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Evaluation of the oxidation stability of jatropha biodiesel/diesel blends

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ABSTRACT

One of the major technical issues facing biodiesel is its susceptibility to oxidation which is due to its content of unsaturated fatty acid chains, especially those with bis–allylic methylene moieties. In addition, the presence of air and other factors also influences the oxidation process of biodiesel including presence of light, elevated temperature, as well as extraneous materials such as metals which may be even present in the container material. The overall objective of this work is to evaluate the oxidation stability of Jatropha biodiesel/diesel blends. An acid–catalyzed pretreatment followed by a standard transesterification procedure in a potassium methoxide solution to produce Jatropha methyl ester (JME) from Jatropha curcas L. oil (JO) with high acid value of 16.25 mg KOH/g was accomplished. The analysis of the physicochemical properties showed JME demonstrated potential as a good candidate for feedstock in biodiesel production because the studied physicochemical properties of JME adequately satisfied the relevant standards for biodiesel quality, with the exception of the kinematic viscosity at 40°C. Also, gas chromatography–mass spectrometry analytical result showed that fatty acid composition of JO was quite similar to that of conventional oils. Especially, the evaluation of oxidation stability of Jatropha biodiesel/diesel blends was accomplished with respect to the change in the quality after oxidation by bubbling oxygen at elevated temperature as well as oxidation of blend fuels in contact with copper plate. The results demonstrated a strong correlation between biodiesel concentration and blend stability; i.e., the increase in biodiesel concentration results in the lower stability in both cases of the copper strip corrosion test and the accelerated oxidation.

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1 INTRODUCTION

Global climate change and fossil fuels depletion are among the most critical issues facing human civilization. The development and use of renewable energy sources have the potential to address both issues. Among these sources, biofuels have been gaining increasing interest in the past decade as a substitute for petroleum in the transportation sector to mitigate the effects of greenhouse carbon dioxide (CO_2) emissions on climate change and offset the depletion of fossil fuels. However, the challenges with biofuels are that their production must be highly scalable and result in minimal environmental

impact. Moreover, their physicochemical properties must be consistent with those of petroleum. Known to be renewable, biodegradable and less pollutant emission, biodiesel, which is prepared from vegetable oils and animal fats, has been studied extensively as an alternative for diesel fuel.

Although biodiesel can be used in its neat form, it is recommended that being used in its blends with petrodiesel at any level leads to the improvement in its quality. Its blend is denoted as "BXX", where "XX" represents the biodiesel fraction (i.e., B20 consists of 20% of biodiesel and 80% of petrodiesel). However, the differences in chemical nature between biodiesel and diesel may lead to differences in the physicochemical properties, affecting engine performance and pollutant emissions. Therefore, the quality control of biodiesel blends should be monitored in several aspects (Benjumea *et al.*, 2008; Jha *et al*., 2008). Oxidation stability of biodiesel has been the subject of extensive studies, primarily in regard to oxidation during extended storage periods. This is one of the major challenges for the use of biodiesel because of its unsaturated fatty acid content, which is especially susceptible to oxidation (Knothe, 2006). There are numerous factors, such as presence of air, elevated temperatures and presence of metals that were found to promote oxidation. According to Knothe and Dunn (2003), the increase in the number of double bonds in biodiesel enhances its oxidation.

The presence of metal, such as copper, can increase the oxidation of biodiesel. Sarin *et al*. (2009) studied the influence of metal contaminants on oxidation stability of JME and reported that even low concentrations of metal contaminants resulted in nearly the same influence as high one. Of all studied metals, copper was found to be the strongest detrimental and catalytic effect on oxidation stability of biodiesel. The oxidative stability significantly decides the fuel quality; therefore, the European Committee for Standardization (CEN) was mandated to develop standard specifications and test methods regarding the biodiesel oxidation stability. This issue has been addressed in the European FAME (free fatty acid methyl ester) standard EN 14214 and in the recent version of the European standard for automotive diesel (EN 590:2009). The latter requires the determination of oxidation stability of Jatropha biodiesel/diesel blends using the modified Rancimat method EN 15751. The finished blends of diesel fuel with biodiesel shall comply with a minimum induction period of 20 hrs. at 110ºC. The established European standard EN 14112 using a Rancimat apparatus is the test method for determining oxidative stability of biodiesel at 110ºC, with a minimum induction period of 6 hrs. However, in order to ensure a high quality biodiesel within the EU, the CEN has already discussed a change in the limit of a minimum induction period of 8 hrs instead of 6 hrs.

Jatropha curcas is a drought–resistant shrub or tree grown in Central and South America, Southeast Asia, India, and Africa. *Jatropha curcas* was propagated from South America to other countries in Africa and Asia by the Portuguese (Gubitz *et al*., 1999). It is well adapted to arid and semiarid regions and often used for soil erosion control. The seeds of Jatropha resemble castor seeds, somewhat smaller in size (0.5 to 0.7 g) and dark brown in color. The oil content of the seed varies from 30 to 40%. The oil is toxic due to the presence of diterpenes, mainly phorbol esters, responsible for tumor–promoting activity.

Oil contents, physicochemical properties, fatty acid composition and energy values of Jatropha species were investigated in many studies (Banerji *et al*., 1985; Kandpal and Madan, 1995; Haas and Mittelbach, 2000; Kumar *et al*., 2003; Pramanik, 2003; Akintayo, 2004; Shah *et al*., 2004) while it is considered that oil from Jatropha has toxic substance (Hirota *et al*., 1988; Gandhi *et al*., 1995; Makkar *et al*., 1998; Abdel Gadir *et al*., 2003). A number of research papers have appeared on the production of biodiesel from Jatropha curcas L. oil (JO) (Berchmans and Hirata, 2008; Lu *et al.*, 2009; Shutt *et al*., 2010). So far, however, there has been little work about the oxidation stability of blending biodiesel from nonedible oilseeds like Jatropha with diesel.

Biodiesel fuels are expected to be used in various forms of blends, thus the quality standardization is necessary. The objective of this research to investigate the oxidation stability of Jatropha biodiesel/diesel blends (B5, B10, and B20) prepared from Jatropha methyl ester (JME). The effects of evaluated temperature (115ºC) and copper metal on the oxidation stability of Jatropha biodiesel/diesel blends were studied further in this work.

2 MATERIALS AND METHODS

2.1 Materials

All the chemicals used (for the biodiesel fuel production or analyses) were analytical reagent grade or equivalent.

JO was obtained from West Nusa Tenggara, Indonesia.

2.2 Methods

2.2.1 Conversion of oil into biodiesel

The used crude oils in this study contained a high concentration of free fatty acids. Therefore, methyl esterification of the free acid was carried out in methanol in the presence of sulfuric acid (1 w/v%) prior to transesterification for biodiesel production, according to method of Ghagde and Raheman (2005). The pre–processed crude oil was then mixed with potassium methoxide solution (1.0 w/v) in a round glass flask at the volume ratio of 1:8 (alkaline methanol to oil), and the mixture was kept to react at 60°C while stirring. After 2 hrs., the product was cooled down and left for separation of the biodiesel in a separating funnel. After removing the glycerol layer at the bottom, the remaining biodiesel was washed twice with an equivalent amount of water to remove residual methanol and alkali. Finally, the biodiesel was vacuum–dried at 60°C until reaching the water content of less than 500 ppm, which is the standard limit of water content.

2.2.2 Fatty acid profile

Fatty acid methyl ester composition was analyzed by a gas chromatograph–mass spectrometer (GC–MS 2010, Shimadzu Co., Japan) equipped with a wax column (Inert–Cap Pure Wax column, 30 m × 0.25 mm–id, GL Sciences Inc., Japan). Helium was used as the carrier at a flow rate of 2 mL/min. One µL of FAME samples was injected through the auto injector (AOL–20i, Shimadzu), and the peaks were observed under the column temperature programmed to start at 50°C, being heated to 260°C at a rate of 5°C/min and held at this temperature for 10 min. The compounds in a biodiesel fuel were identified by the mass spectroscopic peak profile and the molecular weight of parent peak using the chemical library in the workstation system equipped in the present Shimadzu GC–MS apparatus.

2.2.3 Physicochemical properties

Density of the biodiesels and the feedstock oil was determined using a density meter (DMA 4100A, Anton Paar GmbH–Austria).

The kinematic viscosity (40°C) test was carried out using a glass capillary viscometer and evaluated according to American standard ASTM D6751 and JIS K 2390–2008. The kinematic viscosity specifications (determinations at 40°C) in biodiesel standards which are 1.9–6.0 mm^2/s in the American standard ASTM D6751 and 3.5–5.0 mm^2/s in the JIS K 2390–2008. The kinematic viscosity specifications in petrodiesel standards are 1.9–4.1 mm^2/s (No. 2 diesel fuel, to which biodiesel is usually compared; No. 1 diesel fuel is 1.3–2.4 mm^2/s) in the American standard ASTM D975 and minimum value of 1.7 mm^2/s in the JIS K 2204. The viscosity of biodiesel is slightly greater than that of petrodiesel, which is reflected in the specifications in the standards.

Water content was determined by Karl Fisher coulometric titration method using 831 KF coulometer (Metrohm) according to BS EN ISO 12937:2001.

Free fatty acids are formed by the oxidation as well as the hydrolysis of biodiesels, and the degree is usually given in the acid value. Acid value is the parameter showing the content of free acid, and is expressed as the amount of KOH in milligram to neutralize the free acid (mg KOH/g of sample). Acid value was determined by the titration method using potentiometric titration apparatus (Model AT–610, Kyoto Electronic Manufacturing Co Ltd., Japan).

Iodine value is a measure of the total number of double bonds in fat or oil (or its derivatives). Iodine value is given in the amount of iodine which reacts with the unsaturated bonds in oil or fat, and the unit is given in gram of I_2/100 g of sample. Iodine value is analyzed according to the standard of JIS K0070–1992. Briefly, biodiesel is reacted in Wijs reagent and thereafter with an aqueous KI solution. The liberated iodine is then titrated with a 0.01mol/L standard solution of sodium thiosulphate.

Oxidation stability in terms of induction period, expressed in hour unit, was determined following the EN 14112 method using of Rancimat test apparatus (Model 743, Metrohm). Oxidation stability was also identified by the oxygen adsorption method of PetroOXY, operated at 120°C (Petrotest GmbH & Co. KG, Germany), and the oxidation stability data were expressed in the unit of hour and minutes (h:m).

Copper is susceptible to corrosion, and it is used as an indicator of the corrosiveness of a fuel. The copper strip corrosion has also changed physicochemical properties of fuel. Corrosion test was carried out and judged by the surface appearance after the immersion of copper plates in fuels. In the standard of JIS K 2513, a copper plate was immersed in fuels at the temperature of 60°C for 3 hrs, and the appearance of copper at the surface is used for judgment. In this study, the polished copper strip is immersed in a specific volume of biodiesel sample and B5, B10, B20 blends, and kept under at 60°C for 3 hrs, 24 hrs, 120 hrs and 164 hrs, and at 115°C for 3 hrs, 164 hrs to observe the change in the quality. At the end of the treatment, the copper strip was removed, and physicochemical properties of

biodiesel samples were analyzed in terms of oxidation stability, peroxide value, kinematic viscosity at 40°C, and iodine value. Accelerated oxidation method was also employed to evaluate the oxidation stability of Jatropha biodiesel/diesel blends. Oxidation of these fuels was carried out using TOS–10T apparatus (Yoshida Scientific Ltd., Japan) according to JIS K 2514. A 350 mL of filtered middle distillate blended fuels are aged at 115°C for 3 hrs and 16 hrs under bubbling oxygen at a rate of 3 L/h.

3 RESULT AND DISCUSSION

3.1 Characteristics of JO

The physicochemical properties and fatty acid compositions of the JO feedstock are summarized in Table 1.

Table 1: Characteristics of the JO

Test	Unit	Value
Density at 15°C	g/cm^3	0.9200
Kinematic viscosity	mm^2/s	34.99
Water content	mg/kg	980
Acid value	mg KOH/g of oil	16.25
Iodine value	g I_2/100 g of oil	98.0
Fatty acid composition	%	
Palmitic acid (C16:0)		13.37
Stearic acid (C18:0)		5.45
Oleic acid (C18:1)		45.79
Linoleic acid (C18:2)		32.27
Others		3.12
Average molecular weight		847

Composition and proportion of fatty acids in the oil depend on the plant species and the growth conditions. The oil used in this study contains 18.82% of saturated acids (palmitic acid and stearic acid) and 78.06% of unsaturated acids (oleic acid and linoleic acid). The difference in unsaturated content of different raw material would strongly affect the properties of biodiesel produced, especially its oxidation stability. JME, containing high degree of unsaturated carbon, tends to have low oxidation stability. Average molecular weight of JO was calculated based on the fatty acid methyl ester composition of the JME which was identified by GC–MS. The acid value of JO was found to be 16.25 mg KOH/g of oil (free fatty acid corresponds to 8.13%).

3.2 Analysis of key characteristics of JME and its blends

JME was selected because JO is one of the most popular feedstock for biodiesel production at present. Analysis of the physicochemical properties of JME indicated that the produced biodiesels demonstrated potential as candidates to be considered for feedstock in biodiesel production because they exhibited fuel properties within the limits prescribed by the latest American Standards for Testing Material, European standards and Japanese Industrial Standard. However, JME is unsuitable in pure state for its direct use as fuel in internal combustion engines because its kinematic viscosity at 40°C (6.6 mm^2/s) is higher than that of the upper limit of international standard (6.0 mm^2/s). Thus, JME was blended with reference diesel. Biodiesel can be used as a blend with diesel in any proportion; however, according to ASTM D975 and D7467, the maximum proportion of biodiesel is 20% (ASTM D2274, 2005). Biodiesel and diesel are not chemically similar, accordingly, biodiesel is composed of long–chain fatty acid methyl esters, whereas diesel is a mixture of aliphatic and aromatic hydrocarbsons containing approximately 10 to 15 carbons. Because of their differences in chemical compositions, it is not surprised that biodiesel and diesel exhibit different fuel properties. The blend also exhibits some its own properties, which are different from neat biodiesel and diesel fuels. Specifically, the most important fuel properties influenced by blending of biodiesel with diesel are oxidative stability. Therefore, the focus of this work is to evaluate oxidation characteristics of JME blends and compare JME blend properties with those of neat JME. This method is also used for studying the effects of blending ratio to the characteristics of biodiesel diesel mixture.

It is predicted that the oxidation stability of JME will increase by blending with diesel, as hydrocarbon constituents of diesel are more stable to oxidation than FAME (especially in the case of unsaturated FAME). As shown in Table 2, the increase in JME proportion led to significant increases in peroxide value, acid value, and kinematic viscosity at 40°C while decreases in induction period (IP). These results demonstrated that blending with diesel really improved oxidation stability of biodiesel.

Table 2: Analytical data of JME and its blends

Specification	Diesel	B5	B10	B20	B100	Standards for B100		
						ASTM	EN	JIS
Rancimat, h	–	33.5	23.55	16.27	5.68	6.0	3.0	10.0
PetroOXY, h	–	6.17	5.25	4.43	1.34	–	–	–
Acid value, mg KOH/g of sample	0.14	0.0005	0.0019	0.017	0.141	0.5 max	0.5 max	0.5 max
Peroxide value, meq/kg	–	1.0	1.3	2.1	11.7	–	–	–
Iodine value (g I_2/100 g of sample)	–	9.59	14.90	–	97.39	120 max	120 max	120 max
Kinematic viscosity at 40°C (mm^2/s)	3.07	2.95	3.1	3.31	6.6	1.9–5.0	3.5–5.0	3.5–5.0

3.3 Evaluation of the oxidation stability

The stability of the blends is mainly affected by the characteristics of the diesel fuel. Higher refining base diesel with lower sulfur content decreases oxidation stability of the final blend.

The absence of sulfur in the base diesel, which acts as a natural oxidation inhibitor, and the presence of antioxidant additive in the methyl ester have strong effect on the stability of the final blends. Diesel fuel containing catalytically–cracked compounds may be more unstable, compared to hydrotreated diesel fuel. The oxidation stability of these blends was investigated from the two aspects, namely the oxidation under bubbling oxygen at 115°C, and the contact with copper metal plate.

3.4 Oxidation in contact to copper

The appearance of copper surface was practically almost unchanged; however, the fuel quality changed significantly, depending on the immersed conditions.

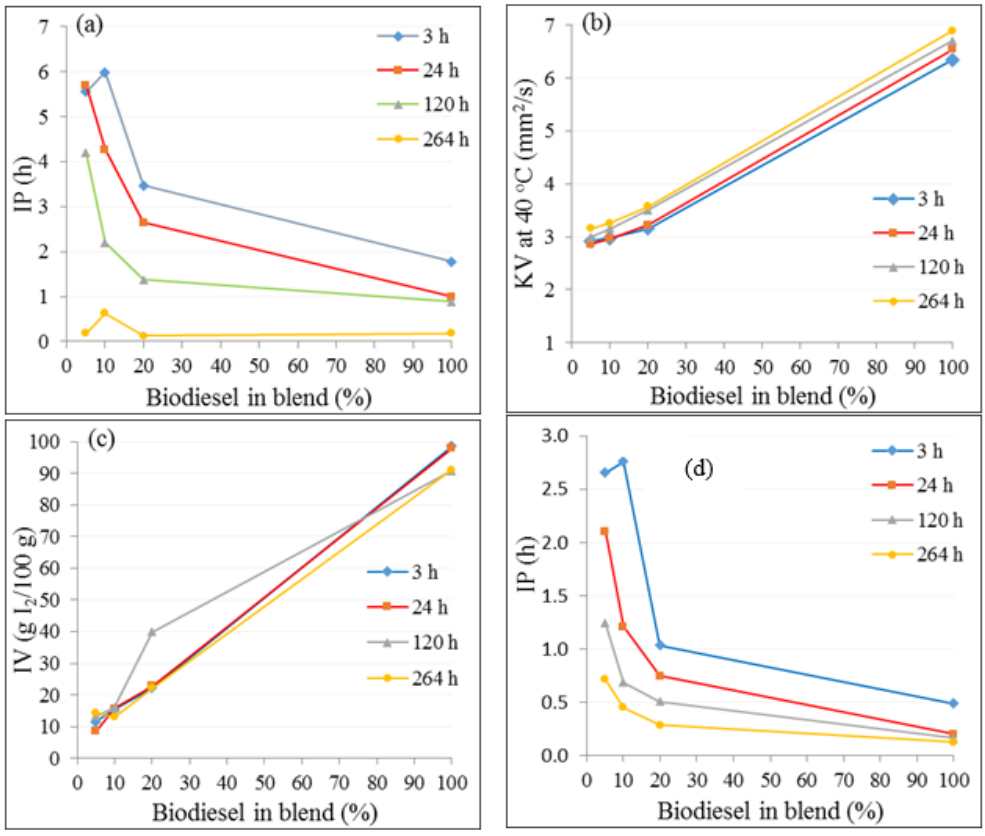

Fig. 1: Results of copper strip corrosion test at 60°C with different time treatment: Rancimat test (a), kinematic viscosity at 40°C (b), iodine value (c), and PetroOXY (d)

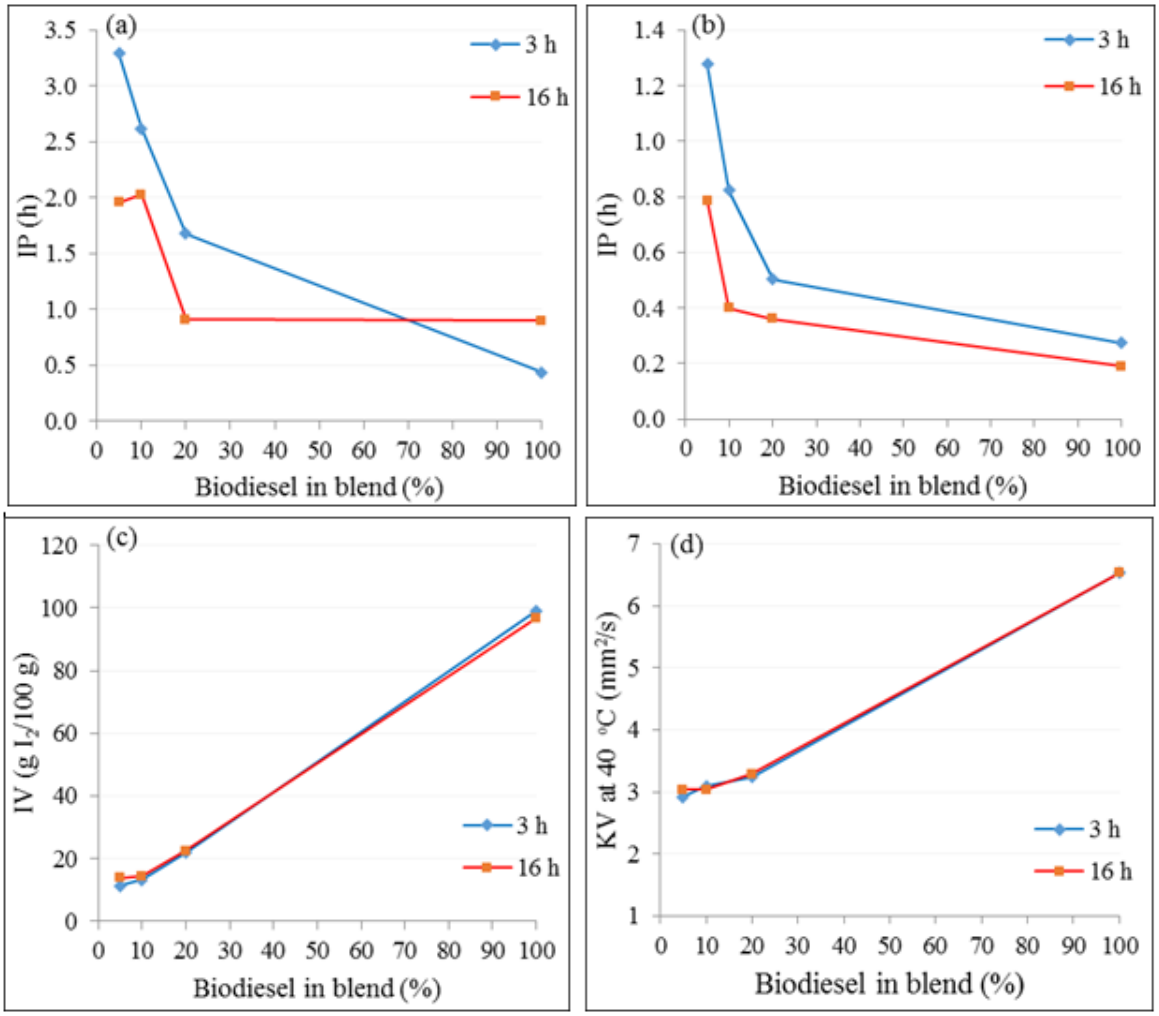

Fig. 2: Results of oxidation stability after strip corrosion test at 115°C: Rancimat test (a), PetroOXY test (b), Iodine value (c), and kinematic viscosity at 40°C (d)

The results revealed the fuel quality changed corresponding to blending ratio, with the higher proportion of JME would negatively affect the oxidation stability (Fig. 1). Moreover, the oxidation of the blends remarkably increased under the contact with copper surface. It is also found that the degree of oxidation correlated with the increase in temperature and contact time (Fig. 2). The increase of peroxide value and the decrease of IP clearly demonstrated for this correlation.

3.5 Accelerated oxidation

Accelerated oxidation method was employed to evaluate the oxidation stability of Jatropha biodiesel/diesel blends. It is suggested that the change in acid value before and after the oxidation can be used as standard indicator for the oxidation. In this study, however, peroxide value was measured before and after the accelerated oxidation, respectively. In addition, the oxidation stability was also examined by monitoring the change in IP. As shown in Fig. 3, peroxide and acid values increased dramatically, indicating the decrease in oxidation stability after the accelerated oxidation. The quality of the Jatropha biodiesel/diesel blend is, in theory, naturally dependent on the blending ratio. The result obtained from the experiments (Fig. 3) is consistent with the theory. Remarkable changes in quality was found in blends with biodiesel proportion ranging from 5 to 20% after the oxidation.

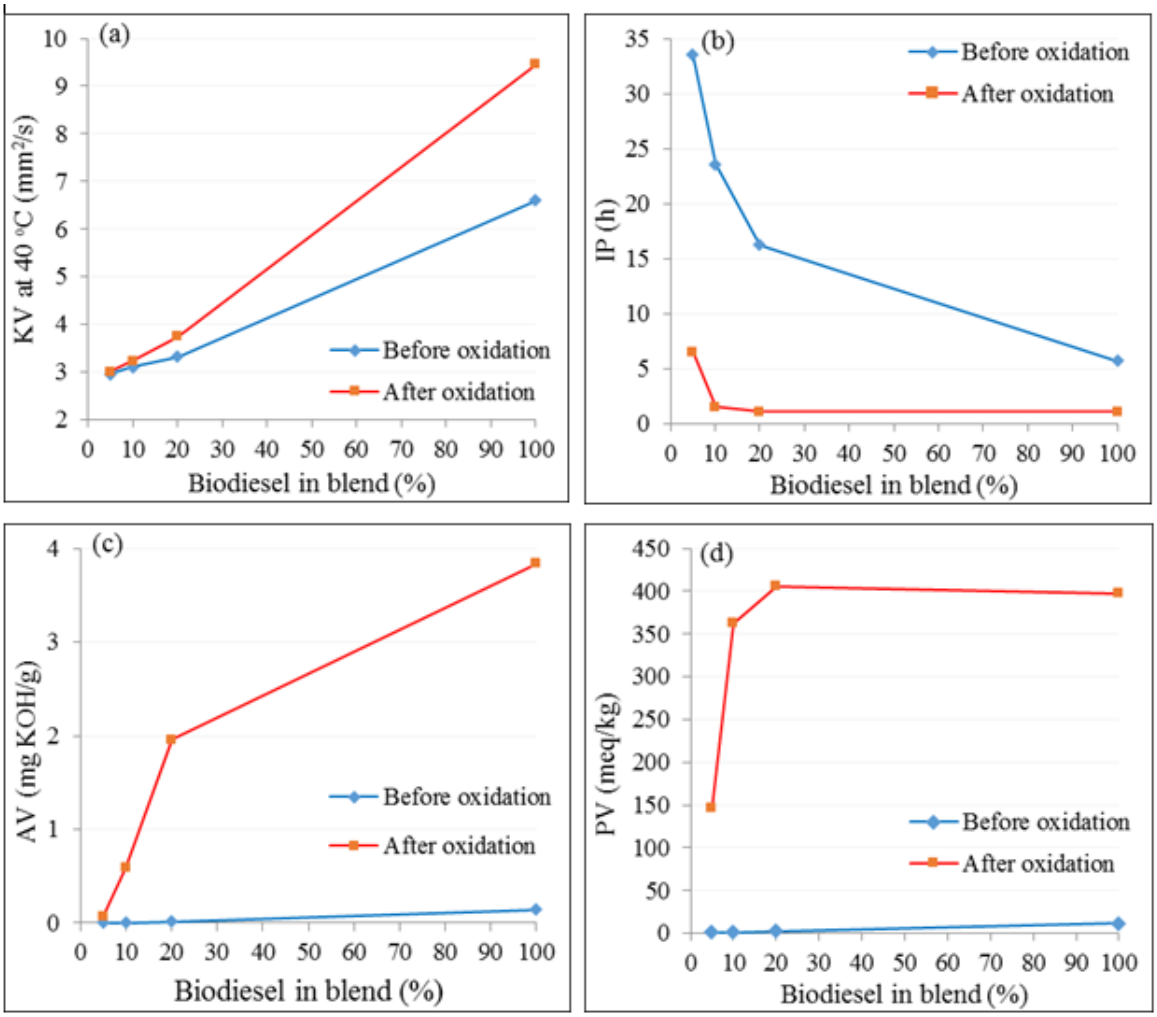

Fig. 3: Results of kinematic viscosity at 40°C (a), Rancimat test (b), acid value (c), and peroxide test (d) before and after the oxidation test at 115°C for 16 hrs. under bubbling oxygen

4 CONCLUSIONS

In summary, the stability of biodiesel is affected by various parameters. In this study, a correlation relationship between the blending ratio and the stability of Jatropha biodiesel/diesel blend was observed. This relationship is demonstrated by the change of IP, iodine value, acid value, peroxide value of Jatropha biodiesel/diesel blends, compared with both neat biodiesel and diesel. In general, the increase in Jatropha biodiesel/diesel ratio results in the lower stability of the blend in both cases of the copper strip corrosion test and the accelerated oxidation. The observation from this study provided useful information for the penetration of biodiesel into the transportation sector.

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