Effect of Storage towards Oxidation Stability and Physical Properties of Biodiesel from Palm Fatty Acid Distillate (PFAD)

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Abstract. Biodiesel is an alternative fuel for diesel machines, forming from vegetable oil, animal fat, and cooking oil. The use of biodiesel increases with the enactment of Indonesian Ministerial Regulation of Energy and Mineral Resources No. 12/2015, which requires the use of biodiesel (B100) by 20% in motorized vehicles, starting from January 2016. Palm Fatty Acid Distillate (PFAD) is a by-product of the vegetable oil industry, that can be converted into biodiesel. PFAD used in this research was obtained from the Palm Oil Plantation Research Center of North Sumatra, with free fatty acid content of 95.2 %mol. PFAD, which was converted to biodiesel through an esterification reaction is 99.6%, with molar ratio of PFAD: Methanol of 1:9 and addition of sulfuric acid catalyst of 0.6% v/v methanol. Analysis of oxidative stability in biodiesel was carried out using Rancimat method. Biodiesel stored for approximately one month has an Induction Period (IP) of 5.25 hours, decreases from 6.15 hours without storage. Storage time for biodiesel can be extended by the addition of antioxidant X. In terms of economy, the optimum antioxidant X concentration added to biodiesel is 0.06 ppm. Biodiesel stored for approximately one month with addition of 0.06 ppm antioxidant X, has an Induction Period (IP) of 6.34 hours. Reaction rate constant of antioxidant X in biodiesel at temperature of 110°C is 0.0042 m⁻¹ and the critical concentration of antioxidant X at 110°C is 7.618 x 10⁻⁶ M.

Keywords: antioxidant, biodiesel, induction period, Rancimat method, storage

1. Introduction

The American Society for Testing and Materials (ASTM) in 2008 defines biodiesel as fuel contains monoalkyl esters of long chain fatty acids, which derived from renewable fats such as vegetable oils or animal fats that meet the ASTM D6751 requirements [1]. The use of biodiesel as an alternative fuel increases with the enactment of the Indonesian Minister of Energy and Mineral Resources Regulation No.12 Year 2015. This regulation obliges the use of biodiesel (B100) by 20% in motorized vehicles, starting from January 2016 [2]. The process of biodiesel production includes reactions between raw materials, which can be in the form of vegetable oils and animal fats, with alcohol compounds to form alkyl (methyl or ethyl) esters. Until now, Crude Palm Oil (CPO) is still a mainstay as a raw material for biodiesel synthesis [3]. The side product of CPO processing, namely Palm Fatty Acid Distillate (PFAD) which is a non-edible material can be used as a raw material for producing biodiesel. The process of processing crude palm oil can produce 73.5% oleate; 21% stearic; 5% palm fatty acid distillate (PFAD) and 0.5% other ingredients.
In general, PFAD contains free fatty acids between 80% to more than 90%. The fatty acids contained in PFAD can be converted into fatty acid methyl esters. With the potential for the availability of PFAD of around 0.21 million tons per year, it can produce 0.189 million tons of fatty acid methyl ester (biodiesel). This value is equivalent to 3.78 million tons or 4195.8 million liters of biodiesel per year [4]. PFAD is very suitable to be used as a raw material for the manufacture of biodiesel. This side product from palm oil processing is toxic so its use does not compete with food needs and the price of PFAD is relatively cheap.

Kivivele et al. [5] mentioned that the shortcomings in biodiesel are in terms of storage and distribution. The double bonds in biodiesel cause biodiesel to be easily oxidized so that antioxidants are needed. Various studies have been carried out on biodiesel from various types of raw materials. Budiastuti et al. [6] obtained the results of Induction Period (IP) on biodiesel made from PFAD raw material at 1.7 hours and with the addition of antioxidant X Induction Period (IP) at 7.1 hours.

With the abundance of PFAD as a biodiesel feedstock, it is important that this research observes the effect of storage on oxidative stability and physical properties of PFAD-based biodiesel to obtain biodiesel that can be stored for a long time with oxidative stability that is still maintained in accordance with the SNI 7182-2015.

1.1. Esterification Reaction

Esterification is the process of forming esters from carboxylic acids. Esterification occurs when carboxylic acids react with alcohol. The esterification reaction can occur and be accelerated with the addition of acid and heat catalysts. The temperature for heating is not too high, which is 55-60°C [7]. The esterification reaction is carried out if the raw material used contains high free fatty acids (> 70%) as in PFAD. Factors affecting esterification reaction includes the catalyst, reaction temperature, stirring and reaction time [8]. The influence of these factors can be explained as follows.

a). Catalyst

The catalyst functions to reduce the activation energy so that at a certain temperature the reaction rate constant is getting higher. Without a catalyst, the esterification reaction can only take place at a minimum temperature of 250°C, however, with a catalyst, the esterification reaction takes place well at temperatures around 100°C. The catalysts used are acids, bases and ion exchangers. The esterification reaction can be carried out by adding acid catalysts such as HCl and H₂SO₄ [9].

b). Reaction temperature

The higher the reaction temperature, the faster the reduction of percentage (%) FFA occurs. The best reaction temperature is reached at 60°C [10]. In accordance with the Arrhenius law (equation 1), that the reaction rate is proportional to the reaction temperature at which the reaction temperature is higher, the reaction rate constant (k) is greater so that the reaction rate is greater.

\[ K = k_0 e^{-E/RT} \]  \hspace{1cm} (1)

where \( K \) = Arhenius constant; \( k_0 \) = collision factor; \( R \) = gas constant (8,314 Jmol⁻¹K⁻¹); \( T \) = temperature (K); \( E \) = activation energy (J) [11].

c). Stirring

Based on Arhenius' Law (equation 1), the reaction rate constant is influenced by the values of \( k_0 \), \( E \), and \( T \) where the greater the collision factor (\( k_0 \)), the greater the constant reaction rate will be obtained. Stirring will increase the frequency of collisions between the reacting molecules so that it speeds up the reaction.

d). Reaction Time

The reaction time directly proportional to the concentration of methyl esters produced. Fast reaction time will save time and reduce production costs. The maximum time is obtained after the reaction equilibrium is reached. After the optimum time is reached, the longer the reaction time takes place, it does not result in much more product [12].

1.2. Biodiesel Quality Standards Based on SNI 7182-2015
The biodiesel quality standards are listed in SNI 7182-2015 [13]. Several quality requirements for biodiesel used for diesel engine fuels are presented in Table 1:

Table 1. SNI 7182-2015 Biodiesel Quality Standards [13].

| No | Parameter and unit                  | Value       |
|----|-------------------------------------|-------------|
| 1  | Density at 40°C, kg/m³              | 850-890     |
| 2  | Kinematic viscosity at 40°C, mm²/s (cSt) | 2.3-6.0  |
| 3  | Cetane number                       | Min. 51     |
| 4  | Flash point (closed bowl), °C       | Min. 100    |
| 5  | Fog point, °C                       | Max. 18     |
| 6  | Water content                       | Max. 0.05   |
| 7  | Acid value (mg-KOH/g)               | Max. 0.5    |
| 8  | Oxidation stability (minutes)       | 480         |

The above parameters are important parameters of 19 parameters on SNI that need to be analyzed so that the biodiesel obtained meets the prerequisites in accordance with the SNI standard. The other parameters considered in the SNI quality standard, include corrosion of copper plates, carbon residues, sulfur content, distillation temperature, sulfulant ash, methyl ester content, iodine number and monoglyceride.

1.3. Antioxidant

Antioxidants are compounds or chemical components which in certain levels or amounts can inhibit or slow down damage due to the oxidation process [14]. Based on the source, antioxidants are divided into two, namely natural antioxidants and synthetic antioxidants. Natural antioxidants are antioxidants derived from the extraction of natural materials. Natural antioxidants can be obtained from everyday foods such as vegetables, fruits, nuts and other plants. While synthetic antioxidants are chemically synthesized compounds. Antioxidants used in this study (antioxidant X) are synthetic antioxidants in the form of organic compounds which are white solids and sensitivity to oxygen so that they can make the sample become brownish in color. Antioxidant X can inhibit or slow down oxidation in substances / ingredients added.

2. Research Methodology

The research is divided into five stages, namely the preliminary research stage; stage of biodiesel processing; antioxidant addition stage, the stage of determining the Biodiesel-Antioxidant Induction Period (IP) value and determining the optimum concentration of antioxidant X; and Determination of IP values in the optimum Biodiesel-Antioxidant mixture after being stored for approximately one month. The research methodology carried out can be seen in Figure 1. PFAD raw materials used were obtained from the North Sumatra Oil Palm Plantation Research Center, Indonesia.

The esterification reaction in producing biodiesel is carried out in batches. The stages of producing biodiesel are presented in Figure 2. The reaction was carried out by mixing PFAD and methanol with the addition of 0.6% v / v H₂SO₄ catalyst, PFAD molar ratio: methanol = 1: 9 [15].
Figure 1. Research Methodology

In the analysis phase, the biodiesel produced is then analyzed for several properties, such as: Induction Period (IP) value, viscosity, density, acid value, moisture content, and alkyl ester content in accordance with SNI 7182-2015 on purified biodiesel. The analysis of IP values is carried out by using...
the Rancimat method. This method is carried out by oxidizing the biodiesel by air pressure of 25 kPa/hour and accelerated in the presence of heat at 110ºC [16].

The addition of antioxidant X was varied by addition of antioxidant at various concentrations (ppm). The IP value of each mixture of biodiesel and antioxidants is measured by the Rancimat method. Variations in antioxidant concentration are 0.1; 0.3; 0.5; 0.7; and 0.9 ppm. The concentration of the mixture which has the optimum IP value is determined its viscosity, moisture content and acid number with the same method in determining the physical and chemical properties of PFAD. Pure biodiesel obtained is then stored for about one month to determine the effect of storage time on the IP value.

3. Results and discussion

3.1. Preliminary research

Based on the results of preliminary research [15] it is known that PFAD used is composed of high free fatty acids, which is as much as 95.2 mol%. The free fatty acid consists of 47.5 %mole of saturated fatty acids and 47.7 %mole of unsaturated fatty acids. Hexadecanoic acid (C\textsubscript{17}H\textsubscript{34}O\textsubscript{2}) is the highest composition of saturated free fatty acids with a composition of 29.11 %mol. While the highest composition of unsaturated free fatty acids is the octadecadienoic acid (C\textsubscript{18}H\textsubscript{34}O\textsubscript{2}), as much as 26.41 %mole. Other compounds found in PFAD are tetracosapentaen at 0.1 %mole and lycopersen at 4.73 %mole.

Tetracosapentaen is called an antioxidant because it is based on its structure, which are phenolic compounds [17]. Phenolic compounds have 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 [14]. The tetracosapentaen content found in PFAD is 0.1 %mole, equivalent to 292 mg/L PFAD.

The PFAD density obtained was 856.974 kg/m\textsuperscript{3}. This is influenced by the molecular weight of PFAD which is represented by the length of the chain of fatty acids and the double bonds in alkyl groups. The higher the molecular weight of fatty acids, the higher the density will be. The PFAD acid value was obtained at 117.636 mg KOH/g. The acid number shows that PFAD has a high free fatty acid content, so the process of making biodiesel must be done by the esterification process as shown in equation (2).

\[
\begin{align*}
R'\textsuperscript{+} &+ \text{CH}_2\textsuperscript{--}\text{OH} &\rightleftharpoons & R'\textsuperscript{+} &+ \text{CH}_2\textsuperscript{--}\text{OH} &\rightleftharpoons & R'\textsuperscript{+} &+ \text{H}_2\text{O} \\
\end{align*}
\]

(2)

The water content obtained in PFAD resulting from the analysis is 49%. The water content in PFAD will affect the reaction process and cause the reaction to shift to the left. This is a process that is avoided because it will reduce the reaction conversion in the reactants so that PFAD is preheated to reduce the water content before the esterification process. The heating is carried out at a temperature of 80º C for 2 hours. Heating temperature must be maintained because heating with higher temperatures will cause color changes in PFAD to be darker (burnt).

3.2. Physical Characteristics

In the process of making biodiesel carried out in batches at 60ºC for 60 minutes, a sulfuric acid catalyst was added to reduce the activation energy because SO\textsuperscript{2−} ion in sulfuric acid can neutralize charged molecules (+2). In this study, the conversion of the esterification reaction was 99.6%. Then analysis of the characteristics of pure biodiesel from PFAD and pure biodiesel mixture from PFAD with 0.1 ppm antioxidant X were conducted. The results of water content analysis on pure biodiesel are not in accordance with the 2015 SNI standard [15].
While the results of the analysis on the biodiesel mixture with 0.1 ppm antioxidant X showed that the density, viscosity, acid number, alkyl ester level, flash point and oxidative stability were in accordance with the 2015 SNI standard. Table 2 shows the results of the water content analysis:

|                  | Pure Biodiesel | Biodiesel + 0.1 ppm Antioxidant X (with storage) | Biodiesel + 0.1 ppm Antioxidant X (without storage) |
|------------------|----------------|--------------------------------------------------|--------------------------------------------------|
| Water content (%)| 0.23           | 0.02                                             | 0.02                                             |

Based on Table 2 it can be seen that biodiesel storage with the addition of 0.1 ppm antioxidant X does not affect the decrease in water content because the biodiesel that has been stored with the new biodiesel (without storage) has the same moisture content, which is 0.02%. When it is compared to the water content in pure biodiesel, biodiesel + antioxidants either with storage or without storage decreased by 0.21%. This may occur due to the pure biodiesel sample phase at the time of testing in the form of solids (frozen) and stored in a container having volume around 3L with a tested sample of 500 mL. Phase of samples of biodiesel + antioxidant X with and without storage is in the form of liquid and volume of sample containers is around 1 L. Air with a volume of about 2.5 L in pure biodiesel containers is likely to condense and mix with pure biodiesel so that the water content in pure biodiesel is greater than the water content of biodiesel + antioxidant X.

3.3. Oxidation Stability
Oxidative stability as indicated by the Induction Period (IP) value of biodiesel as a fuel has a minimum limit of 6 hours [13]. This IP value shows the stability of oxidation in oil or fat which is the resistance of biodiesel to not degrade due to oxidation by oxygen in air in a certain period of time [15]. In determining this IP value, the data obtained by the Rancimat method is in the form of biodiesel conductivity value. The conductivity value is then made with a curve on time and the point of intersection of two line equations is obtained to get the value of oxidative stability.

Determination of oxidative stability was carried out on pure biodiesel, and a mixture of pure biodiesel with antioxidant X both with storage and without storage. Figure 3 shows the curve of time versus conductivity of pure biodiesel, which results in the IP value of pure biodiesel. It shows that the IP value of pure biodiesel is 6.03 hours. To obtain an objective conclusive result, the second run of determination of oxidative stability was then carried. With the same Rancimat method, IP value of pure biodiesel obtained was 6.28 hours. Therefore, the average of IP value for pure biodiesel is 6.15 hours, which fulfills the IP value based on the SNI standard.

Since the IP value of pure biodiesel has fulfill the SNI standard, the addition of small amount of antioxidant (0.1 ppm) was then applied, as shown in Figure 4.
Figure 3. IP value determination for pure biodiesel

From Figure 4, it is obtained the IP value of mixture of biodiesel and 0.1 ppm antioxidant X, i.e. 11.75 hours. A drastic increase in IP value is obtained when only 0.1 ppm antioxidant X is added. The second run of measuring the IP value of biodiesel + 0.1 ppm antioxidant X was conducted to check the repeatability of the result. By the same Rancimat method, the second measurement resulted in the IP value of biodiesel + 0.1 ppm antioxidant X of 10.35 hours. Therefore, the average IP value of biodiesel + 0.1 ppm antioxidant X is 11.05 hours. Comparing the IP value of pure biodiesel and mixture of biodiesel + 0.1 ppm antioxidant X, it can be stated that with the addition of a low antioxidant concentration, an increase in IP value is very significant. The oxidative stability of pure biodiesel which was originally 6.15 hours, after addition of 0.1 ppm antioxidants X it has an average IP value of 11.05 hours [15].

A measurement of the reaction rate constant of the antioxidant was conducted to obtain the optimum concentration of antioxidant added. From Figure 5, it is obtained the reaction rate constant of antioxidant X in biodiesel at a temperature of 110 °C, which is 0.0042 m³. The study conducted by
Xiong et al. [18] obtained the reaction rate constant of biodiesel which used cooking oil raw materials with the addition of antioxidants at a temperature of 110º C of 0.00688 m\(^{-1}\). It can be interpreted that biodiesel with raw materials for cooking oil is oxidized faster than biodiesel with PFAD raw materials. In addition, in Figure 6 it is known that the critical concentration of antioxidant X at 110ºC is 7.618 x 10\(^{-6}\) M (0.06 ppm). Therefore, this antioxidant concentration was chosen as the optimum concentration.

![Figure 5. Reaction rate constant determination for pure biodiesel](image)

Observation on Induction Period (IP) value for biodiesel, which has been stored at room temperature for around a month was carried out to observe the effect of storage towards the oxidation stability of biodiesel (Figure 6). Based on this figure, the IP value of pure biodiesel decreased to bec 5.25 hours. The IP value of pure fresh biodiesel (without storage) was 6.15 hours [15]. It means that after storage for about one month, the biodiesel became oxidized. Natural antioxidants found in raw materials can inhibit oxidation only in a short time period of time.

The mixture of biodiesel and 0.06 ppm antioxidant X was also checked its IP value after it was stored at room temperature for around a month (Figure not shown). With the addition of antioxidant concentration of 0.06 ppm, an increase in IP value was obtained. The oxidative stability of pure biodiesel which was originally 5.25 hours after the addition of antioxidants had an IP value of 6.34 hours. The addition of antioxidants could slow down the oxidation in biodiesel as well as increase the value of oxidative stability in biodiesel. Thus, if biodiesel is to be stored, it is necessary to add synthetic antioxidants in various concentrations according to how long storage will be carried out. Table 3 shows IP values for biodiesel with and without storage and fulfillment of SNI.

It is clear from Table 3 that even though the pure biodiesel produced has a value of oxidative stability that fulfills the SNI standard and has natural antioxidants in raw materials but synthetic antioxidants are needed to increase the value of oxidative stability in the biodiesel, especially when the biodiesel is planned to be stored.
Figure 6. IP determination for pure biodiesel after a month storage

Table 3. SNI 7182-2015 Biodiesel Quality Standards [13].

| No | Biodiesel with & without storage | IP (hours) | Fulfilment of SNI |
|----|---------------------------------|-----------|------------------|
| 1  | Pure biodiesel (without storage)| 6.15      | Yes              |
| 2  | Biodiesel + 0.1 ppm antioxidant X (without storage) | 11.05     | Yes              |
| 3  | Pure biodiesel (stored for a month) | 5.25      | No               |
| 4  | Biodiesel + 0.06 ppm antioxidant X (stored for a month) | 6.34      | Yes              |

Conclusion

PFAD used is suitable as a raw material for producing biodiesel. It is composed of high free fatty acids of 95.2 % mole, consisting of 47.5 % mole of saturated fatty acids and 47.7 % mole of unsaturated fatty acids. Hexadecanoic acid (C16H34O2) is the highest composition of saturated free fatty acids with a composition of 29.11 % mole. While the highest composition of unsaturated free fatty acids is the octadecadienoic acid (C18H34O2), i.e. 26.41 % mole. Other compounds found in PFAD are tetracosapentaen at 0.1 % mole and lycopersen at 4.73 % mole.

Pure biodiesel produced from PFAD, with conversion through an esterification reaction is 99.6%, fulfills the Indonesian standard (SNI 7182-2015). However, when this biodiesel needs to be stored, addition of antioxidant is needed to maintain its oxidative stability. IP value for pure biodiesel is 6.34 hours and decreases to become 5.25 hours after 1 month storage. IP value for biodiesel + 0.06 ppm antioxidant X after 1 month storage is 6.34 hours. Reaction rate constant of antioxidant X in biodiesel at temperature of 110°C is 0.0042 m$^{-1}$ and the critical concentration of antioxidant X at 110°C is 7.618 x 10$^{-6}$ M.
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