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Application of Tocopherol as Antioxidant to Reduce Decomposition Process on Palm Oil Biodiesel

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***Abstract*—**Biodiesel is one of the alternative fuels promising for substituting petrodiesel as energy source which has an advantage as it is sustainable and eco-friendly. Due to the raw material that tends to decompose during storage, biodiesel also has the same characteristic that tends to decompose during storage. Biodiesel decomposition will form higher acid value as the result of oxidation to double bond on a fatty acid compound on biodiesel. Thus, free fatty acid value could be used to evaluate degradation of biodiesel due to the oxidation process. High free fatty acid on biodiesel could impact on the engine performance. Decomposition of biodiesel due to oxidation reaction could prevent by introducing a small amount of antioxidant. The origin of raw materials and the process for producing biodiesel will determine the effectiveness of antioxidant. Biodiesel made from high free fatty acid (FFA) crude palm oil (CPO) by using two steps esterification is vulnerable to oxidation process which is resulted in increasing on the FFA value. Tocopherol also known as vitamin E is one of the antioxidant that could improve the stability of biodiesel due to decomposition by the oxidation process. Tocopherol 0.5% concentration on palm oil biodiesel could reduce 13% of increasing FFA under temperature 80 °C and exposing time 180 minute.

***Keywords*—**Antioxidant, biodiesel, decomposition, oxidation, tocopherol.

I. Introduction

BIODIESEL is one of the promising alternative energy to overcome the lack between supply and demand of hydrocarbon fuel, especially for the automotive engine. The advantage of biodiesel is on the sustainability and renewability. Different kind of raw materials source were used for biodiesel production, it is spread from the seed of plant both edible and non edible oil, used frying oil, fats from slaughterhouses and also microalgae that could growth in a very fast way [1]-[3]. While there are also some many routes to produce biodiesel, transesterification, reactive distillation, microwave assist, both thermal and catalytic cracking and so on [4]-[6]. With all the various feedstock and process to produce biodiesel there is still a problem appear in biodiesel application, it is the stability to oxidation process [7], [8].

Biodiesel is vulnerable to oxidation because most of the biodiesel feedstock composed by partly unsaturated fatty acid. The compositions of feedstock then lead to the product of biodiesel with unsaturated chain which is easily reacted with oxygen. Oxidation of biodiesel will produce some compound that affect to other quality parameter of biodiesel such viscosity, acid value, esters content, cloud point [9]. Thus, the stability of biodiesel from oxidation process should be maintained to ensure quality of biodiesel itself. One of the efforts to achieve high stability on biodiesel in stability to oxidation process is by introducing a small amount of antioxidant into biodiesel.

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A. Biodiesel

Biodiesel is a substance made from lipid that came from vegetable oil and animal fat which is similar properties to biodiesel. The most common route to produce biodiesel is conversion of the lipid into esters, known as fatty acid alkyl ester. In case the alkyl ester was derivate of methanol it was named fatty acid methyl ester. Both physical and chemical properties of biodiesel depend on their feedstock source [10].

For the feedstock that originally came with high FFA (usually more than 1%), in the alkaline transesterification process, feedstock should be pretreatment to reduce the FFA on the feedstock. Thus for the high FFA feedstock, biodiesel production consists of two simultaneous reaction, esterification step as shown in (1) and transesterification step as shown in (2) [11]-[13]:

$$R_1COOH + CH_3OH \underset{}{\overset{\text{Acid catalyst}}{\rightleftharpoons}} R_1COOCH_3 + H_2O \quad (1)$$

$$TG + 3\ CH_3\ OH \underset{}{\overset{\text{Alkali catalyst}}{\rightleftharpoons}} \text{Gliserol} + 3\ \text{FAME} \quad (2)$$

B. Biodiesel Oxidation

Biological, physical and chemical processes are several sources for biodiesel decomposition. Microorganism activity is the main source for biodiesel decomposition by biological source, while heat, metals and light are physical source. Water, oxygen and FFA are chemical source for biodiesel decomposition [14], [15]. These sources could work separately or simultaneously on biodiesel and result in decomposition of biodiesel. Unsaturated fatty acid on biodiesel is vulnerable to oxidation reaction. Decomposition due to oxidation reaction on biodiesel could bring a serious problem on the engine because biodiesel could change viscosity, acid value, water content cetane number, and also its caloric value. Oxidation on biodiesel was reaction between oxygen and double bond chain on biodiesel compound. There are three steps on the oxidation reaction, namely initiation, propagation and termination step and shown in (3)-(7) [16]:

Initiation:

$$RH + O_2 \rightarrow R^* + H_2O \quad (3)$$

$$RH + O_2 + RH \rightarrow R^* + H_2O + R^*$$

Propagation:

$$R^* + O_2 \rightarrow ROO^* \quad (4)$$

$$ROO^* + RH \rightarrow ROOH + R^* \quad (5)$$

Peroxide decomposition:

$$ROOH \rightarrow RO^* + {}^*OH$$

$$2\,ROOH \rightarrow RO^* + ROO^* + H_2O$$

Termination:

$$ROO^* + ROO^* \rightarrow \text{inactive product} \quad (6)$$

$$ROO^* + IH \rightarrow ROOH + I \quad (7)$$

where, RH= organic matter (Alkyl lipid), ROO^*= Peroxide radical, ROOH= Hydroperoxide, I= Stable radical or inactive radical, IH= free radical inhibitor. The series of the reaction also known as auto oxidation reaction.

In the oxidation process, oxygen will react with the components that have double bond on the molecular chain. In biodiesel, double bond was found in the unsaturated chain on biodiesel component. This means that the oxidation reaction to biodiesel will reduce the number of double bond in biodiesel compound. The changes on the percentage of unsaturated chain could be analyzed by evaluation on iodine number.

C. Antioxidant

Most of the oil and lipid came with their original antioxidant, it was namely natural antioxidants. Tocopherols, ascorbic acid, ascorbic acid ester, and carotenoids are example of natural antioxidants that exist in lipid [17], [18]. Natural antioxidants decrease significantly in biodiesel due to the process steps from raw material oils to final biodiesel product. The process steps include oil extraction, pretreatment to remove gums and phospholipid also esterification process to reduce high FFA. In case that biodiesel production uses transesterification route with alkali catalyst, purification of biodiesel to fulfill the standard requirement also contributes to the decreasing of natural antioxidant. For this reason, new antioxidant should be introduced to improve biodiesel quality in a view of oxidation stability.

There are two classifications of antioxidants; primary and secondary antioxidant. Primary antioxidant refers to chain breaking antioxidants; because of the chemical nature of these molecules, they can act as free radical acceptors and delay or inhibit the initiation step or interrupt the propagation step of auto-oxidation. Mechanism of primary antioxidant is shown in (8)-(10) [19]:

$$R\bullet + AH \rightarrow RH + A\bullet \quad (8)$$

$$RO\bullet + AH \rightarrow ROH + A\bullet \quad (9)$$

$$ROO\bullet + AH \rightarrow ROOH + A\bullet \quad (10)$$

where R•, RO•, ROO• = free radical.

Radical from the antioxidant will react with radical from fatty acid to form stable complex compound as shown in (11)-(l3):

$$R\bullet + A\bullet \rightarrow RA \quad (11)$$

$$RO\bullet + A\bullet \rightarrow ROA \quad (12)$$

$$ROO\bullet + A\bullet \rightarrow ROOA \quad (13)$$

II. Material and Method

A. Material

CPO was supplied by PT Inti Indosawit Subur, Medan, North Sumatra, Indonesia. Initial FFA of CPO is 6.7%. All chemicals used in the research are analytical grade.

B. Method

1) Esterification of Raw CPO

The reaction was performed in a three neck round-bottom glass flask (1 L), equipped with a water controlled condenser and a magnetic stirrer that was immersed in a thermostatic bath. A series of batch experiments using 500 mL of oil were conducted to obtain 2 L, for oxidation stability studies. Sulfuric acid (3 wt.%) was dissolved in methanol (20% V/V relative to oil) and then poured into reactor which was previously filled with the raw CPO, at 65 ºC. Reaction temperature was maintained at 65 ˚C and a vigorous magnetic stirring was performed. To determine the optimum reaction time, the reaction was conducted for 4 h and the acid value was monitored at different time intervals, by removing 2 mL of sample from the reactor each time and further analyzing the acid value. After the end of the reaction, the products were poured into a separation funnel to separate the oil phase from the water/acid/alcohol phase; settling lasted 12 h. The oil phase, shortly written as mixture (composed of by palm oil and palm oil biodiesel), was then submitted to vacuum distillation (using a rotary evaporator) at 65 °C and using a maximum vacuum of 200 mbar to recover the excess of methanol used. The acid value was determined to confirm the effectiveness of the reaction and the absence of residual sulfuric acid.

2) Transesterification of the Mixture

The reaction flask and setup was similar to the one used for the esterification step. Sodium hydroxide (1% w/w) was dissolved in methanol (6:1 molar ratio relative to oil) then poured into the reactor which was filled with the product resulted from the previous step. Reaction was performed at 60 °C, for 90 minute, using vigorous stirring. After the end of the reaction, the products were poured into the separation funnel to separate the biodiesel phase and the glycerol phase, for 2 h. Excess methanol removal both from the biodiesel and the glycerol phase was also performed by vacuum distillation at 65 °C and at a maximum of 200 mbar of vacuum pressure (using a rotary evaporator). Biodiesel was further purified by acid and water washing and dried using an anhydrous salt as

follows: Biodiesel was washed one time using 50% V/V (relative to oil) of an hydrochloric acid solution (0.5% V/V), to neutralize the catalyst, and then repeatedly with 100% V/V (relative to oil) of distilled water until the pH of the washing water was close to the pH of the distilled water (clear water). Small amounts of sodium chloride were slowly added to break the emulsion, when appeared during washing, being removed in the subsequent water washing step. After water washing, the residual biodiesel water was absorbed by using 25% w/w of anhydrous sodium sulfate, vigorous stirred for 10 min and finally left overnight. The biodiesel was after filtered by vacuum to obtain the final product. To avoid any oxidation of the product, after purification, the product was left in the freezer at -20 ºC.

3) Influence of Tocopherol on the FFA Value of Palm Oil Biodiesel

Five gram of tocopherol was accurately weighted, added to 1000 gram of biodiesel to prepare mother solutions. For the purpose of determining the effectiveness of the antioxidants, 10 gram of sample was taken from mother solution, placed it in reaction tube and heated in thermostatic water bath in certain temperature (70 ºC and 80 ºC). After certain time of heating (30, 60, 90, 120, 150, 180 minute) sample was taken from water bath and the FFA value was further analyzed.

III. Result and Discussion

A. Esterification of CPO

Through the esterification of CPO, percentage of FFA could decrease from 6.7% to 1.8% after 280 minute reaction time as shown in Fig. 1. On the esterification process FFA was converted to fatty acid methyl ester (FAME), thus on esterification process, formation of FAME was already started, and will complete in transesterification step.

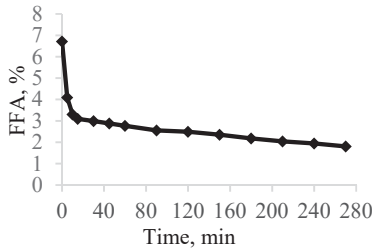

Fig. 1 Esterification of CPO

B, Transesterification of Palm Oil

Palm oil from esterification process is converted to FAME during 90 minute of reaction in 65 ºC. At the end of reaction, it was found that the yield of reaction is 92%. After purification, FAME content on the final product is 99%. Analyzing on the total acid value of biodiesel lead to the conclusion that FFA on palm oil biodiesel is 1.8%.

C. Influence of Temperature on FFA in Biodiesel

Correlation between temperature of the oxidation reaction to the increasing of the FFA value of biodiesel was shown by Figs. 2-4. In a palm oil biodiesel without antioxidant, after 180-minute oxidation reaction at 70 °C, FFA will increase 12.3% from the initial value, while oxidation reaction at 80 °C, FFA will increase 19.7%. It makes sense due to classical kinetic theory that increasing temperature will promote to higher rate of reaction and in this case it is oxidation reaction of the double bond of unsaturated compound in palm oil biodiesel.

D. Influence of Tocopherol

Tocopherol was introduced to palm oil biodiesel to reduce decomposition of biodiesel by oxidation reaction on unsaturated compound on biodiesel. From Figs. 3 and 4, it was shown that at the end of oxidation reaction, FFA on palm oil biodiesel will increase. At 70 ºC, biodiesel without tocopherol will increase 12.3% from the initial value of FFA, while on biodiesel with tocopherol 0.2% and 0.5% will increase the FFA as 8.3% and 5.8%. It was shown that by introducing tocopherol as antioxidant, stability of biodiesel could improve significantly.

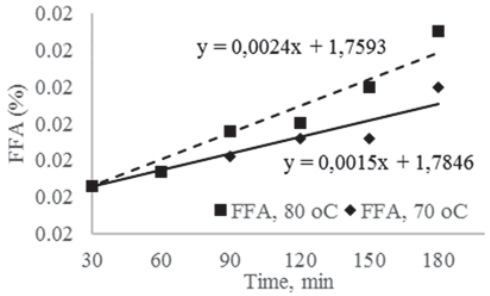

Fig. 2 Correlation between time of reaction and percentage of FFA on palm oil biodiesel without tocopherol

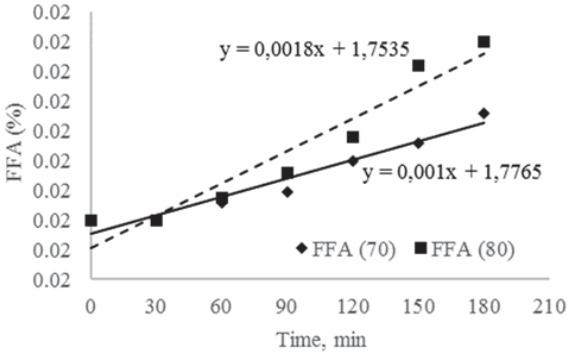

Fig. 3 Correlation between time of reaction and percentage of FFA on palm oil biodiesel with tocopherol 0.2%.

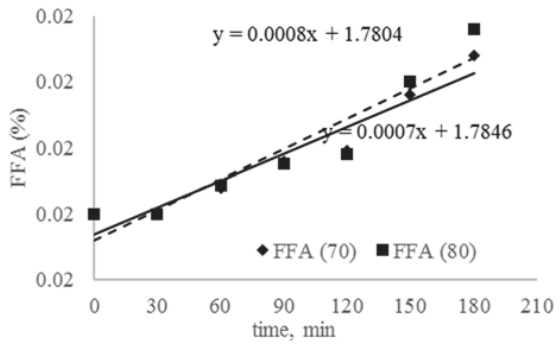

Fig. 4 Correlation between time of reaction and percentage of FFA on palm oil biodiesel with tocopherol 0.5%.

Analyzing the FFA after 180-minute oxidation reaction at 80 °C on biodiesel shows that FFA will increase. The increasing of FFA is 19.7% from the initial value in the biodiesel without tocopherol. On biodiesel introduced by 0.2% tocopherol, increasing of FFA is 14.9%. While on biodiesel introduced by 0.5% tocopherol, increasing of FFA is 6.7% correspond to the initial value of FFA.

Fig. 4 shows the correlation between increasing of FFA on biodiesel to the time of oxidation reaction at 70 and 80 °C. Extrapolation of this data to the ambient temperature 30 ºC will found that after 180 minute, FFA value of biodiesel will increase 2.5%.

IV. Conclusion

Tocopherol is one of the alternative sources of antioxidant to prevent increasing value on FFA in palm oil biodiesel. In the same amount that introduced to biodiesel, tocopherol will work better to prevent increasing of FFA on palm oil biodiesel in higher temperature. Extrapolating data of the experiment to the ambient temperature 30 ºC shown that after 180 minute exposing palm oil biodiesel contain 0.5% tocopherol, FFA will increase 2.5% correspond to initial value.

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