BLENDING OF JATROPHA OIL WITH OTHER VEGETABLE OILS TO IMPROVE COLD FLOW PROPERTIES AND OXIDATIVE STABILITY OF ITS BIODIESEL

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ABSTRAK

Minyak jarak pagar kaya akan asam lemak tidak jenuh, sedangkan minyak tropis lainnya, seperti minyak sawit dan kelapa, kaya akan asam lemak jenuh. Pencampuran biodiesel jarak pagar dengan biodiesel kedelai, biji rapa, sawit dan kelapa menghasilkan sifat yang beragam, yang berada di antara sifat masing-masing komponen murninya. Biodiesel jarak pagar pada konsentrasi 50 – 70% dalam campuran jarak pagar-kelapa memiliki nilai titik awan dan titik tuang yang lebih baik (masing-masing 9 ^{o}C dan -6 ^{o}C), dibandingkan biodiesel jarak pagar (12 ^{o}C, 0 ^{o}C) dan biodiesel kelapa (15 ^{o}C, 9 ^{o}C). Pencampuran jarak pagar dengan kelapa selanjutnya dipelajari menggunakan dua metode yakni metode 1 adalah pencampuran dalam bentuk biodiesel dan metode 2 adalah dalam bentuk minyak sebelum proses biodiesel. Pencampuran metode 2 menghasilkan titik awan yang lebih tinggi dan titik tuang yang lebih rendah dibanding metode 1 dan nilainya relatif konstan. Pencampuran 55% biodiesel jarak pagar dengan biodiesel laurat (75% laurat metil ester) menunjukkan titik awan dan titik tuang minimum (-3 ^{o}C; -18 ^{o}C). Titik minimum ini disebut titik *eutectic* yang mencerminkan keseimbangan yang ideal dari cair-padat di antara metil ester jenuh rantai sedang dan metil ester tidak jenuh rantai panjang. Komposisi metil ester biodiesel ini adalah laurat 34,03%, miristat 0,31%, palmitat 8,91%, stearat 3,82% dan oleat 46,17%. Hasil ini juga menunjukkan peran laurat, suatu asam lemak jenuh rantai sedang, yang dominan dalam biodiesel kelapa (48,11%).

Kata Kunci: biodiesel jarak pagar, pencampuran, titik awan, titik tuang

ABSTRACT

Jatropha oil has rich in unsaturated fatty acids, but other tropical oils, such as palm oil and coconut oil, have high saturated fatty acid. Blending of jatropha biodiesel with soybean, rapeseed, palm and coconut biodiesels resulted in different propertie, between properties of each pure compounds or even better than pure biodiesel. Jatropha biodiesel in concentration of 50-70% jatropha-coconut blend had better cloud point and pour point (9 ^{o}C and -6 ^{o}C, respectively), compare to jatropha biodiesel (12 ^{o}C, 0 ^{o}C) and coconut biodiesel (15 ^{o}C, 9 ^{o}C). Blending of jatropha and coconut were further investigated using two methods, namely methods 1 was in the form of biodiesel and method 2 was in the form of oil before biodiesel processing. Blending method 2 resulted in higher cloud point and lower pour point compared to method 1 and the values were relatively constant. Blending of 55% of jatropha biodiesel with lauric biodiesel (75% lauric methylester) showed a minimum cloud point and pour point (-3^{o}C; -18^{o}C). This minimum point called eutectic point expressed an ideal equilibrium of liquid-solid among saturated medium chain alkyl esters and unsaturated long chain alkyl esters. Methylester composition of this biodiesel was 34.03% lauric, 0.31% miristic, 8.91% palmitic, 3.82% stearic and 46.17% oleic acids. This proved the important role of lauric acid, a medium chain saturated fatty acid, which was dominant in coconut biodiesel (48.11%).

Keyword: jatropha biodiesel, blending, cloud point, pour point

INTRODUCTION

Biodiesel is an alternative for petroleum fuel that can be commercially produced through transesterification of vegetable oils with alcohol and alkaline catalyst. Utilization of biodiesel fuel will greatly contribute to mitigation of environmental issues such as global warming and air pollution since its feedstock of biomass is carbon neutral and low in sulfur content.

Cold flow properties of biodiesel are depending on properties of fatty acid composition in vegetable oil (Goering *et al.,* 1982). Usually, unsaturated fatty acid has lower cloud point and pour point compare with saturated one, but it more susceptible to oxidation (Mittelbach and Remschmidt, 2004). These oils are characterized according to their cold flow properties and oxidative stability, which are attributed to their fatty acid composition. In general, unsaturated fatty acids are

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low in melting point, while saturated ones high. The high degree of unsaturation makes a melting point lower, and simultaneously, causes high vulnerability to oxidation (Kazancev *et al.*, 2006).

Improvement of low temperature flow characteristic still remains one of the major challenges while using biodiesel as an alternative fuel for diesel engines. The biodiesel fuels derived from oils with significant amounts of saturated fatty acid compounds will display higher cloud points and pour points. The cloud point, which usually occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons causes fuel starvation and operability problems as solidified material clog fuel lines and filters. With decreasing temperature more solids form and material approaches the pour point, the lowest temperature at which it will cease to flow.

Jatropha oil is one of the prospective biodiesel feedstock among several options currently developed in Indonesia. The plant is known to tolerate varying weather conditions and soil types. Soybean and rapeseed oil are common feedstock for biodiesel production in USA and Europe, respectively. Due to substantial amount of unsaturated fatty acids in that oil, they have good low temperature properties. On the other hand, palm and coconut oil were also abundance feedstock in Indonesia, but they have high pour point and cloud point because of high saturated fatty acid content. The advantage of this oil is good in oxidative stability and high cetane number (Sarin *et al.*, 2007).

In order to improve characteristics of jatropha oil as biodiesel feedstock, trade off relation between fluidity in cold climate and oxidation stability can be achieved by blending jatropha with other vegetable oils. Binary mixtures of Jatropha with palm and coconut have been examined to get an optimum mix to achieve better low temperature properties and to improve oxidative stability from tropical oils. Blending of jatropha with soybean and rapeseed was also used as comparison. The first objective of this study is to improve jatropha fuel properties by blending with various source of vegetable oil. The second is to examine the effects of fatty acid compositions in the blended biodiesel on the cold flow properties and oxidative stability, and third, to find out the role of lauric acid in decreasing pour point and cloud point of jatropha-coconut biodiesel mixture.

RESEARCH METHOD

Material

Jatropha curcas seed was obtained from farmers plantation. Crude palm oil, refined coconut, soybean and rapeseed oil were obtained from local market. KOH, sulfuric acid and methanol for biodiesel processing were technical grade. Phenolphtalein, neutral 95% ethanolic solution, 0.1 N $Na_2S_2O_3$, 5% KI, chloroform, and amylum were used for analysis free fatty acid and iodine value. Instrument for analysis was GC HP 6980 series (Agilent Technology, Hewlett-Packard), other equipments were glass capillary viscometer, picnometer, four-necks vessel, condensor, thermometer, magnetic stirer, and glassware.

Methods

Two methods were used to prepare mixture of biodiesel fuels. In method 1, crude jatropha oil, crude palm oil and refined oils of rapeseed oil, soybean oil, and coconut oil were converted to their methyl esters with alkali-catalyzed method. Esterification process using acid catalyst as pretreatment was done for crude oil of jatropha (Tiwari *et al.*, 2007) and palm due to high acidic content. These methyl esters were mixed at various molar ratios to make binary mixture with jatropha methyl ester in the concentration of 0–100% jatropha biodiesel with increment of 10%. The mixture was then stirred thoroughly. Second step was to compare biodiesel jatropha-coconut mixture from this method with biodiesel prepared by method 2. Method 2 was blending the oil of jatropha and coconut before transesterification. The concentration of jatropha oil in mixture were 0-100% with increment of 10%. Transesterification was then conducted to convert oil blends into its methyl ester. Analysis of clouding time was carried out for this blends.

The selected range of jatropha concentration in jatropha-coconut blends was 50-70% with increment of 5% for method 1, while the selected range of method 2 was 35–55% with increment of 5%. Lauric acid with concentration of 75% in oil was converted to methyl ester by esterification process. Its biodiesel was used for further study of the capability of coconut biodiesel which has high lauric methylester content to improve cold flow properties of jatropha biodiesel mixture. Selected range for jatropha biodiesel volume in jatropha-lauric mixture was 35-65% with increment of 5%. Sample from two methods of blending and jatropha-lauric biodiesel were analysed for their pour point, cloud point, and some physical characteristics to compare with biodiesel standard.

Biodiesel samples have been prepared using alkali catalyzed method. Methanol (1:3 molar oil: alcohol) was mixed with NaOH/KOH (1 wt% of oil) added to the reactor containing oil slowly along with stirring. The reaction mixture was heated at 65 ^{o}C for 2 h. After completion of the reaction the material was transferred to separating funnel and both the phases were separated. Upper phase was biodiesel and lower part was glycerin. Upper phase i.e. methyl ester (biodiesel) was washed with the water twice to remove the traces of glycerin, unreacted catalyst and soap formed during the transesterification. The residual product was heated to get rid of residual moisture.

Yield of methyl esters and their composition were analyzed by Gas Chromatography system with HP FFAP column (25 m x 0.32 µm film thickness) and FID detector. Methyl esters standards for GC were C8-C22, all purchased from Nu Chek Prep (USA).

The cloud point and pour point were measured by ASTM D2500 and D 97, respectively. The pour point is defined as the temperature at which the fuel can no longer be poured due to gel formation. The observation of the samples starts at a temperature that is at least 9 ^{o}C above the expected pour point. The sample was immersed into a 18^{o}C cooling bath and temperature was cooled to about -20 ^{o}C in cooling bath. Readings were taken for every 3 ^{o}C decrease in the temperature until the sample totally ceased to flow (the sample was held in horizontal position for 5 s). Readings of the test thermometer were taken and 3 ^{o}C was added to the temperature recorded as the result of the ASTM D-97 pour point.

The cloud point is defined as the temperature at which a cloud of wax crystal first appears in a liquid when it is cooled under controlled conditions during a standard test. The same cooling procedure as described in ASTM D-97 was followed; the samples were examined at intervals of 1 ^{o}C, until any cloud was observed at the bottom of the test jar. The cloud point was reported to the nearest 1 ^{o}C as ASTM D-2500 cloud point.

RESULTS AND DISCUSSION

Table 1 shows methyl esters composition of jatropha, coconut, palm, rapeseed, and soybean biodiesel. It is clear that most of the feedstock, except for coconut oil, consist mainly of palmitic (C16:0), stearic (C18:0), oleic (C18:1) and linoleic (C18:2) acids, in which the first number in the bracket is total number of carbon atoms in the fatty acid unit of the molecule, while the second is that of double bonds.

Some physical characteristics of biodiesel is shown in Table 2. Jatropha, rapeseed, and soybean biodiesel has lower cloud point and pour point than coconut and palm. Rapeseed has the lowest temperature because of the highest degree of unsaturated fatty acid. Cloud point of coconut biodiesel was lower than palm, it caused by the content of medium chain fatty acid, lauric acid, which in palm, the dominant fatty acid is long chain palmitic and stearic acid. Cloud point and pour point increase along with length of fatty acid chain. Saturated methylesters tend to form crystal at low temperature because they have high intermolecular forces. Methyl esters molecules have sufficient polarity in carboxylic group for giving them an amphiphilic nature and allowing the formation of bi-layer structures with the head groups aligned next to each other inside the crystal and away for non-polar bulk liquid.

Table 1. Methyl esters composition (wt%)

VEGETABLE OIL	**Number of Carbon Atoms : double bonds**									
	(8:0)	**(10:0)**	**(12:0)**	**(14:0)**	**(16:0)**	**(18:0)**	**(18:1)**	**(18:2)**	**(18:3)**	**(22:1)**
Jatropha	-	-	0.09	0.08	15.7	-	45.1	38.3	-	-
Coconut	8.3	6	46.7	18.3	9.2	2.9	6.9	1.7	-	-
Palm	1.0	0.1	0.9	1.3	43.9	4.9	39	9.5	0.3	-
Rapeseed	-	-	-	-	2.7	2.8	21.9	13.1	8.6	50.9
Soybean	-	-	-	0.1	10.3	4.7	22.5	54.1	8.3	-

Table 2. Biodiesel physical characteristics

BIODIESEL	**CloudPoint (^{o}C)**	**Pour Point (^{o}C)**	**Viscosity (cSt, 40 ^{o}C)**	**Density (g/ml, 40 ^{o}C)**
Jatropha	12	0	8.557	0.8765
Coconut	15	6	5.679	0.8805
Palm	18	12	8.566	0.8756
Rapeseed	0	-6	8.523	0.8800
Soybean	9	0	8.498	0.8826

Low Temperature Properties

Jatropha biodiesel has good low temperature properties measured in terms of cloud point, and pour point, comparable to conventional biodiesel feedstocks like soybean and rapeseed. Binary mixtures of jatropha biodiesel with other biodiesel samples were therefore examined for their low temperature properties, to study the effect of other vegetable oil biodiesel on Jatropha biodiesel properties.

Figure 1 shows changes in cloud point and pour point of blending biodiesel in different ratio of jatropha biodiesel with other biodiesel. Figure 1a. showed that cloud point of soybean was 9 ^oC and increased slightly to 12 ^oC even in addition of only 20% jatropha biodiesel. The same trend was found in cloud point. The lowest cloud point and pour point was 9 ^oC and -3 ^oC, respectively, at 10% jatropha in soybean biodiesel. It can be shown that soybean and jatropha have almost similar cloud point and pour point, whereas rapeseed biodiesel has the lowest. Blending of palm biodiesel in jatropha biodiesel exhibits additive response in cloud and pour point properties and worsen the low temperature properties of jatropha biodiesel. Similar behaviors were also observed by Imahara (2006) for binary mixtures of saturated and unsaturated esters, such as pure methyl palmitate (C16:0) and methyl oleate (C18:1). These results mean that saturated esters, which have higher pour point than unsaturated ones, have a significant effect on characterizing its cold properties.

In the case of the mixtures consisting of coconut oil and jatropha biodiesel, dissimilar behavior was observed. Pour point of mixture was gradually decreased to the eutectic point (-6 ^oC), and then increased. The same curve was also found in cloud point. This tendency in cloud point and pour point change is very similar with cloud point of other mixtures of two saturated esters. It indicates that binary mixture of saturated esters has the lower pour point at a eutectic point than that of either component of esters. The existence of such eutectic point indicates that the first crystal formed at the cloud point consists of only a single pure methyl ester especially for saturated one having high melting point. In this case, interaction among lauric acid from coconut and saturated fatty acid from jatropha (C16:0, C18:0) could be having an important role.

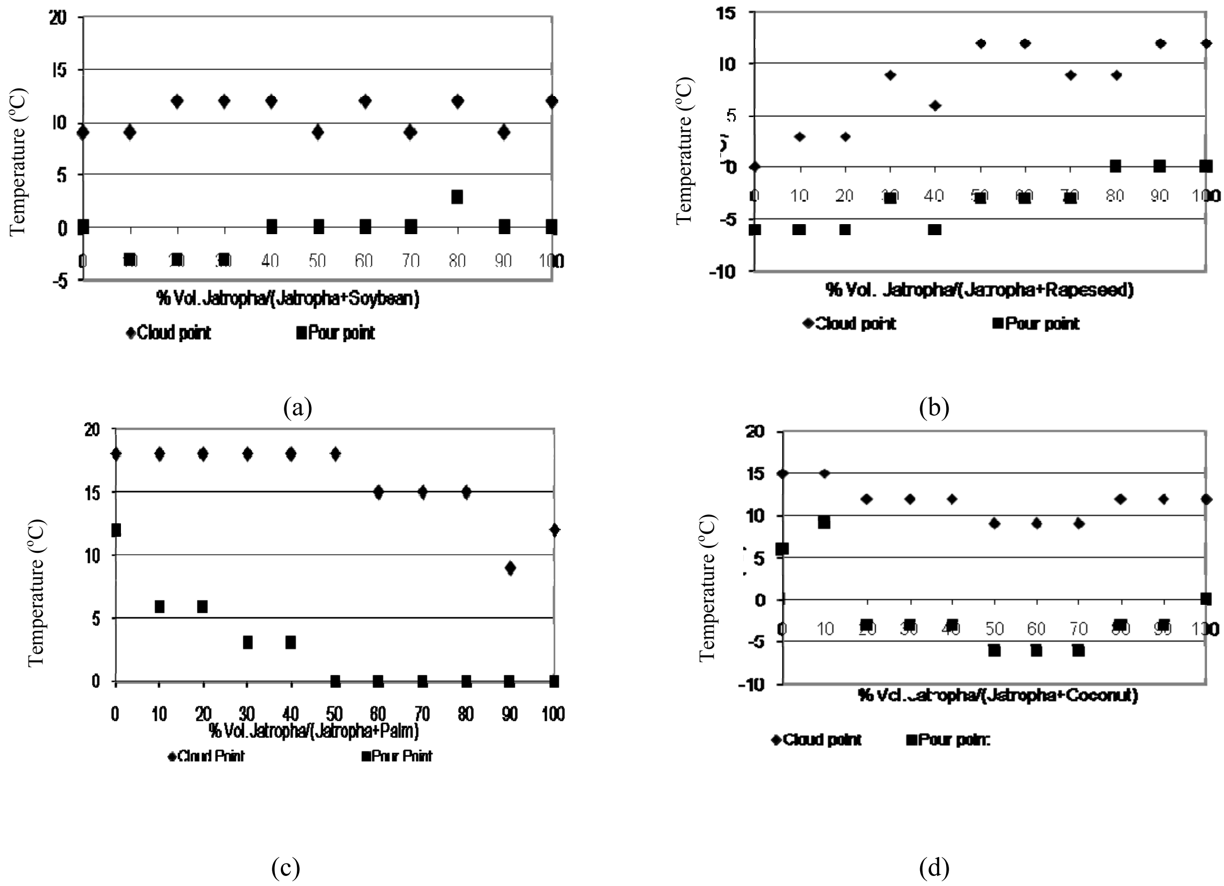


Figure 1. Cloud point and pour point of various blending biodiesel: a. Jatropha-soybean, b. jatropha-rapeseed, c. jatropha-palm, d. jatropha-coconut

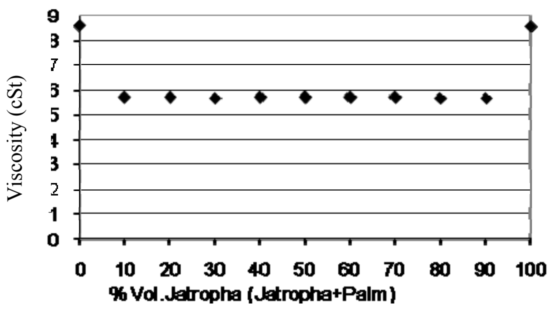
Other important fuel properties at low temperature of biodiesel derived from vegetable oil is viscosity. The viscosity kinematic is ratio of dynamic viscosity and density (Knothe *et al.*, 2004). Jatropha, rapeseed, and soybean biodiesel was dominated by unsaturated methylester, consist of oleic (C18:1), linoleic (C18:2), and linolenic (18:3) ester. The kinematic viscosity of unsaturated fatty compounds strongly depends on the nature and number of double bonds with double bond position affecting viscosity less. Effect of blending palm, coconut, rapeseed and soybean biodiesel with jatropha biodiesel at various concentrations showed at Figure 2a-d.

Figure 2 shows non-linear value of viscosity with added concentration of jatropha biodiesel in mixtures. Almost in all cases, blending will decrease kinematic viscosity of biodiesel mixture below its intrinsic value and then increase to the jatropha biodiesel viscosity. Value of kinematic viscosity in all blended was lower than parent biodiesel and that was in range ASTMD 6751 with limited 2,3 – 6,0 mm^2/s. Density order from the highest to the lowest value was coconut, soybean, rapeseed, jatropha and palm. Mixture with jatropha decreased the density, except for palm biodiesel.

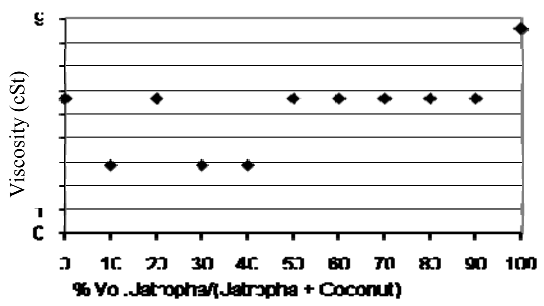
Futher investigation was done to jatropha-coconut blend prepared by biodiesel blend (method 1) and oil blend (method 2). Biodiesels from method the two was evaluated for clouding time. A time when clouds start to appear in clear biodiesel liquids at low temperature. Concentration of 50% jatropha showed the longest clouding time either in method 1 or method 2. Clouding time for pure jatropha and coconut biodiesel were 21.11 and 10.23 minutes, respectively. Further investigation was done in selected range of 50-70% jatropha in mixture for method 1 and 35-55% jatropha in mixture for method 2, with smaller increment of 5%. At these concentrations, clouding time relatively longer than others. The clouding time of 50, 55, 60, 65 and 70% biodiesel method 1 were 25.3, 21.42, 19.04, 18.23, and 17.56 minutes, respectively. While in the concentrations of 35, 40, 45, 50, and 55% jatropha in mixture for method 2 were 19.08, 23.51, 21.35, 25.41, and 20.12 respectively.

Figure 3 shows cloud point and pour point from different method of biodiesel preparation. Blending was done in the form of oil before biodiesel process, in the range of 35%-55% jatropha in blends (method 2). Different method of blending caused slightly different in cloud point and pour point. Blending in the form of oil resulted in higher cloud point and lower pour point compare to in the form of biodiesel (method 1) and the values were relatively constant. Blending 55% of jatropha biodiesel with lauric biodiesel (75% lauric methylester) showed a minimum cloud point and pour point (-3 ^oC, -18 ^oC).

This minimum point called eutectic point expressed an ideal equilibrium of liquid-solid among saturated medium chain alkyl esters and unsaturated long chain alkyl esters. Methylester composition of this biodiesel was 34.03% lauric, 0.31% miristic, 8.91% palmitic, 3.82% stearic and 46.17% oleic. This proved the important role of lauric, a medium chain saturated fatty acid, which was dominant in coconut biodiesel (48.11%).



(a)



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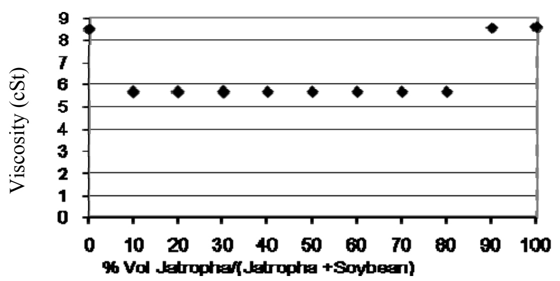

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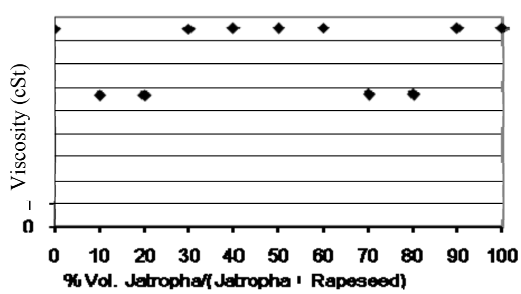
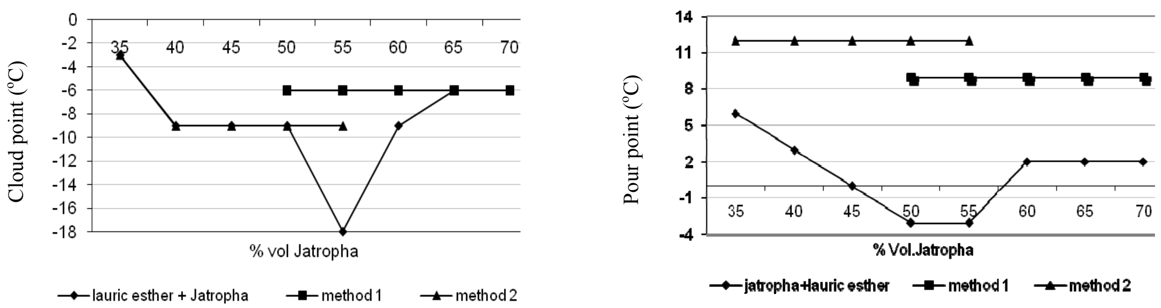


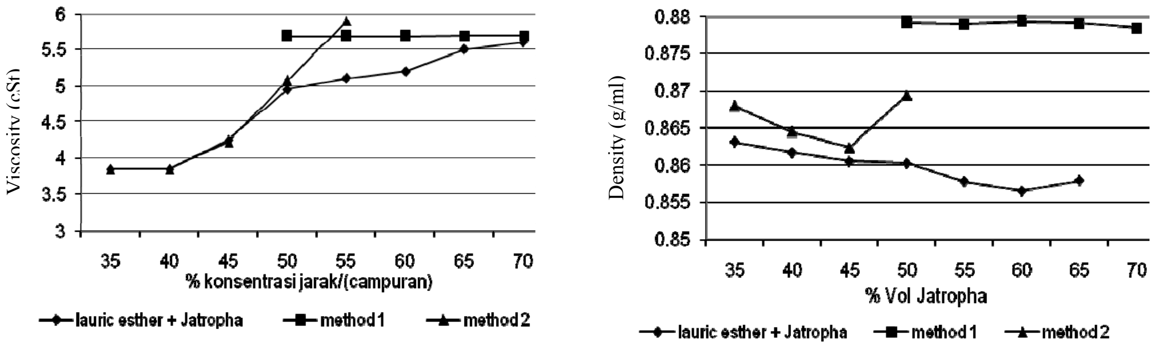
(d)

Figure 2. Changes viscosity at various blending of biodiesel: a. jatropha-palm, b. jatropha-coconut, c. jatropha-soybean, d. jatropha-rapeseed



(a) (b)

Figure. 3. Cloud point and pour point of jatropha–coconut biodiesel and jatropha-lauric ester



(a) (b)

Figure 4. Kinematic viscosity (a) and density (b) of jatropha–coconut biodiesel and jatropha-lauric ester

Viscosities of pure jatropha and coconut biodiesel were 8.55 cSt and 5.67 cSt at 40 ^oC. Jatropha has higher viscosity than coconut because it contains unsaturated oleic ester which has viscosity of 4.51 cSt, while coconut contains lauric ester which has viscosity of 2.43 cSt. All biodiesel mixture were in the range of kinematic viscosity requirement of biodiesel standard which is 2.4 - 6.0 cSt at 40 ^oC (Figure 4a). High viscosity affected the fuel injection and lubricity in an engine (Allen *et al.*, 1999).

Densities of pure jatropha biodiesel, coconut biodiesel and lauric ester were 0.8765, 0.8805, and 0.8727 g/m^3, respectively. Increasing concentration of jatropha biodiesel tend to decrease density of the mixture. Mixture of jatropha with lauric ester gave the lowest density which was significantly lower than the pure biodiesel itself (Figure 4b).

Iodine value of pure jatropha biodiesel and coconut biodiesel were 82.53 g I_2/100 g and 9.41 g I_2/100 g, respectively. Therefore, increasing concentration of jatropha biodiesel will increase the iodine value (Figure 5). High iodine value represent high degree of unsaturation. According to methylesters composition with GC, jatropha biodiesel had 83.35% (w/w) unsaturated ester and coconut biodiesel had only 1.84% (w/w). Unsaturated esters can improve low temperature properties because they have lower melting point (Gerpen *et al.*, 2004; Knothe *et al.*, 2004), but on the other hand, unsaturated esters can easily react with oxygen in the atmosfer, formed polymerized oxidative compounds (Knothe, 2007). Maximum iodine value according to European standards (EN 14214) is 115 to maintain oxidative stability and prevent high carbon deposite in engine. In addition, concentration of linolenic acid and four double bond ester are not exceed than 12 and 1%, respectively. All the values were in accordance with European standard.

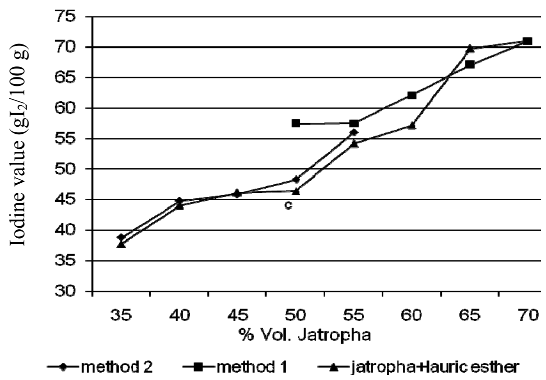


Figure 5. Iodine value of jatropha – coconut biodiesel and jatropha-lauric ester

CONCLUSION AND RECOMMENDATION

Conclusion

Blending of jatropha biodiesel with soybean, rapeseed, palm and coconut biodiesels resulted in different properties, between properties of each pure compounds or even better than pure biodiesel. Jatropha biodiesel in concentration of 50-70% jatropha-coconut blend had better cloud point and pour point (9 °C and -6 °C, respectively), compare to jatropha biodiesel (12 °C, 0 °C) and coconut biodiesel (15 °C ,9 °C).

Blending in the form of oil before biodiesel process gave wider range of cloud point and pour point than in the form of its biodiesel. Minimum point was in the range of 40 – 55% jatropha oil in blends. Blending of lauric ester and jatropha biodiesel gave the lowest cloud point and pour point (-3 °C and -18 °C) at 55% jatropha in blends. This proved that there was an equilibrium between saturated and unsaturated fatty acids in eutectic point and lauric acid from coconut had an important role. Therefore, mixture of jatropha biodiesel with coconut biodiesel can lead to a synergistic combination with improved low temperature property and oxidation stability.

Recommendation

The mixture of jatropha with coconut was the best combination in term of cold properties and axidative stability. However, it should be further evaluated for its chemical stability and performance on diesel engine.

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