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Influence of Synthetic Antioxidant in the Iodine Value and Acid Number of Jatropha Curcas Biodiesel

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***Abstract*—**Biodiesel is one of the alternative fuels that promising for substituting petro diesel as energy source which is advantage on sustainability and ecofriendly. Due to the raw material that tend to decompose during storage, biodiesel also have the same characteristic that tend to decompose and formed higher acid value which is the result of oxidation to double bond on a chain of ester.

Decomposition of biodiesel due to oxidation reaction could prevent by introduce a small amount of antioxidant. The origin of raw materials and the process for producing biodiesel will determine the effectiveness of antioxidant. The quality degradation on biodiesel could evaluate by measuring iodine value and acid number of biodiesel.

Biodiesel made from high fatty acid *Jatropha curcas* oil by using esterification and transesterification process will stand on the quality by introduce 90 ppm pyrogallol powder on the biodiesel, which could increase Induction period time from 2 hours to more than 6 hours in rancimat test evaluation.

***Keywords*—**Acid value, antioxidant, biodiesel, iodine value.

I. Introduction

INCREASING in biodiesel production shown the acceptance of consumer to the alternative energy for substituting petro diesel as a fuel. Total biodiesel production in 2013 was 400 000 barrel per day, it was grown almost 12 times from 2003 production [1], [2]. The advantage of biodiesel is in renewability and sustainability and this is very attractive factor on the biodiesel grown [3], [4], thus tend also support by new biodiesel production technology such reactive distillation, solid state catalyst [5], thermal and catalytic cracking [6], [7], and microwave assist [8]. While from the feedstock of biodiesel increasing production also support by research on microalgae which could result on higher solid density of algae culture and also higher oil yield [9]. Thus there is a wide range of biodiesel feedstock, from vegetable oil both edible oil and non-edible oil, waste frying oil, animal fat and also microalgae [10]-[13]. For all the biodiesel feedstock, in the composition of fatty acid always appear unsaturated fatty acid [14], [15]. Higher unsaturated fatty acid has shown by higher iodine value. Unsaturated fatty acid is fatty acid with one or more double bond on carbon chain in which is vulnerable to react with other compound such oxygen or hydrogen. In a case double bond on fatty acid chain oxidized by oxygen it will form free fatty acid. Further reaction will formed aldehyde and also polymer compound. Reaction of double bond with hydrogen will increase significantly biodiesel viscosity. Higher viscosity will disturb flowing operation of the fuel and burner system. Higher free fatty acid in biodiesel will promote corrosion in metal part of engine [16]

There is some effort to reduce the negative impact of unsaturated fatty acid content on biodiesel; one of them is by introduce antioxidant on biodiesel which is stabilized biodiesel from the influence of oxidation process. Antioxidant is naturally presence in the vegetable oil, however due to its extraction and other processes natural antioxidant could decrease, inactivated and useless. Processes such heating, pressing, exposure to air is significantly decrease effectiveness of natural antioxidant, thus to maintain biodiesel quality and to protect biodiesel from oxidation process synthetic antioxidant should be introduce. For every single feedstock source of biodiesel they have a specific antioxidant that could work better than other antioxidant. Table I listed result of some research work in the effectiveness of antioxidant application on biodiesel. It is concluded that composition of biodiesel feedstock is strongly influence on the effectiveness of antioxidant, while the purification process with and without distillation is also influence too. Distillation process could almost totally remove natural antioxidant that exist in biodiesel, thus stability of biodiesel due to oxidizing process is depend only on introducing of synthetic antioxidant on distilled biodiesel. While on biodiesel without distillation process (undistilled biodiesel) stability of biodiesel is depend both on natural antioxidants that originally came from the plant and also from synthetic antioxidant that introduced into biodiesel. Correlation of the mixture between natural antioxidant and synthetic antioxidant in the effectiveness on antioxidant action is varied from mutualism to interfere each other [17]-[19]. There are three steps in the oxidation process on biodiesel as shown as follows [20].

Initiation : $RH + I \rightarrow R^* + IH$
Propagation : $R^* + O_2 \rightarrow ROO'$
: $ROO^* + RH \rightarrow ROOH + R'$
Termination : $R^* + R^* \rightarrow R\text{-}R$
: $ROO^* + ROO^* \rightarrow$ Stable product

The first step, Initiation will take a time and reaction is slow, while after enough free radical was accumulated, propagation reaction will go fast as shown in Fig. 1.

In the analyses, the point where the second step is named Induction Period, For this purpose the analyses was held on Rancimat test equipment which is operated on 110°C and 10 L min^{-1} air flow.

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TABLE I
ANTIOXIDANT EFFECTIVENESS ON BIODIESEL

Methyl Ester	Result	Concentration
Rapeseed (UD)	TBHQ>PG>PY>BHA>BHT	1000
Rapeseed (D)	PY>PG>BHA>TBHQ>BHT	1000
Used Frying oil (UD)	PY>PG>TBHQ>BHA>BHT	1000
Sunflower seed (UD)	PY>PG>TBHQ>BHA>BHT	1000
Sunflower seed (D)	TBHQ>PG>BHA>PY>BHT	1000
Animal Fat (UD)	PY>TBHQ>PG>BHA>BHT	1000
Animal Fat (D)	PG>PY>TBHQ>BHT>BHA	1000
Used Palm Oil	PG>BHA>TBHQ+BHT>αTocferol>γTocoferol> δtocoferol>α tocoferol	1000
Soya bean	BHT>BHA>TBHQ	1000
Ethyl Ester from Soya Bean	TBHQ>BHT>α tocoferol	1000
Palm Oil Biodiesel	TBHQ>PG>THBP>BHT>DLTDP>BHA	1000
Palm Oil Olein	TBHQ>BHT>BHA	-

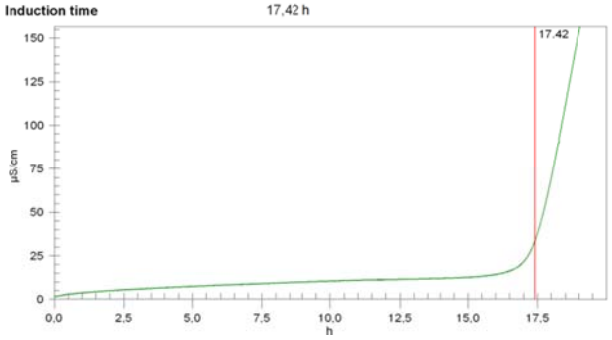

Fig. 1 Result of Rancimat test analyses

II. MATERIALS AND METHOD

A. Materials

High Free Fatty acid (14%) *Jatropha curcas* oil was purchase from PT Jatropha Green Energy Indonesia use as biodiesel feedstock. Commercially antioxidants t use in the experiment is Pyrogallol. Chemicals for oil pretreatment, biodiesel preparation and purification and all chemical for analyses are analytical grade.

B. Methods

1. Esterification of Raw *Jatropha curcas* Oil

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 use in characterization and oxidation stability studies. Sulfuric acid (3 wt.%) was dissolved in methanol (20% V/V relative to oil) and then poured in to reactor which was previously filled with the raw *Jatropha curcas* oil, at 65°C. 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 an 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 (2.2.3). 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 oily phase, named mixture (mixture of *Jatropha curcas* oil and 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 that resulted from previous step. Reaction was performed at 60°C, during 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, during 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 during 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°C.

3. Influence of Synthetic Antioxidants on the Oxidation Stability of Biodiesel

The antioxidant was accurately weighted, added to the biodiesel obtained to prepare 90 ppm concentrated solutions For the purpose of determining the effectiveness of the antioxidants, the Rancimat test was performed using the equipment 837 Biodiesel Rancimat®, from Metrohm. In

agreement with the standard, 3 g of sample were used each time. The test was conducted in duplicate for each antioxidant, at each concentration. Following the study, correlations were found between the concentration of antioxidant and the induction period. After determining from the predictive models the best concentration to reach the minimum of 6 hours of induction period according to the standard, experiments were performed (in duplicate) to validate the results.

III. Result and Discussion

Esterification step could decrease free fatty acid on *Jatropha curcas* oil from 14% to less than 1%. While as a result of esterification reaction, 12% Methyl ester was yielded.

Transesterification step was performed with Methanol as alcohol source with consideration that Methanol is more reactive than Ethanol, and Methanol also less hygroscopic. After purification step, biodiesel that come from transesterification reaction has 99.6% purity.

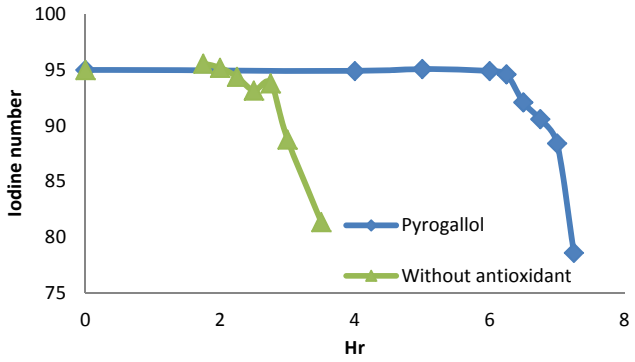

Fig. 2 Correlation of Induction time to Iodine number of biodiesel

It was shown on Fig. 2 that introduction of pyrogallol to biodiesel could improve stability of biodiesel significantly. Iodine number, start to change after 2 hours for biodiesel without antioxidant, while on biodiesel with pyrogallol 90 ppm the changes on iodine number will start after 6 hours. The result also agrees with European Standard EN 14214-2006.

From Fig. 3 it was shown that acid value on biodiesel without antioxidant will increase to more than 1% after 2 hours of oxygen exposure on Rancimat equipment which is operated on 110^{o}C and dry air flow 10 L.min.$^{-1}$.

From Fig. 4 it was shown that Acid Value of biodiesel will reach more than 1% after 6 hours exposure of Oxygen on Rancimat test equipment. The result is significantly increase stability of biodiesel from 2 hours to 6 hours stability test. Fig. 4 also has shown that slope of acid value increase is lower than slope of acid value increase in biodiesel without antioxidant.

Introducing antioxidant on biodiesel also concluded that antioxidant could maintain stability of biodiesel from oxidizing process, thus less free fatty acid that formed and mean that biodiesel could storage in a longer period.

This research work uses pyrogallol as a source on antioxidant considerate that pyrogallol has higher performance to use as antioxidant on *Jatropha curcas* biodiesel.

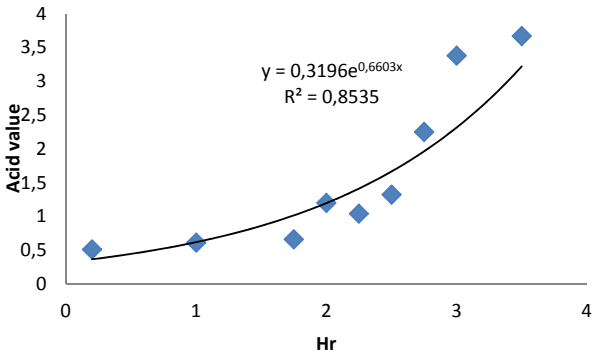

Fig. 3 Acid value analyses after oxygen exposure on biodiesel without antioxidant

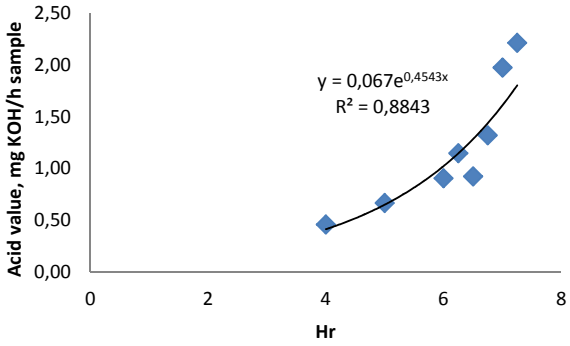

Fig. 4 Acid value analyses after oxygen exposure on biodiesel with Pyrogallol 90 ppm

IV. Conclusion

Application of antioxidant pyrogallol could improve and increase stability of *Jatropha curcas* biodiesel significantly. *Jatropha curcas* biodiesel without antioxidant could not fulfill requirement of biodiesel standard EN 14214-2006 while introducing 90 ppm pyrogallol could improve to the standard requirement.

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