Increase of Oxidation Stability of Biodiesel from Palm Fatty Acid Distillate (PFAD) by Antioxidant Additions

Herawati Budiastuti, Sri Widarti, and Riniati

***Abstract*—Biodiesel is a renewable energy, possesses high cetane number and flash points, resulting in its suitable uses in diesel machines and its safe distribution and storage, as well as low gas emission, and its function as lubricant. Disadvantages of the biodiesel include its high density and viscosity, resulting in plug and ineffective injection system, and low oxidation stability. This research studied about antioxidant additions to maintain oxidation stability of biodiesel. Induction period (IP) measuring kit, to measure oxidation stability, was constructed by using modified Rancimat principle. The best operation conditions were at temperature of 110^{0}C and pressure of <100 Kpa/h, resulting in relation coefficient (r) of 0.996 and detection limits of 6.54 ppm of oil samples. Palm fatty acid distillate (PFAD) used contains free fatty acids (FFA) of 86.43%. The IP of the biodiesel was only 1.7 hours. The optimum concentration of pyrogallol (PY) antioxidant added into biodiesel was 20 ppm whereas of propylgallate (PG) was 40 ppm. At these concentrations, the biodiesel IP increased to become 7.1 and 6.5 hours, respectively. Additions of these antioxidants fulfill the IP requirement of biodiesel measured by European Standard of EN 14214 (> 6 hours).**

***Index Terms*—Antioxidant, biodiesel, oxidation stability, PFAD.**

I. Introduction

Mandatory of minimum biodiesel consumption in transportation based on Indonesian Ministerial Decree of Energy and Mineral Resources No. 25/2013 is 10% starting from September 2013 and will increase to 20% in 2016 [1]. Reference [2] obtained that addition of 10% biodiesel into petroleum diesel decreases biodiesel viscosity to become 5.65 cst so that fulfilling its standard. However, mixture of biodiesel from fatty acid methyl ester (FAME) produced from crude palm oil (CPO) ≥ 20% results in viscosity higher than biodiesel viscosity required by Indonesian National Standard (INS).

Advantages of biodiesel compared with diesel fossil fuel include its renewable energy and unique since depending on the areas where the plantation grow, high cetane number and flash point so that easy in auto ignition and safe distribution and storage, respectively, as well as its low gas emission, and its function as lubricant. However, disadvantages of the biodiesel usage include its high density and viscosity, resulting in plug and ineffective injection system, and low oxidation stability, resulting from unsaturated fatty acid methyl ester (FAME) [3].

Renewable fuel type such biodiesel is easy to oxidize during storage and distribution since it possesses double chains in carbon chains of FAME. Mechanism occurred is the mechanism of radical formation, producing dimer, trimer or oligomer of FAME, possessing high molecular weights. The formation of macro molecules results in high viscosity of the fuel so that it is not appropriate for the injection system of the fuel into machineries and it may form plug which endangers the machineries. Besides, secondary oxidation of fuel may occur as a result of ethanol and aldehyde, which may produce acids such as acetatic and formic acids. The acid formation may increase acid number of the fuel. Time consumed for occurrence of secondary oxidation is defined as induction period (IP) [4].

To avoid the above problems, addition of antioxidant is commonly used. Several types of antioxidant usually added include butylated hydroxyanisole (BHA), pyrogallol (PY), propylgallate (PG), tert-butyl hydroquinone (TBHQ). The type and doses of antioxidant applied depend on raw materials of biodiesel, as well as its composition and mixture [5], [6]. This research studied about type and doses of antioxidant added into the biodiesel produced from crude palm oil (CPO) quality 4 or called palm fatty acid distillate (PFAD). By proper addition of type and doses of certain antioxidant, it may guarantee that the biodiesel produced may be stable up to consumers or buyers and may increase its uses in the market.

II. Research Method

A. Raw Materials, Operating Conditions, Antioxidant, and Analyzed Parameters

Raw materials of biodiesel were obtained from Palm Oil Plantation, Riau, Indonesia in the form of crude palm oil (CPO) quality 4 or called palm fatty acid distillate (PFAD). PFAD was initially analyzed for its content of free fatty acids (FFA). To obtain biodiesel, the operating conditions were maintained at temperature of 60^{0}C, molar ratio of CPO: methanol = 1:9.5, sulphuric acid catalyst loading of 0.5% (v), and operation time of 1 hour.

The reactor was set up from a three neck rounded flask, completed with reflux condenser, thermometer, and magnetic stirrer. To maintain the constant operating temperature, the oil bath was heated by an automatic temperature heater. Antioxidants studied were pyrogallol (PY) and propylgallate (PG).

Several parameters analyzed to measure the quality of biodiesel were viscosity, density, pour point, flash point, cetane number, and induction period (IP). IP is the value

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showing oxidation level of biodiesel during certain period of storage.

B. Induction Period (IP) Measuring Kit

Principle of modified Rancimat equipment was applied to design the tool/kit to measure IP of biodiesel. The principle of modified Rancimat is measurements of conductivity of substances resulting from oxidation of biodiesel. The resulted product of biodiesel is in the form of short carbon chain volatile substances, for example organic acids capable to ionize in water, and therefore could be measured their conductivities in the absorbed media. Various temperatures chosen to conduct conductivity measurements were at 100, 110, and 120^{0}C at pressure of <100 Kpa/h. Measurements resulting in the highest relation coefficient (r) were chosen as the best operation conditions to measure IP.

III. Results and Discussion

A. PFAD and Biodiesel Production

PFAD used to produce biodiesel was analyzed for its content of free fatty acids (FFA). PFAD is the fourth quality of CPO containing > 70% FFA. The other three Indonesian CPO are CPO containing < 5% FFA, off grade CPO with 5-20% FFA, and channel CPO containing 20-70% FFA [2].

PFAD was chosen as the raw material in producing biodiesel in this study based on its lower price compared to the other CPO types and by using PFAD it won't compete with food consumption. FFA containing in the PFAD obtained from Riau are shown in Table I.

TABLE I: Composition of PFAD

No.	Compounds	% mole
1	Palmitic Acid	41.46
2	Oleic Acid	43.02
3	Stearic Acid	1.95
4	Diglyseride	6.68
5	Docenal/Dodecane-11-al	3.25
6	Cyclotetradecane	3.64

Since total FFA containing in the PFAD accounted to 86.43%, estherification reaction is the reaction chosen to produce biodiesel. In the estherification reaction, the FFA will react with methanol resulting in methyl esther and H_2O with sulphuric acid as the catalyst.

TABLE II: Characteristics of Biodiesel

No.	Parameter	Unit	SNI-04-71 82 -2006	Biodie -sel
1	Cetane number	-	min 51	37
2	Flash point	^{0}C	min 100	254
3	Pour point	^{0}C	max 18	9
4	Viscosity	mm^2/s	2.3 – 6.0	-
5	Density	kg/m^3	850 – 890	896.6
6	IP	hours	> 6	> 9

The biodiesel produced possess characteristics as shown in Table II. Compared to the Indonesian standard for biodiesel (SNI-04-7182-2006), biodiesel produced in this study fulfils the parameters of flash point, pour point, and IP.

B. IP Measuring Kit and Limit of Detection

The modified Rancimat equipment designed in this study applied the principle of conductivity measurements towards substances produced during oxidation of biodiesel. Biodiesel samples were oxidized at 110^{0}C by purging air. Vapour produced during oxidation reaction from the biodiesel samples were flown together with air and collected in the flash containing distilled water. This flash was completed with conductivity meter to measure conductivity of produced oxidation samples in the reaction flash [5], [7].

By constructing the IP Measuring Kit, conductivity measurements of oxidation results from biodiesel can be conducted in any laboratory using simple glass wares and tools which can be easily found. For further usage, this IP Measuring Kit can not only be used for IP measurements of biodiesel but also measurements of edible or non edible oil.

Acetic acid was chosen to determine detection limit of the modified Rancimat based on several reasons. The main reason is that acetic acid is one example of a short chain organic acid as a result of biodiesel oxidation, which will ionize and release H^+ ion in water. The other reasons include its low price and availability in the market.

Acetic acid was analogized as a simple organic acid as a result of biodiesel oxidation so that during determination of detection limit there won't be oxidation occurred. Air used in this study was applied as driving force for acetic acid to reach absorbed media but not as an oxidiser. Acetic acid was only evaporated and flown to absorbed media to be measured its conductivity. Acetic acid in methanol was allowed to completely evaporate until the measurement of conductivity was constantly obtained. The constant conductivity of acetic acid was collected and statistically determined to obtain the detection limit.

The operation conditions were varied at 100, 110 and 120^{0}C at an average pressure lower than 100 Kpa/h to obtain the optimum temperature so that it can be used as the temperature standard. Limit detection was determined from the slope of linear regression curves using equations 1 and 2.

$$\text{Limit of Detection (LOD)} = \frac{3\times SD}{\text{slope}} \quad (1)$$

$$\text{Deviation Standard (DS)} = \sqrt{\frac{\sum(Y-Yi)^2}{n-2}} \quad (2)$$

Table III shows conductivity measurements at various temperatures and calculation of limit detection using equations (1) and (2). It shows that correlation coefficients (r) resulting from concentrations of acetic acid at temperatures of 100, 110 dan 120^{0}C vs their conductivities fulfil the requirement of Indonesian National Standard (INS), that is ≥ 0.97. Research result shows the tight correlation between measurement variables at operation temperature of 110^{0}C, possessing r very close to 1; i.e 0.996, with detection limit of 6.54 ppm. This operation temperature was chosen to be the optimum temperature. It fulfils the requirement to check stability tests of biodiesel oxidation [7] based on Europe standard of EN 14214. This detection limit result shows that the modified Rancimat designed can be used to measure oil

samples with fatty acid contents ≥ 6.54 ppm.

TABLE III: CONDUCTIVITY MEASUREMENTS AT VARIOUS TEMPERATURES

Acetic acid (ppm)	Temperature (^{0}C)		
	100	110	120
0	0.4	0.5	0.4
10	3.4	2.2	2.0
20	4.1	3.7	5.4
30	5.3	5.3	6.2
40	5.6	6.8	7.9
50	7.3	9.0	8.9
60	8.9	9.4	10.3
70	10.1	11.6	12.6
r	0.980	0.996	0.989
LOD (ppm)	14.67	6.54	12.70

C. Addition of Antioxidant

1) Addition of pyrogallol (PY)

After detection limit using the modified Rancimat was conducted, determination of IP for biodiesel resulted from this study and antioxidant addition was followed. The IP was obtained from the curve of conductivities vs time. The conductivities of compound observed were collected every 15 minutes until the conductivities raise drastically. The cross-section between linear horizontal curve and linear slope curve of the conductivities shows the IP (in minutes) of compound. The IP was converted to unit of hours to comply with the standard of EN 14214. Duplo (double) measurements of each IP determination were done. The IP of biodiesel and biodiesel with addition of antioxidant is shown in Fig. 1. The average IP of pure biodiesel (without addition of antioxidant) was at 103 minutes (1.7 hours). The average IP of biodiesel and 20 ppm PY was much higher at 425 minutes (7.1 hours). Addition of PY antioxidant at concentration of 20 ppm into biodiesel from this research could increase IP and fulfil the EN 14214 standard > 6 hours.

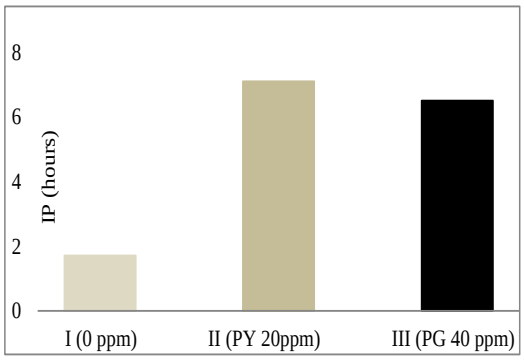

Fig. 1. IP of pure biodiesel and with antioxidant additions.

In general, addition of PY antioxidant at various concentrations (10, 20, 30, 40, and 50 ppm) resulted in trend of IP increase with the increase of antioxidant concentration (Fig. 2) with the exception of PY addition at 30 ppm. At 30 ppm PY, it resulted in lower IP than its addition at 20 ppm (6.1 compared to 7.1 hours). The reason for the decrease is still unknown.

From Fig. 2, it can be concluded that concentration of 20 ppm of PY is the optimum PY concentration, providing the IP of 7.1 hours. Reference [5] obtained IP increase from 4 hours to become 12.1 hours when biodiesel from *Croton Megalocarpus Oil* (COME) was added 200 ppm PY antioxidant. Addition of PY antioxidant for biodiesel resulting from this study (PFAD or CPO quality 4) only consumed 1/10 of PY concentration added into COME. Even though IP obtained from this study is lower than IP obtained from their study [5], however, IP as high as 7.1 hours has fulfil the IP standard requirement for biodiesel in Europe countries (EN 14214), which is > 6 hours. This requirement is to fulfil the required biodiesel stability [7], [4].

2) Addition of propylgallate (PG)

Addition of PG antioxidant at concentration of 50 ppm could increase biodiesel IP more than three times the IP of pure biodiesel; 5.4 hours compared to 1.7 hours. However, if it is compared to the biodiesel IP standard based on EN 14214, the addition of 50 ppm PG has not increased to the required IP > 6 hours. By decreasing addition of PG concentration to become 40 ppm, it could conversely increase the biodiesel IP to become 6.5 hours (Fig. 2). Addition of 80 ppm PG resulted in the same IP at 40 ppm addition; i.e 6.5 hours. Therefore, 40 ppm PG addition is selected as the optimum antioxidant concentration to obtain the oxidation stability of biodiesel from PFAD (Fig. 1).

In general, the increase of PG antioxidant addition concentrations could result in the increase trend of biodiesel IP (Fig. 2). Addition of PG antioxidant higher than 80 ppm was not conducted with consideration that addition of 40 ppm PG could fulfil the IP standard requirement for biodiesel based on EN 14214 (> 6 hours). From the curve in Fig. 2, it can be drawn conclusion that 40 ppm of PG addition is the optimum concentration addition and this addition is the minimum addition in providing IP fulfilling the IP standard of biodiesel.

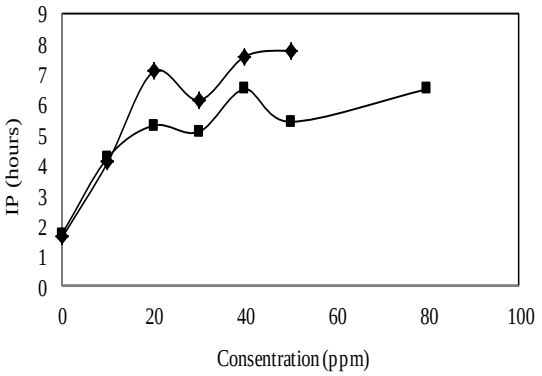

Fig. 2. IP of biodiesel with PY (♦) and PG additions (■).

Addition of 200 ppm PG antioxidant for biodiesel resulting from *Croton Megalocarpus Oil* (COME) increases its IP from 4 hours to become 7.6 hours [5]. Addition of PG antioxidant for biodiesel resulting from this study (PFAD from CPO quality 4) only consumed 1/5 of PG concentration added into COME.

Comparison between PY and PG in term of prices of these antioxidants (1.6:1), addition of PY, which is needed only a half of concentration of PG, is considered to be the antioxidant chosen to stabilize the oxidation stability of the biodiesel.

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