2015. This might be due to not enough preheating time to reduce water content in the PFAD before esterification process [9].

3.3. Determination of IP of biodiesel

Measurement of the value of the average Induction Period (IP) on pure biodiesel has reached the minimum standard of 6.15 hours, as shown in Table 2 Variations of antioxidant concentrations were applied to resulting biodiesel and its IP were measured to observe the effect of addition of increasing antioxidant concentrations. Table 3 shows that the higher the antioxidant concentrations added, the higher IP obtained. From this Table and in terms of economics, it can also be concluded that the best concentration of antioxidant Z added to the biodiesel complying with the SNI 7182-2015 is 0.1 ppm.
Table 3. Induction Periods of Biodiesel with and without antioxidant addition.

| No | Antioxidant Z concentration (ppm) | IP (hours) |
|----|----------------------------------|------------|
| 1  | 0                                | 6.15       |
| 2  | 0.1                              | 11.05      |
| 3  | 0.3                              | 13.10      |
| 4  | 0.4                              | 13.83      |
| 5  | 0.5                              | 15.34      |
| 6  | 0.7                              | 17.93      |
| 7  | 0.9                              | 19.09      |

4. Conclusion
The biodiesel making and determination of effect of addition of increasing antioxidant concentrations have been successfully carried out. The biodiesel produced meets the SNI 7182-2015 from parameters of density, viscosity, alkyl ester content, and oxidative stability, but does not fulfill the requirement of water content and value of acid numbers. The average IP in pure biodiesel has reached the minimum standard of 6 hours, which is 6.15 hours. The best antioxidant concentration in increasing IP of biodiesel, fulfilling the SNI 7182-2015 is 0.1 ppm, which gave an IP of 11.05 hours.

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