Effect of Soybean Biodiesel Addition on the Quality of Palm Stearin Biodiesel

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ABSTRACT

Cold flow properties and oxidation stability are two important biodiesel characteristics. Usually biodiesel has these two properties in opposing qualities. Palm stearin biodiesel contains high levels of saturated fatty acid methyl esters (FAME) in the form of 63% palmitic acid methyl ester. Thus this type of biodiesel has bad cold flow properties and good oxidation stability. On the other hand, soybean biodiesel has a high level of unsaturated FAME in the form of 53% linoleic acid methyl ester. Hence it has good cold flow properties whereas the oxidation stability is bad. According to SNI 7182:2015 the maximum temperature of cloud point is 18 °C and minimum value for oxidation stability is 8 hours. The cloud point of palm stearin biodiesel (PSB) can be lowered to below 18 °C, while keeping the oxidation stability at 8 hours, by blending it with soybean biodiesel (SB). In this experiment, cold flow properties and oxidation stability of PSB are 17.4 °C and 17 hours respectively while for the cold flow properties of SB are 0.8 °C and oxidation stability 4.5 hours. The blending was done continuously for 15 minutes with variations in PSB/SB mass ratio 97.5:2.5, 95:5, 92.5:7.5 and 90:10. The cloud point and oxidation stability were analyzed using ASTM D 5773 and EN 15751 respectively. The results showed that by lowering the mass fraction of PSB, the biodiesel blend would have lower values for cloud point while still having good properties in term of oxidation stability. In this study the PSB/SB ratio that resulted in the lowest cold flow property i.e. 16.8 °C was 90:10 with 8.53 hours of oxidation stability.

Keywords: Cloud point, FAME, Oxidation Stability, SNI 7182:2015

INTRODUCTION

Biodiesel is a form of diesel fuel consisting of fatty acid methyl esters (FAME), obtained from vegetable oils or animal fats. Various fatty acid chains in different vegetable oils are accounted for different physical and chemical properties in biodiesel. Cold flow properties and oxidation stability are two important biodiesel characteristics that generally depend on fatty acid composition of the feedstock. Usually biodiesel has these two properties in opposing qualities (Joelianingsih *et al*. 2015).

The cold flow properties are properties that describe the fluidity of biodiesel in low temperature. These cold flow properties

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of biodiesel are assessed by the following temperatures: cloud point (CP) at which crystals begin to form, pour point (PP) at which fuel no longer pours and cold filter plugging point (CFPP) at which fuel crystals begin to stop up a fuel filter. This test is regarded as a better indicator of low temperature operability than cloud point (Isioma *et al*. 2013). According to SNI 7182:2015 (Biodiesel Standard in Indonesia), cold flow properties of biodiesel are assessed only by cloud point.

Oxidation stability is one of the major issues affecting the use of biodiesel mainly because of its unsaturated fatty acid chains and the double bonds in the chains of many fatty compounds. Therefore, oxidation stability is one of the most important characteristics in view of the practical use of FAME (Ramos *et al*. 2009).

Biodiesel is made of feedstock containing higher concentrations of saturated long chain fatty acids tends to have relatively poor cold flow properties and good oxidation stability. While the feedstock that contains higher concentrations of unsaturated (mono and polyunsaturated) long chain fatty acids tends to have relatively good cold flow properties and poor oxidation stability (Edith *et al*. 2012).

Good quality biodiesel has high oxidation stability but is low in CP. Cloud point and oxidation stability are the two significant problems that are often encountered in the use of biodiesel. Biodiesel with high CP cannot be used in an area with a cold climate because it tends to form wax deposits hence blocking the fuel filter in cars. On the other hand if the biodiesel has low oxidation stability, it cannot be stored for a long period since it may degrade and can cause problems in the diesel engine (Shahabuddin *et al*. 2012). Palm stearin biodiesel (PSB) is produced from palm stearin which can be obtained from crude palm oil (CPO). It has a high content of saturated FAME i.e. 63% of palmitic acid methyl ester (PAME), with CP 19.4 °C and oxidation stability 11 hours (Udomsap *et al*. 2008). According to SNI 7182:2015 the maximum temperature for CP is 18 °C and the minimum value for oxidation stability is 8 hours. The cloud point of PSB can be lowered to below 18 °C, while keeping the oxidation stability at 8 hours, by blending it with soybean biodiesel (SB). SB has 53% of unsaturated FAME in the form of linoleic acid methyl ester. The CFPP value of SB is -5 °C and oxidation stability is 1.3 hours (Ramos *et al*. 2009). The aim of this research is to study the characteristic changes of PSB after blending with SB. The quality of biodiesel can be stated by the mass ratio of PSB/SB that will produce biodiesel mixture with cloud point ≤ 18 °C and oxidation stability ≥ 8 hours.

MATERIALS AND METHODS

Materials

PSB used in this study was obtained from one of the Indonesian biodiesel producers whose product has been certified to meet the SNI 7182:2015 standard. SB (Agnique ® ME18S – U Methyl Soyate) used in this experiment was a commercial product purchased from BASF (Mississauga, Canada). The internal standard solution used for characterizing methyl ester composition was nonadecanoic acid methyl which is produced by SIGMA (St. Louis, Missouri, USA).

Biodiesel Blending

PSB and SB were mixed with a variation in PSB/SB mass ratio as follows, 97.5:2.5; 95:5; 92.5:7.5 and 90:10. The mixing process was performed in a continuous agitated beaker glass for 15 minutes.

Analytical Methods

FAME composition and FAME contents in biodiesel was analyzed using gas chromatography (GC) which was conducted at Chemical Engneering laboratory of Institut Teknologi Indonesia. The GC analysis method to determine the methyl ester contents in biodiesel complies with EN14103:2011 method. This method is suitable for FAME which contains methyl esters between C6 and C24. The substrate that was used for FAME analysis was carried in a split injection into an analytical column Rtx®-WAX, RESTEK (Pennsylvania, USA) with a polar stationary phase and flame ionization detector (FID). The GC configuration used in this study was Shimadzu GC-2010 (Kyoto, Japan), fitted with a capillary split/splitless injector and FID. In order to determine the retention time of the FAME, this GC was calibrated using nonadecanoic acid methyl esters (FAME C19) as the internal FAME standard. The ester C content, expressed as mass percentage, was calculated using equation (1).

$$C = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{W_{EI}}{W} \times 100 \quad \cdots (1)$$

where:

$\sum A$ is the total peak area of the methyl ester in C6:0 to that in C24:1;

A_{EI} is the peak area corresponding to nonadecanoic acid methyl ester;

W_{EI} is the weight, in milligrams, of the nonadecanoic acid methyl ester being used as the internal standard;

W is the weight, in milligrams, of the sample.

Several parameters of the biodiesel sample that were analyzed included kinematic viscosity (ASTM D 445), cloud point (ASTM D 5773) iodine value (AOCS Cd 1-25), and oxidation stability (EN 15751). Especially for pure PSB and SB the analyzed parameters were density (ASTM D4052), cetane number (ASTM D 613) and monoglyceride content. The latter analysis was conducted using the titration method listed in SNI biodiesel 7182:2015 clause 9.18. All analyses were conducted at the LEMIGAS Research and Development Centre for Oil and Gas Technology, Jakarta.

RESULTS AND DISCUSSION

The FAME Profile of PSB and SB

The chromatogram of FAME content in PSB and SB are shown in Figures 1 and 2 respectively. These figures show that SB has higher C18:0 and C18:1 compared to PSB. On the other hand, PSB has

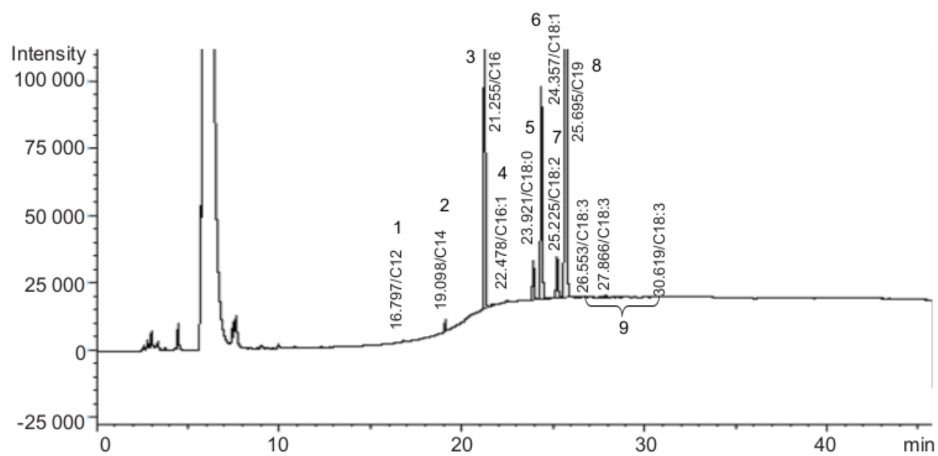

Figure 1 The chromatogram results of fatty acid methyl esters profile of palm stearin biodiesel.

higher C14 and C16. This proves that SB has the potency to be blended in PSB. Table 1 compares the FAME composition of PSB used in this experiment with those found in three references. The comparison of FAME composition of SB used in this study with compositions found in other references is presented in Table 2. The FAME compositions in Table 1 and Table 2 are the result of normalization (FAME content is 100%).

From Table 1 it can be seen that the largest FAME content in PSB is palmitic acid methyl ester (PAME) followed by oleic acid methyl ester (OAME) and linoleic acid methyl ester (LAME). From the table it can also be seen that the FAME content of PSB used in this study is similar to the content of PSB found in three other references. The largest FAME content for SB is LAME followed by OAME and PAME. The composition of those

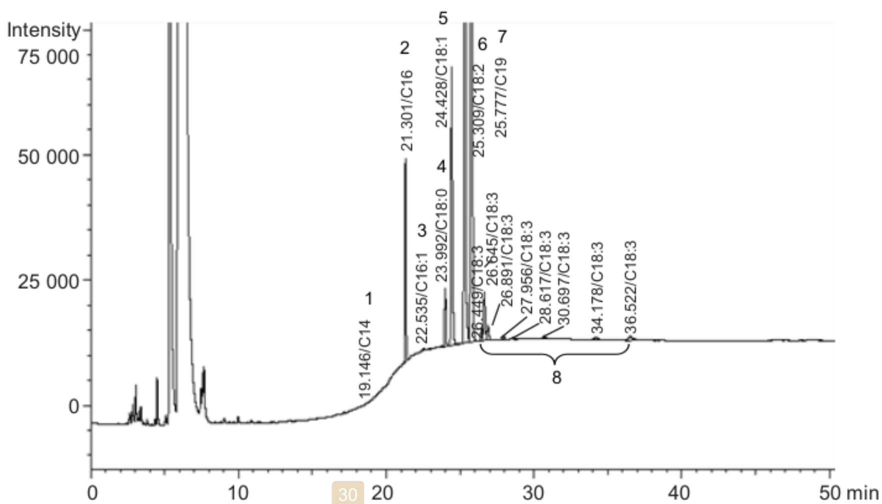

Figure 2 The chromatogram results of fatty acid methyl esters profile of soybean biodiesel.

Table 1 The fatty acid methyl esters composition of the palm stearin biodiesel compared with other references

FAME	Composition (%w w^{-1})			
	Experiment results	References		
		1	2	3
Lauric	0.13		0.100	0.10–0.60
Myristic	1.11	1.21	0.796	1.10–1.90
Palmitic	56.26	61.21	63.131	47.20–73.80
Palmitoleic	0.21		0.093	0.05–0.20
Stearic	5.15	4.0	4.454	4.40–5.60
Oleic	29.93	27.54	25.467	15.60–37.00
Linoleic	6.38	6.05	4.703	3.20–9.80
Linolenic	0.83		0.053	0.10–0.60
Arachidic			0.058	0.10–0.60

[1]Che *et al.* 1999; [2]Udomsap *et al.* 2008; [3]Koushki *et al.* 2015.

Table 2 The fatty acid methyl esters composition of the soybean biodiesel compared with another references

FAME	Composition (%w w^{-1})				
	Experiment results	References			
		1	2	3	4
Lauric			0.1		
Myristic	0.07		0.1		
Palmitic	10.83	11.3	10.2	10.7	7-14
Palmitoleic	0.21	0.1	0.0	0.0	
Stearic	4.18	3.6	3.7	3.2	1.4–5.5
Oleic	22.73	24.9	22.8	25.0	19–30
Linoleic	53.17	53.0	53.7	53.3	44–62
Linolenic	8.81	6.1	8.6	5.4	4–11
others		1.0		2.5	

[1]Ramos *et al.* 2009; [2]Udomsap *et al.* 2009; [3]Isioma *et al.* 2013; [4]Zahan & Kano 2018.

components are also similar to the compositions found in other four previous works.

The compositions of FAME in biodiesel blends a various PSB/SB mass ratio are listed in Table 3. The theoretical compositions were calculated using FAME composition of pure PSB and SB as listed in Tables 1 and 2. The FAME composition of biodiesel blend resulting from the experiment are similar to the compositions that were obtained theoretically through calculation.

Biodiesel Characteristics

Tabel 4 lists the characteristics of biodiesel samples including viscosity, cloud point, iodine value and oxidation stability.

The density of PSB and SB at 40 °C were 865.6 kg $m^{3\ -1}$ and 868.4 kg $m^{3\ -1}$ respectively. The cetane value for PSB was 56.6 while for SB it was 55.8. It was found that PSB and SB have 0.33% and 0.22% (w w^{-1}) for monoglyceride content. Monogliceride content is important because it affects the cloud point of biodiesel, pure or blended. If the monogliceride is higher (higher than the SNI standard), the cloud point is also higher (Kalligeros *et al*. 2014; Aisyah *et al*. 2018). The quality standard for 7 parameters of biodiesel according to SNI 7182:2015 are presented in Table 5. The cloud point of SB as mentioned in several literatures ranges from -2 °C to 2 °C (Mittelbach & Remschmidt 2004; Wang *et al*. 2010).

Table 3 The fatty acid methyl esters composition of blending palm stearin biodiesel and soybean biodiesel

FAME	Experiment results (% w w^{-1})				Theoretical (calculated) (% w w^{-1})			
	97.5:2.5	95:5	92.5:7.5	90:10	97.5:2.5	95:5	92.5:7.5	90:10
Capric	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00
Lauric	0.12	0.13	0.12	0.13	0.12	0.12	0.12	0.11
Myristic	1.09	1.00	1.06	1.16	1.09	1.06	1.04	1.01
Palmitic	57.35	55.33	55.77	51.47	55.13	53.99	52.85	51.72
Palmitoleic	0.27	0.33	0.11	0.40	0.21	0.21	0.21	0.21
Stearic	3.93	4.97	4.15	5.27	5.13	5.11	5.08	5.06
Oleic	30.40	29.65	29.47	28.54	29.75	29.57	29.39	29.21
Linoleic	6.27	7.86	8.80	11.86	7.55	8.72	9.89	11.06
Linoleic	0.70	0.86	0.63	1.17	1.03	1.23	1.42	1.62
Total	100	100	100	100	100	100	100	100

Table 4 Characteristic results of palm stearin biodiesel, soybean biodiesel and blending biodiesel

Mass ratio PSB:SB	Viscosity ($mm^2\ s^{-1}$)	Cloud point (°C)	Iodine value (g I_2 100 g^{-1})	Oxidation stability (hours)
100:0	4.74	17.40	44.75	17.00
97.5:2.5	4.71	17.30	49.44	9.95
95:5	4.58	17.20	50.63	9.85
92.5:7.5	4.56	17.10	52.31	9.07
90:10	4.50	16.80	55.20	8.53
0:100	4.19	0.80	103.94	4.50

Table 5 The quality standard of biodiesel according to SNI 7182:2015

Parameter/Properties	Limits	Units max/min
Density, (40 °C)	850–890	kg $m^{3\ -1}$
Kinematic viscocity (40 °C)	2.3–6.0	$mm^2\ s^{-1}$ (cSt)
Cetane number	51.0	min.
Could point	18.0	°C, max
Iodine value	115.0	(g-I_2 100 g^{-1}) max
Oxidation Stability	480.0	minutes, min
Monoglycerides	0.8	% (w w^{-1}) max

From Tables 4 and 5 it can be seen that blending PSB with SB, where the mass composition of SB ranges from 2.5-10% (w w^{-1}), produces a biodiesel blend with a quality that meets the SNI requirements. Viscosity, cloud point, and oxidation stability of biodiesel blend are inversely proportional to the composition of SB in the blend. On the other hand, the iodine value is higher as the SB composition increases. These results are in agreement with FAME profiles listed in Tables 1-3. As the unsaturated FAME content increases, the iodine value and oxidation stability increases while the cloud point decreases (Knothe 2005; Refaat 2009).

In accordance with the aim of this research, i.e. to know the changes in blend biodiesel properties, the results show that cloud point decreased insignificantly, but unfortunately, it also decreases oxidation stability significantly. Thus to achieve low cloud point and high oxidation stability, the recommended maximum mass composition for SB in PSB/SB biodiesel blend is 10%.(w w^{-1}).

CONCLUSION

PSB has high oxidation stability (17 hours) but low cold flow properties (17.4 °C). Blending PSB with SB is a practical method to decrease its cloud point but maintain the oxidation stability more than 8 hours. The recommended maximum mass concentration of SB in PSB/SB blend is 10% or the ratio of PSB/SB is 90:10. The SB composition more than 10% can reduce oxidation stability significantly even it can be below the standard value. This blending method produced blend biodiesel with characteristics that still comply with the SNI requirement i.e. cloud point of 16.8 °C and oxidation stability of 8.53 hours where the maximum cloud point is 18 °C and minimum oxidation stability is 8 hours.

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