OXIDATION STABILITY IMPROVEMENT FOR JATROPHA BIODIESEL TO MEET THE INTERNATIONAL STANDARD FOR AUTOMOTIVE APPLICATIONS

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ABSTRACT

Biodiesel from Jatropha oil has several advantages compared to which from Palm oil, among others better cold flow properties (lower cloud point, pour point and CFPP). However, Jatropha biodiesel has an oxidation stability that is too low (2-3 hours) so that its application in the diesel engine is not acceptable. This paper reports the effect of addition of Palm bodiesel and commercial anti-oxidant on the oxidation stability of Jatropha biodiesel. The objective of this research is to find the formulation for Jatropha biodiesel which will meet the oxidation stability determined by World Wide Fuel Charter 2009 (WWFC) of min.10 hours. The required addition of BHT into Jatropha biodiesel is more than 10000 ppm to meet the WWFC specification. The addition of BHT will decrease to less than 10000 ppm if the Jatropha biodiesel was blended with Palm biodiesel as much as 60% v/v. Addition of antioxidant should be limited to a minimum value because there are also concerns about the negative effects of antioxidants on the engine components

Keywords: *jatropha & palm biodiesel, oxidation stability, anti-oxidant*

I. INTRODUCTION

Jatropha oil is a potential raw material for biodiesel other than Palm oil. The advantage of using Jatropha oil for biodiesel production compared to Palm oil is because it is non edible material so that its utilization will not interfere with the need of raw materials for food industries. In addition, the use of Jatropha oil as raw material could drive economic growth, particularly in rural or critical land areas. The weakness of biodiesel from Jatropha is that it shows very low oxidation stability. Its use as a fuel can lead to the engine failure.

The results of research have shown that biodiesel with low oxidation stability leading to corrosion of moving parts of pump and fuel lines [1]. The oxidation of biodiesel produces organic acids which are corrosive. These organic acids also form solids that can clog fuel filters. Oxidation of biodiesel also produces polymers that form deposits in the nozzle and combustion chamber. Thus, oxidation stability becomes one of the most important quality parameters of biodiesel. Oxidation stability is determined by Rancimat method and the specification for oxidation stability varies among the referenced standards. The specification of oxidation stability for biodiesel in Europe is at least 6 hours (EN 14214-2003), whereas the current standard in the US is at least 3 hours (ASTM D6751-07b). International standards issued by the Association of American automotive industry, Europe and Japan (WWFC 2009) establish the oxidation stability of at least 10 hours[2]. Biodiesel with high content of double bond such as Jatropha is more susceptible to oxidation. However, oxidation of biodiesel is affected not only by the content of double bonds but also by temperature, moisture content and water content. Indonesia has a very extreme condition where the ambient temperature and humidity are relatively high and these conditions will accelerate the oxidation process of biodiesel. Biodiesel with high oxidation stability is therefore necessary for safe diesel engine operations in Indonesia. Indonesia biodiesel standard SNI 04-

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7182 (2006) has not adopted the oxidation stability yet. The authors suggested that Indonesia should refer any of the international standards. Given the extreme environmental conditions and vehicle population in Indonesia which mostly uses metal fuel tank, the specification of WWFC with high oxidation stability (min 10 hours) is highly recommended by practitioners of the national automotive industry.

This paper will describe how the oxidation stability of Jatropha biodiesel can be improved by blending with materials of higher oxidation stability such as Palm biodiesel. Blending with Palm biodiesel will increase the content of saturated fatty acids. The saturated fatty acids are known to show high oxidation stability, while the unsaturated fatty acids have lower oxidation stability, especially poly-unsaturates. The oxidation stability of Jatropha biodiesel can be enhanced further by the addition of anti-oxidant. Several studies have reported that anti-oxidants are very effective in improving the oxidation stability of biodiesel[3,4]. Other study has reported the chemical modification of biodiesel to improve the oxidation stability through hydrogenation, hydroxylation and epoxidation[5] .The purpose of this research is to improve the oxidation stability of Jatropha biodiesel by blending with Palm biodiesel and the addition of anti-oxidant to meet international specifications, especially WWFC (min. 10 hours). To achieve this goal, the study was conducted in the following stages:

- Make a prediction of oxidation stability of Jatropha-Palm biodiesel blend
- Measure the oxidation stability of Jatropha-Palm biodiesel blend with and without anti-oxidant
- Determine the biodiesel formulations that have oxidation stability meets the international standards

II. MATERIALS AND METHOD

Biodiesel used in the study is made from Jatropha and Palm oil and manufactured at the BTMP BPP Teknologi Indonesia. Jatropha and Palm biodiesel is made from two types of different oils (A and B). The properties of the Jatropha biodiesel (type A & B) and the Palm biodiesel (type A & B) can be seen in Table 1 and 2. Furthermore, a biodiesel blend is made by mixing Jatropha biodiesel type A (40% v/v) with Palm biodiesel type A (60% v/v). The second blend is made by mixing Jatropha biodiesel type B (40% v/v) with Palm biodiesel type B (60% v/v). The addition of 60% v/v Palm biodiesel into Jatropha biodiesel was made to obtain the sample variation with higher different oxidation stability and it is expected that there will be a reduction in anti-oxidant addition when compared with pure Jatropha biodiesel.

Measurement of oxidation stability was carried out using the Rancimat method (EN-14112). About 3 g of biodiesel sample is heated at 110^{o}C with a constant air flow of 10 L/hour. The effluent air from the

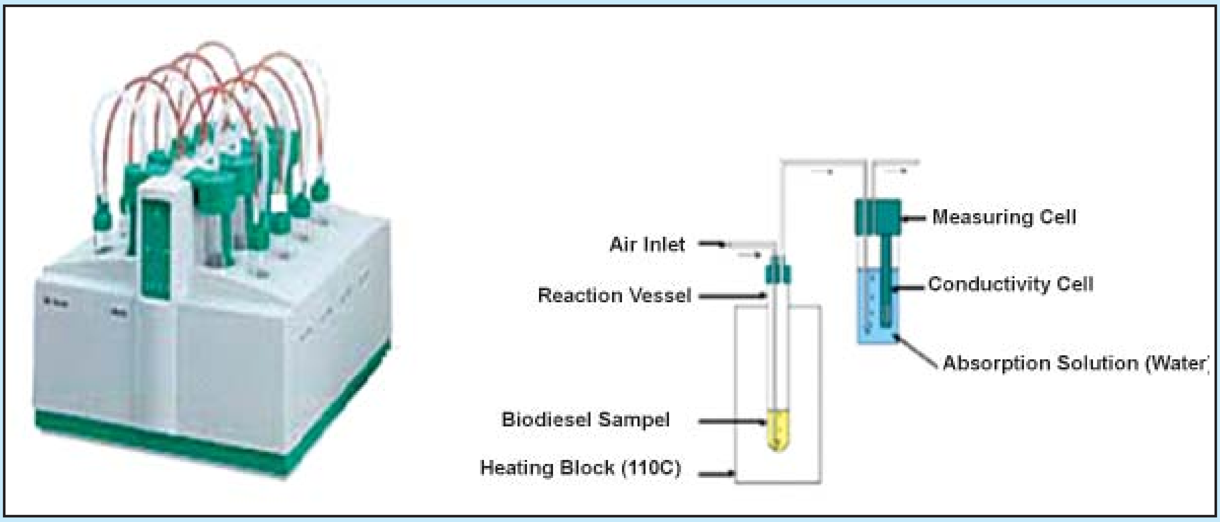

Figure 1
Equipment used for oxidation stability testing (Rancimat method)[6]

Table 1
Physical & chemical properties of Jatropha & Palm biodiesel (Type A)

Properties	Unit	Jatropha	Palm	SNI 04-7182
Viscocity 40°C	cSt	46.679	45.478	2.3-6
Density	kg/m^3	863	858	850-890
Acid Number	mg KOH/g	0.617	0.510	Max. 0.8

Tabel 2
Physical & chemical properties of Jatropha & Palm biodiesel (Type B)

Properties	Unit	Jatropha	Palm	SNI 04-7182
Viscocity 40°C	cSt	46.713	45.312	2.3-6
Density	g/cm^3	0.8617	0.8561	850-890
Acid Number	mg KOH/g	0.687	0.384	Max. 0.8

biodiesel sample is then bubbled through a vessel containing de-ionized water. The conductivity of the water is continually monitored and stored by the software on the attached PC. Oxidation stability (induction time) is measured based on the time required for the appearance of maximum increase of the organic acid content as a result of oxidation or the time that conductivity begins to increase rapidly.

III. RESULTS AND DISCUSSION

A. The properties of biodiesel

The physical and chemical properties of Jatropha and Palm biodiesel for both type A and B are seen in Table 1 and 2. Biodiesel type A and B are made from different raw materials. As seen from Table 1 and 2 measurement values for viscosity, density and acid number meet the specifications of SNI 04-7182-2006. Biodiesel specification for viscosity according to SNI is 2.3 to 6.0 (at 40 °C) and the specification for density is 850-890 kg/m^3 at 40°C. While the specification for the acid number is max. 0.8 mg KOH/g sample.

The typical compositions of saturated and unsaturated of fatty acids of Jatropha and Palm oil are shown in Table 3

Table 3
Compositions of fatty acids in Jatropha and Palm Oil[7]

Fatty Acids	Jatropha (% w/w)	Palm (% w/w)
Laurat (C12/0)	-	0.2
Myristat (C14/0)	-	0.5
Palmitat (C16/0)	12.7	43.4
Palmitoleat (C16/1)	0.7	0.1
Stearat (C18/0)	5.5	4.6
Oleat (C18/1)	39.1	41.9
Linoleic (C18/2)	41.6	8.6
Linolenic (C18/3)	0.2	0.3
Arachidic (C20/0)	0.2	0.3
Behenic (C22/0)	-	0.1
Saturated	**18.4**	**49.1**

B. Prediction of oxidation stability of Jatropha-Palm biodiesel blend

J.Y. Park *et al.*[8] has conducted studies on the effect of blending for various types of biodiesel on the oxidation stability. The study shows that the relationship between oxidation stability and poly-unsat-

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urated fatty acid content can be described using the following model:

$$Y = \frac{117.9295}{X} + 2.5905 \quad (1)$$

X is the content of poly-unsaturated fatty acids (linoleic and linolenic acid in % w/w) and Y is the oxidation stability (hours). If the content of these two unsaturated fatty acids are known, the oxidation stability of biodiesel mixture can be predicted. Table 4 shows the content of poly-unsaturated fatty acids of Jatropha, Palm and the blends of both biodiesels at various compositions. The oxidation stability in Table 4 is calculated using equation (1). The prediction on oxidation stability can be used as a guideline for preparation of Jatropha-Palm biodiesel blends. As a comparison, the results of oxidation stability measurement in the literature[9] for the blend 40% Jatropha and 60% Palm biodiesel is about 6 hours, while the prediction using equation (1) produces the value of 7.94 hours.

The differences in oxidation stability between measurements and predictions using equation (1) could be caused by the variations in the fatty acid compositions or by the presence of impurities (organic acids). From the prediction results in Table 4 it is clear that addition of Palm biodiesel can improve the oxidation stability of Jatropha biodiesel significantly. In this study the use of Palm biodiesel in the blend is limited to maximum 60% v/v. The reasons for the limitation of Palm biodiesel content in the blend are the following:

- The addition 60% of Palm biodiesel has met the ASTM D-6751 for oxidation stability min. 3 hours (lowest value among the international standards)
- Increasing of oxidation stability for Jatropha-Palm biodiesel up to min. 10 hours can done by adding the commercial anti-oxidant

The effect of anti-oxidant treatment on the increase of oxidation stability for Jatropha-Palm biodiesel will be described as follows:

C. Oxidation stability improvement of Jatropha-Palm biodiesel

This study uses anti-oxidant BHT (Butylated Hydroxy Toluene) which is widely available in Indonesian market. Addition of BHT up to 10000 ppm (1%) is expected to increase the oxidation stability up to 10 hours to meet the WWFC specification. Figure 1 shows the effect of addition of BHT on the oxidation stability of Jatropha as well as Jatropha-Palm biodiesel (Type A). The relationships between the oxidation stability and the addition rate of BHT are obtained from the following simple linear regression:

$$Y_1 = 0{,}000498.X + 0{,}447 \quad (2)$$

$$Y_2 = 0{,}000661.X + 1{,}995 \quad (3)$$

Where Y1 is oxidation stability of Jatropha biodiesel (hours), Y2 is the oxidation stability of Jatropha-Palm biodiesel and X is the concentration of BHT.

Figure 1 shows that the oxidation stability of Jatropha-Palm biodiesel higher than that of Jatropha biodiesel after the addition of BHT. The slope of the

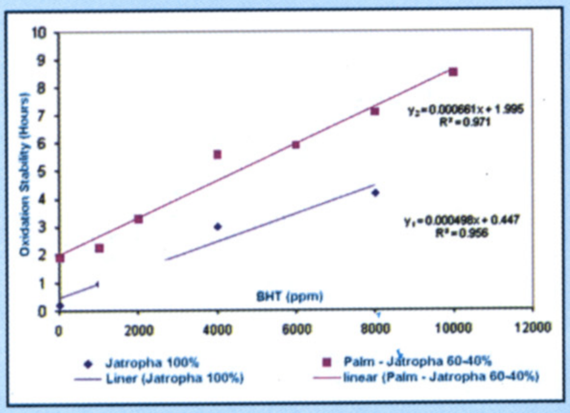

Figure 1
The effect of BHT on the oxidation stability of biodiesel (Type A)

Table 4
Predictions of oxidation stability for Jatropha-Palm biodiesel using equation [1]

Blend Composition	linoleat + linolenat (X, %w/w)	Oxidation Stability (Y, hr)
Jatropha 100%	41.8	5.41
Jatropha-Palm 80-20%	35.22	5.94
Jatropha-Palm 60-40%	28.64	6.71
Jatropha-Palm 40-60%	22.06	7.94
Jatropha-Palm 20-80%	15.48	10.21
Palm 100%	8.9	15.84

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equation (3) is slightly higher (0,000661) compared to the slope of the equation (2) which is 0,000498. The difference in the oxidation stability of the two biodiesels as a function of BHT treatment can be calculated by subtracting the equation (2) from equation (3). This result is as follows:

$$Y = Y2-Y1 = 0,000163.X + 1,547932 \quad (4)$$

Y is the difference in oxidation stability between Jatropha-Palm and Jatropha biodiesel. The factor of 0.000163 can be associated as a contribution of BHT addition to the oxidation stability, while the constant of 1.547932 is the contribution of Palm biodiesel to the oxidation stability of the biodiesel blend. Contribution of Palm biodiesel can be caused by higher content of saturated fatty acids or lower content of polyunsaturated fatty acids. This leads to the increase of the oxidation stability of the biodiesel blend (Jatropha-Palm).Table 5 shows the difference in the effectiveness of the addition of BHT between Jatropha and Jatropha-Palm biodiesel. Effectiveness of BHT addition is calculated using equations (2) and (3), also based on the oxidation stability taken from international standards (ASTM, EN and WWFC).

The data from Table 5 show that the addition of BHT to the Jatropha-Palm is more effective compared to Jatropha biodiesel to fulfill minimum standard in WWFC-2009, EN 14214 and ASTM-6751. Addition of BHT on Jatropha-Palm biodiesel is fewer in quantity (about 37%, 46% and 70%) compared to Jatropha biodiesel. It is known that making Palm biodiesel is cheaper than that of making Jatropha biodiesel because of the limitation of availability of Jatropha oil. Thus the cost to make Jatropha-Palm

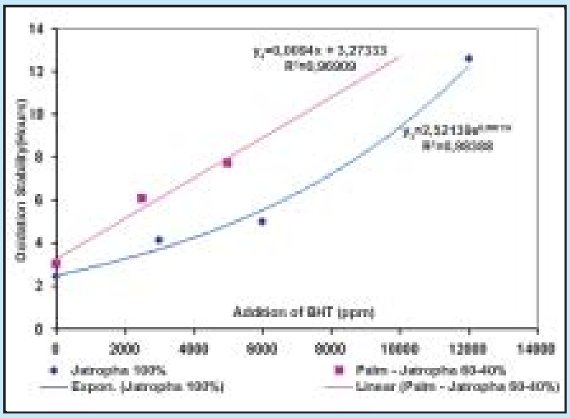

Figure 2
The effect of BHT on the oxidation stability of biodiesel (Type B)

Table 5
The effectiveness of BHT on oxidation stability of biodiesel Type A

Standard for Oxidation Stability	Min. Value	Amount BHT needed (ppm)	
	(hours)	Jatropha	Jatropha-Palm (40:60%)
ASTM 6751	3	5127	1521
EN-14214	6	11151	6060
WWFC 2009	10	19183	12110

Table 5
The effectiveness of BHT on oxidation stability of biodiesel Type B

Standard for Oxidation Stability	Min. Value	Amount BHT needed (ppm)	
	(hours)	Jatropha	Jatropha-Palm (40:60%)
ASTM 6751	3	1337	0
EN-14214	6	6669	2901
WWFC 2009	10	10598	7156

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biodiesel that meets the WWFC specification also lower, especially when using additional anti-oxidant BHT. Therefore, the provision of biodiesel in Indonesia still requires the contribution of edible material such as Palm oil.

Figure 2 shows the effect of BHTaddition on the oxidation stability of biodiesel from Jatropha and Jatropha-Palm (Type B). It can seen that the effectiveness of BHT addition varies from sample to sample, it depends on the raw material used. Table 6 shows the effectiveness of the BHT addition on the oxidation stability of Jatropha and Jatropha-Palm biodiesel (type B) to meet the standards of ASTM, EN and WWFC.

Effectiveness of BHT addition is calculated using equations obtained from regression analysis (depicted in Figure 2). Data from Table 6 show that the effectiveness of BHT in increasing the oxidation stability of Jatropha and Jatropha-Palm biodiesel (Type B). It is concluded that the effectiveness in biodiesel type B is much higher compared with biodiesel Type A. It requires less BHT to improve oxidation stability to meet the standards of ASTM, EN and WWFC.

IV. CONCLUSION

1. The oxidation stability of Jatropha biodiesel can be enhanced to meet the ASTM 6751 with the addition of BHT as much as 1000-5000 ppm. To meet EN-14214 the addition of BHT as much as 7000-11000 ppM is required. Meanwhile, to meet the WWFC 2009 the required addition of BHT is much higher which is about 10000-19000 ppm. To achieve the WWFC standard, the addition of BHT is considered too high (> 10,000 ppm). High concentrations of BHT in biodiesel have a risk of damaging the engine components.
2. The oxidation stability of Jatropha-Palm biodiesel (40-60% v/v) can meet ASTM 6751 with the BHT addition of approximately 2900-6000 ppm and meet the EN-14214 with the BHT addition of approximately 3000-6000 ppm To meet WWFC, the BHT addition of about 7000-12000 is required.
3. The addition of Palm into Jatropha biodiesel biodiesel can reduce the amount of BHT needed to comply with WWFC to less than 10000 ppm. The minimum addition of Palm biodiesel required is 60% v/v. Nevertheless the addition of BHT will depend also of the quality of raw materials used for making biodiesel.
4. Addition of anti-oxidants into the biodiesel should be minimized, this is to reduce costs and the risk of damage to engine components. There is a need for alternative solutions such as the use of anti-oxidant that is more effective than BHT and chemical modifications of biodiesel that can reduce the content of unsaturated fatty acids by hydrogenation, epoxydation and hydroxylation.

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