EFFECT OF BLENDING AND ANTIOXIDANTS ON THE STORAGE STABILITY OF BIODIESEL PRODUCED FROM NIGERIAN GROWN JATROPHA *CURCAS*

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ABSTRACT

Biodiesel consists long chain fatty acid alkyl esters produced from animal fat, vegetable oils or used cooking oils. It is eco-friendly and regarded as a promising renewable fuel substitute for diesel. However, the major drawback of biodiesel is its susceptibility to oxidation due to the presence of unsaturated fatty acids in the parent oil. The Nigerian Jatropha curcas

Introduction

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters or alkyl esters of fatty acids. It is a non-toxic, biodegradable and renewable fuel which can be used in compression ignition engines with little or no chemical modifications with significantly lower emissions than petro-diesel when it is burnt. In addition it does not contribute to the increase in carbon dioxide levels in the atmosphere and thus minimizes the intensity of the green house effect. It is also better than petro-diesel in terms of its properties such as sulphur content, flash point, aromatic content and biodegradability (Patil and Deng, 2009). Biodiesel is a drop-in replacement for petro-diesel that can be derived from renewable sources, including a wide range of plant-seed oils, animal fats and even certain

biodiesel (NJCB) fails to meet the minimum oxidation stability limit (IP of 6 hours) without antioxidant. Blending with petro-diesel as well as the addition of antioxidants leads to a composition having efficient and improved oxidation stability. The results have shown that blending of NJCB with diesel with less than 20% (v/v) would not need any antioxidants. Varying quantities (50 ppm, 100 ppm and 150 ppm) of Pyrogallol (PY) antioxidant were added to the pure biodiesel B100 and blends B10, B20 and B30. The optimum amount of antioxidant (PY) for the samples was found to be 100 ppm.

(Keywords: jatropha curcas, biodiesel, oxidation stability, blends, antioxidants)

lipid-rich algal species. Biodiesel is made via the transesterification of the range of vegetable feedstock oils or animal fats with alcohol; usually methanol to yield fatty acid methyl esters (FAME). Therefore, the chemical composition of biodiesel can vary significantly resulting in extremely varied physical properties (Pullen and Saeed, 2014). However, several important issues including oxidation stability still demand special interest. Lack of stability is one of the major drawbacks for commercialization of such biodiesel (Bouaid *et al*, 2007). Stability of biodiesel refers to the general resistance to change its fuel properties. It is desirable for biodiesel to resist the deteriorating effect of oxygen during storage over an extended period of time or due to elevated temperature. Three stability terms viz., oxidation stability, storage stability and thermal stability are used to describe oxidation affinity of biodiesel fuel in presence of oxygen (Mittelbach and Remschmidt, 2004). It has been conclusively proved that susceptibility to oxidation or autoxidation during long term storage depends upon the composition of biodiesel (Karavalakis *et al*, 2010).

Unsaturated fatty acids are significantly more prone to oxidation than saturated compounds. Again, polyunsaturated fatty esters are

approximately twice as reactive to oxidation as monounsaturated esters (Dunn, 2005). For example, amongst the unsaturated fatty acids, linolenic acid exhibits the highest instability followed by linoleic and oleic.

This is attributed to the fact that these unsaturated fatty acid chains contain the most reactive sites, which are particularly susceptible to free-radical attack. The growth of oxidation process starts by reacting with oxygen via autoxidation mechanism, with the radical chain reaction following the steps of initiation, propagation, chain branching and termination (Frankel, 2005). During these reactions, several products such as peroxides, hydroperoxides, aldehydes, ketones, alcohols and some polymerization byproduct (such as dimmers, trimers and cyclic acid) are formed. Further, it is reported that oxidation rate of biodiesel was mainly influenced by environmental factors like ambient temperature, storage condition and exposure of light etc. (Sarin *et al*, 2009).

The prevention of oxidation of biodiesel is difficult during natural storage condition, as because exposure to oxygen, light, heat and storage container are inevitable during storage, handling and usage of biodiesel fuel (Dunn, 2008). However, some antioxidant additives could play a role to slow down the rate of oxidation. It is also stated that antioxidants inhibit the oxidation rate by slowing down the formation of free radicals. Careful selection of antioxidants is stressed, because the improper type or concentration of antioxidant could act as prooxidant under certain condition (Karavalakis *et al.*, 2011.

Materials and Methods
Collection and Preparation of Jatropha *Curcas* Seed Oil
Collection of Jatropha *Curcas* Seed Oil
Jatropha *curcas* seed oil was obtained from National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria.
Analysis of Jatropha *Curcas* Seed Oil
The crude Jatropha *curcas* seed oil was analyzed in terms of its physiochemical properties in accordance with American Society of Testing Material (ASTM) standard.

Determination of Acid Value

The acid value is defined as the mg of potassium hydroxide necessary to neutralize fatty acids in 1g of sample and is measured as per AOCS Method la – 64. It reflects the amount of free fatty acid content in Jatropha oil. The indicator solution (1.0% phenolphthalein indicator in isopropyl alcohol) was added to the required amount of solvent (equal parts by volume of isopropyl alcohol and toluene) in ratio of 2ml to 125ml and neutralized with alkali to a faint but permanent pink colour. 5g of the well mixed sample was weighed into an Erlenmeyer flask and 125ml of the neutralized solvent mixture was added. It was well shaken and ensured that the sample was completely dissolved before titration. The sample was shaken vigorously while titrating with the standard alkali (0.1M KOH) until the first permanent pink colour was observed. The acid value was calculated as follows:

$$\text{Acid value} = \frac{\text{Titre value} \times \text{Normality of KOH}}{\text{Mass of Jatropha oil}} \qquad (2.1)$$

Determination of Viscosity

The viscosity of Jatropha oil was measured at $24.^\circ C$ using a digital rotary viscometer. The sample cup was removed and the spindle CP-40 was carefully attached to the lower shaft and inserted into the cup containing 25g of the oil sample. The motor switch was turned "on" and rotated at a speed of 60 rpm and sufficient time was allowed for the display reading to stabilize.

Determination of Free Fatty Acid

The method employed for this analysis was AOCS method Ca-5a-40. It gives the percentage by weight of specified fatty acid present in the oil. 5g of the Jatropha oil was weighed into 250 ml conical flask. 25 ml diethyl ether with 25 ml ethanol mixture was added to the Jatropha oil. The mixture was boiled on a hot plate until all the oil dissolved completely. 3 drops of indicator phenolphthalein was added to the mixture and titrated with 0.1 M sodium hydroxide with constant shaking until a pink colour persisted for 30 minutes. The percentage of FFA was calculated using Equation 3.2.

$$\% \text{ FFA} = \frac{Titre\ value \times Normality\ of\ KOH \times 56.1}{Mass\ of\ Jatropha\ oil} \qquad (3.2)$$

Esterification of the oil

The oil was esterified to reduce the percentage of free fatty acid in it. The esterification process was carried out using methanol and sulphuric acid catalyst. About 1000 g of the Jatropha oil was heated to a temperature of 60 $^{\circ}$C in a conical flask and a mixture of methanol (30% by weight of oil) and sulphuric acid (1% by weight of oil) was added to it. The resulting mixture was then heated but maintained at a temperature of 60 $^{\circ}$C with stirring at 600 rpm for one hour. The %FFA was then determined as in section 3.1.2.3 above.

Transesterification of the oil to Biodiesel

The standard alkali-catalyzed transesterification process was used for the conversion of the Jatropha oil to biodiesel. The transesterification process was carried out using methanol and potassium as catalyst.

500 g of the esterified oil was heated to a temperature of 60 $^{\circ}$C in a conical flask and a mixture of methanol and calcium oxide catalyst (8% by weight of oil) was added to it. The resulting mixture was then heated but maintained at a temperature of 60 $^{\circ}$C with stirring at 700 rpm for one hour.

The mixture was thereafter poured into a separating funnel where the biodiesel and glycerol were separated on standing. The solid catalyst was recovered by filtration.

Blend Preparation

The Jatropha *curcas* biodiesel and petro-diesel were mixed in specified proportions ($^{v}/_{v}$) to obtain the blends. For example, 10% biodiesel was mixed with 90% petro-diesel to obtain B10. Similarly, B20 and B30 were also prepared.

Evaluation of Fuel Properties

The major fuel quality parameters viscosity, acid value, peroxide value and induction period of the pure Jatropha *curcas* biodiesel and its blends with petro-diesel with and without antioxidants, were determined during 24 weeks of storage at periodic intervals.

Results and Discussion

Analysis of Crude Jatropha Oil

The results of crude Jatropha oil analysis are presented in Table 3.1 These show that the properties of Jatropha seed oil used in this work are in conformity with literature values. The oil sample has a high value of FFA (16.4 %) much higher than the 1% specified limit, hence the oil needs to be esterified before transesterification. High value of FFA > 1% adversely affect the transesterification reaction in which the FFA in the oil reacts with the alkali catalyst to produce soap (saponification) hence decreasing the catalyst amount needed for the transesterification reaction (Muazu K., 2013).

Table 1: Properties of the crude Jatropha *curcas* seed oil

Parameter	Unit	Value	Test method	ASTMD Standard
Density	kg/m^3	872	ASTMD 287	860 – 933
Viscosity @ 40 °C	mm^2/s	4.3	ASTM D6751	4.0 – 6.0
	mgKOH/g	0.97	AOCS Te 1a-64	0.92 – 6.16
Acid Value	mgKOH/kg	16.4	AOCS(Ca5a-40)	-
Free Fatty Acid	%	7.5		-
Moisture content			Karl Fisher	

Analysis of the fatty acid composition (Table 3.2) of the crude Jatropha oil indicates that the oil consisted principally of linoleic acid (40.39%) followed by oleic acid (38.14%), palmitic acid (14.43%) and stearic acid (7.04 %).This is in conformity with that reported by Siddharth and Sharma (2011). It indicates that the oil contains more unsaturated fatty acids (linoleic acid and oleic acid) than the saturated fatty acids (palmitic acid and stearic acid). The oxidative stability of biodiesel is a function of the fatty acid composition of the parent oil (Zahira *et al.*, 2013) and decreases with larger amount of unsaturated fatty acids in the parent oil.

Table 2: Free fatty acid composition of the Jatropha oil

Fatty Acid	Value (wt. %)
Palmitic acid (16:0)	14.43
Stearic acid (18:0)	7.04

Oleic acid (18:1)		38.14
Linoleic acid (18:2)		40.39
Linolenic (18:3)		-
Saturates	21.47	
Unsaturates	78.53	

Evaluation of Fuel Properties of Fresh Jatropha *Curcas* Biodiesel

The fuel properties of freshly prepared Jatropha biodiesel and its blends in comparison to petro-diesel are presented in Table 3.3. It is found that the fuel properties of jatropha curcas biodiesel and its blends satisfy biodiesel standards. (EN 4214 and ASTM D6751)

Table 3: Fuel properties of Jatropha biodiesel and blends

Parameter	Unit	B100	B10	B20	B30	ASTMD Standard	Petro-diesel
Density	kg/m^3	872	826	832	843	860 – 933	835.12
Viscosity	mm^2/s	4.35	2.77	3.34	3.52	1.9 – 6.0	2.78
Acid Value	mgKOH/g	0.35	0.22	0.27	0.28	0.5 (max)	0.10
Peroxide Value	mg/kg	4.71	2.99	3.61	3.81	-	-
Induction period	Hours	3.31	26	22	17	6 (B100) 20 (blends)	-

Changes in Fuel Properties of Jatropha *Curcas* Biodiesel and its Blends on Storage

The change in fuel quality during storage due to oxidation is evaluated through monitoring the changes in viscosity (a physical property), acid value (based on secondary oxidation products) , peroxide value (based on primary oxidation products, Rancimat induction period (based on accelerated oxidation) and cetane number.

The quality deterioration regarding these specific parameters up to 24 weeks of storage is presented below.
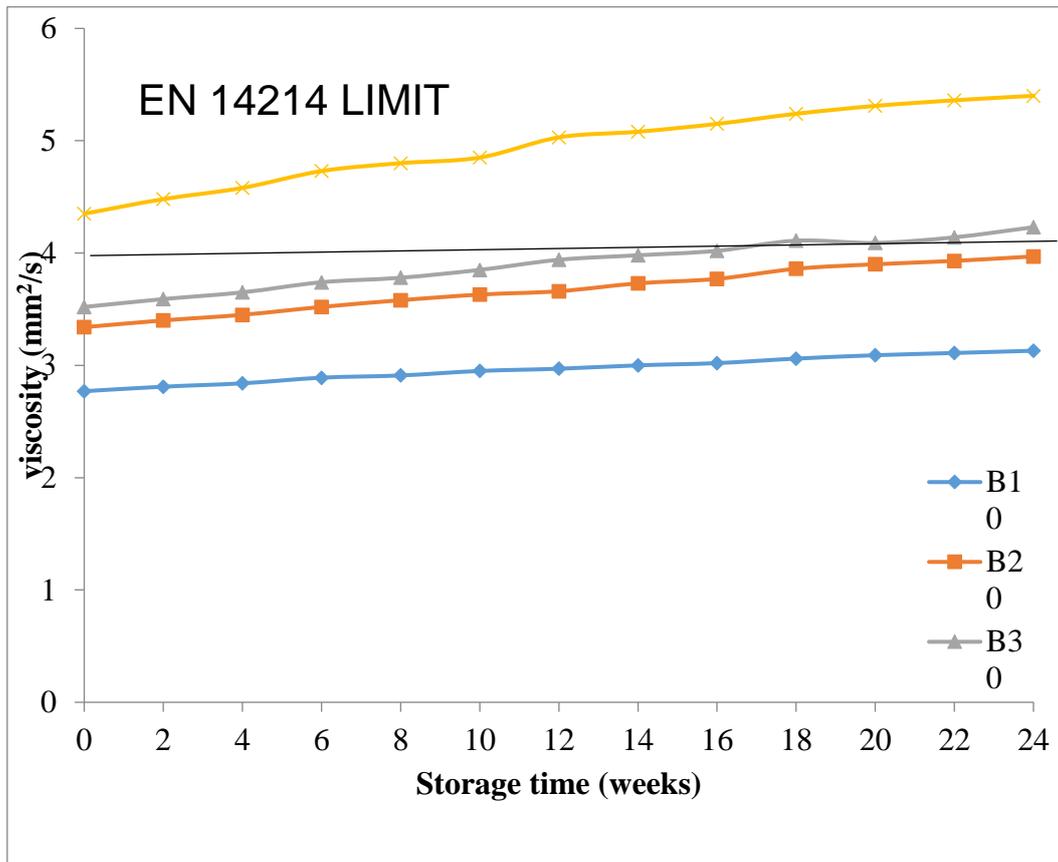
Viscosity

Fig. 1: Variation in the viscosity of blend samples with storage period

The variations in viscosity with storage period are presented in Fig. 1 for all the samples under investigation. Generally, the viscosity values of all the samples are found to increase with period of storage. This can be attributed to the formation of oxidized products which lead to the formation of sediments and gum (Das *et al.*, 2009).

The rates of increase in viscosity of the samples however are not uniform. Pure biodiesel (B100) which increased from 4.35 mm^2/s to 5.40 mm^2/s during the 24 weeks shows a higher rate of increase compared to the blended samples.

Chemical reaction and the formation of products during interaction of biodiesel and petro-diesel is a likely reason for the different rates of increase in viscosity amongst the samples.

Viscosity of B100 is above that of petro-diesel throughout the 24 week storage period while that of B30 goes beyond the viscosity of petro-diesel after the 16th week of storage.

All the samples are within the EN 14214 limit of 5 mm²/s up to 11 weeks but B100 goes above the minimum limit after the 11th week.
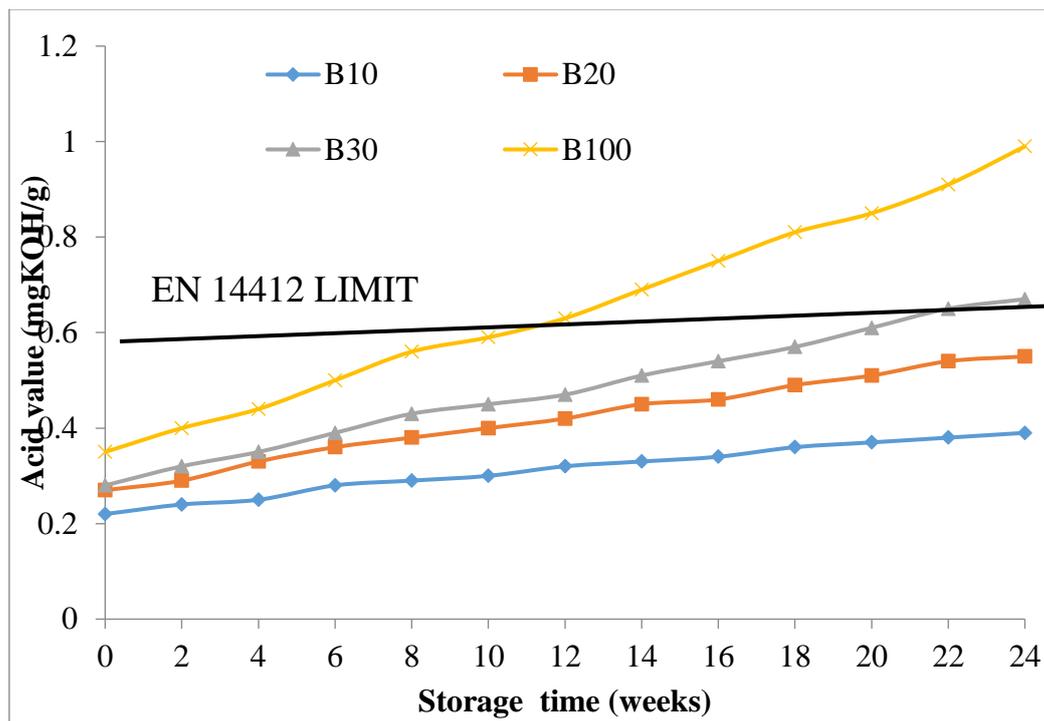
Acid value

Fig. 2: Variation in acid value of blend samples with storage period

The variations in acid value (AV) with storage period are presented in Fig. 2 for all the samples under investigation.

The results show an increase in AV for all the samples.

Similar rate of increase in AV is observed for the two blend samples B30 and B20. The rate of increase in the AV of B10 during storage is the least of all the samples while pure biodiesel B100 exhibited the highest rate of increase from 0.35 mgKOH/g to 0.99 mgKOH/g during the 24-week storage period. The AV for B100 is within the EN 14412 limit of 0.5 mgKOH/g (max) up to 7 weeks; B30 up to 16 weeks; B20 up to 24 weeks; B10 within limit throughout the 24 week storage period.

During storage, the esters are first oxidized to form peroxides, which then undergo complex reaction and further oxidize into acids, and hence increase the acid value. Also, the hydrolysis of esters into alcohol and acid by the traces of water present in the sample increases the acid value (Mittelbach, 2004)
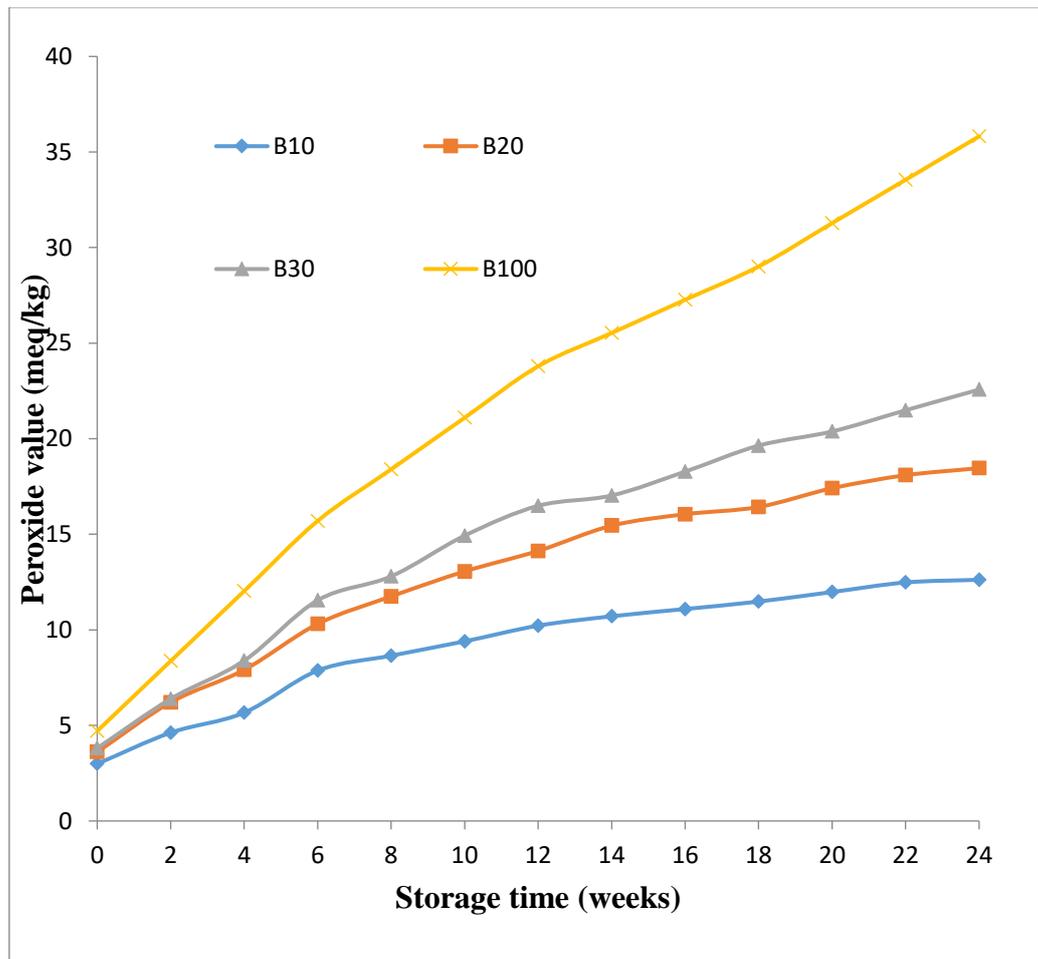
Peroxide value

Fig. 3: Variation in peroxide value of blend samples with storage period

Fig. 3 shows the variation in peroxide values (PV) of the samples under investigation during the 24 weeks period of storage.

Although PV is not specified in biodiesel fuel standards, it is an important indicator of oxidation of biodiesel during storage.

A higher value of PV indicates greater formation of hydro-peroxide through the peroxide chain mechanism (Chakraborty, 2011)

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Peroxide value of pure biodiesel B100 increased from 4.71 meq/kg to 35.82 meq/kg.

Rate of increase in the peroxide value of the pure biodiesel B100 is different from that of the remaining samples. Blends B20 and B30 show similar rate of increase in peroxide value while B10 exhibited the least. This can be attributed to the formation of varying amount of peroxide due to blend dependent reaction.

Effect of Antioxidant Additives on Storage of Jatropha *Curcas* Biodiesel and its
Blends

Further investigation was carried out to check the effectiveness of pyrogallol (PY) antioxidant additives on the pure biodiesel and its blends. PY antioxidant is found to be the most effective antioxidant for jatropha *curcas* biodiesel (Siddharth and Sharma, 2013). The different samples were doped with varying concentrations of PY antioxidant of 50 ppm, 100 ppm and 150 ppm.

Effect of PY Antioxidant on the Viscosity of Samples

Fig. 4 (a – c) shows the effect of PY antioxidant on the viscosity of jatropha *curcas* biodiesel and its blends at varying concentrations. The viscosity of pure jatropha biodiesel without antioxidants is found to increase by 24% while the viscosity of the blends B20 and B30 showed a lower rate of increase of 20% and 19% respectively over a period of 24 weeks. The addition of PY antioxidant however slowed down the rate of increase in viscosity in all the three samples due to deceleration in the oxidation process, which in turn decreases the peroxide formation (Jain and Sharma, 2010).

Without antioxidants, the viscosity of the pure biodiesel B100 goes above the 5mm^2/s EN 14214 limit while the viscosity of the blends B10, B20 and B30 fall within the limit.

Application of antioxidants suppresses the viscosity of all the samples and this increases with the quantity of antioxidant. Antioxidant dose of 100 ppm and 150 ppm exhibited similar rate of retarding the rate of increase in viscosity for all the samples.
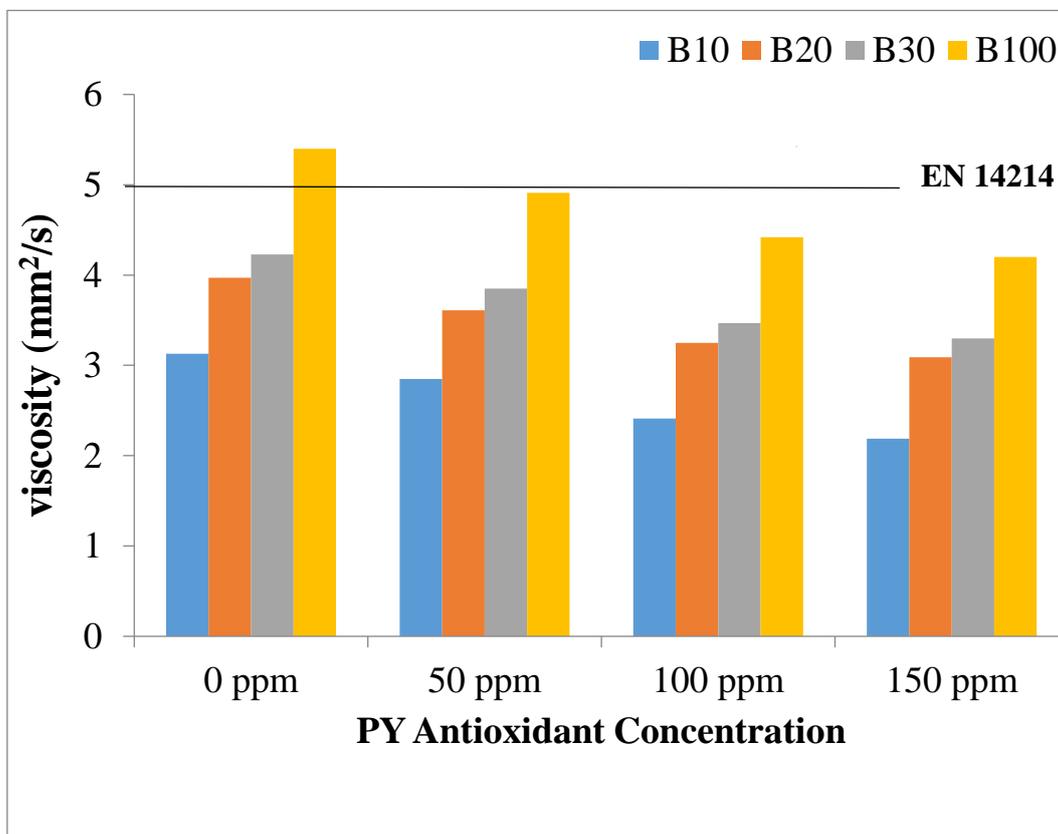
Fig. 3.5 Effect of PY antioxidant on the viscosity of pure Jatropha biodiesel and blends

Effect of PY Antioxidant on the acid value of Samples

Fig. 3.6 shows the effect of PY antioxidant on the acid value of jatropha *curcas* biodiesel and its blends at different concentrations. The AV of pure jatropha biodiesel without antioxidant increased from 0.35 mgKOH/g to 0.99 mgKOH/g over a storage period of 24 weeks. The acid values of the blends B20 and B30 without antioxidant exceeded the maximum limit of 0.5 mgKOH/g after the 20th and 16th weeks respectively. The addition of PY antioxidant significantly decreased the rate of increased in acid value of all the samples due to deceleration in the oxidation process.

Without antioxidant, only B10 falls below the minimum 0.5 mgKOH/g set by EN 14412. Application of PY antioxidant decreases the acid value of all

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samples, indicating a reduction in oxidation. 50 ppm is adequate for B20, blend B30 requires up to 150 ppm while B10 does not require any antioxidant. B100 requires more than 150 ppm.
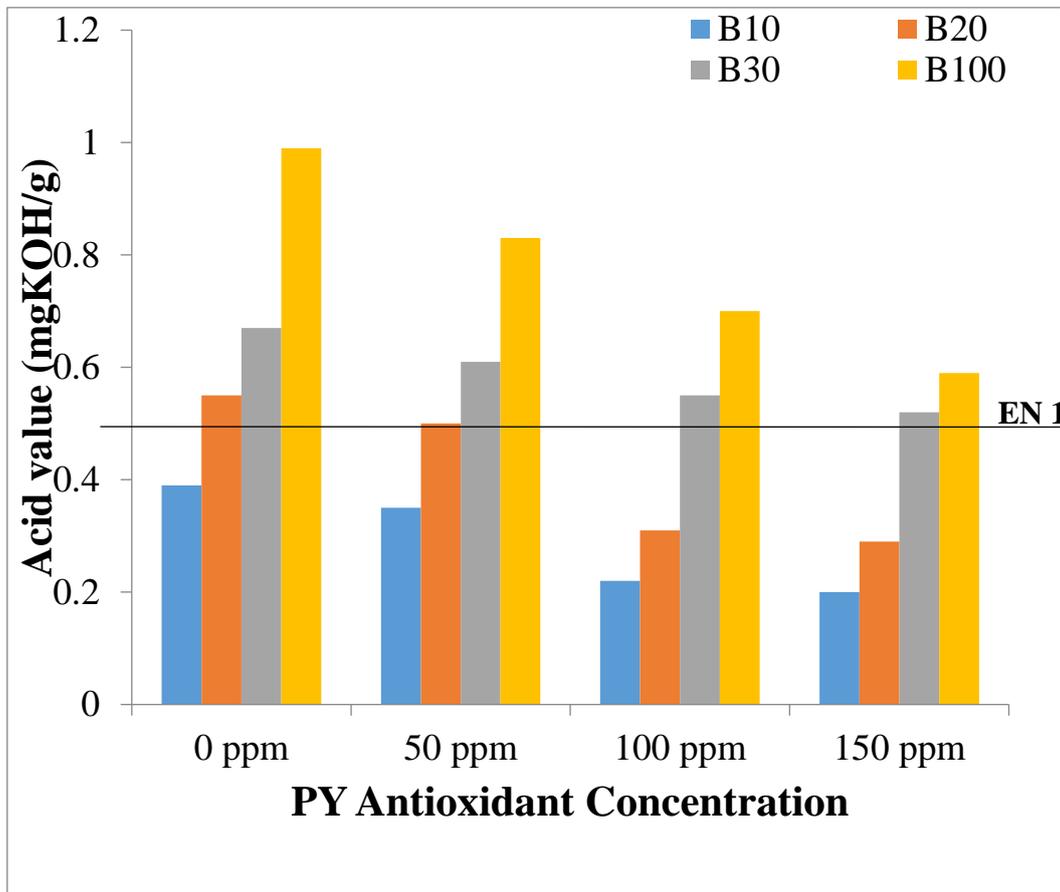

Fig. 3.6 Effect of PY antioxidant on the acid value of Jatropha biodiesel and blends

Effect of PY Antioxidant on the induction period of Samples

Fig. 3.7a and 3.7b show the effect of PY anti-oxidant concentration on the induction period of pure jatropha biodiesel and its blends.

Without antioxidant, the induction period (IP) of 3.31 hours for the pure biodiesel B100, falls short of the minimum IP of 6 hours set by EN 1214.

Without antioxidant, both B10 (IP 26.17 hours) and B20 (IP 22.23 hours) go above the minimum of 20 hours set by EN 14214 while B30 (IP 17.13 hours) falls below the 20 hours standard. The IP increases with increase in antioxidant concentration.
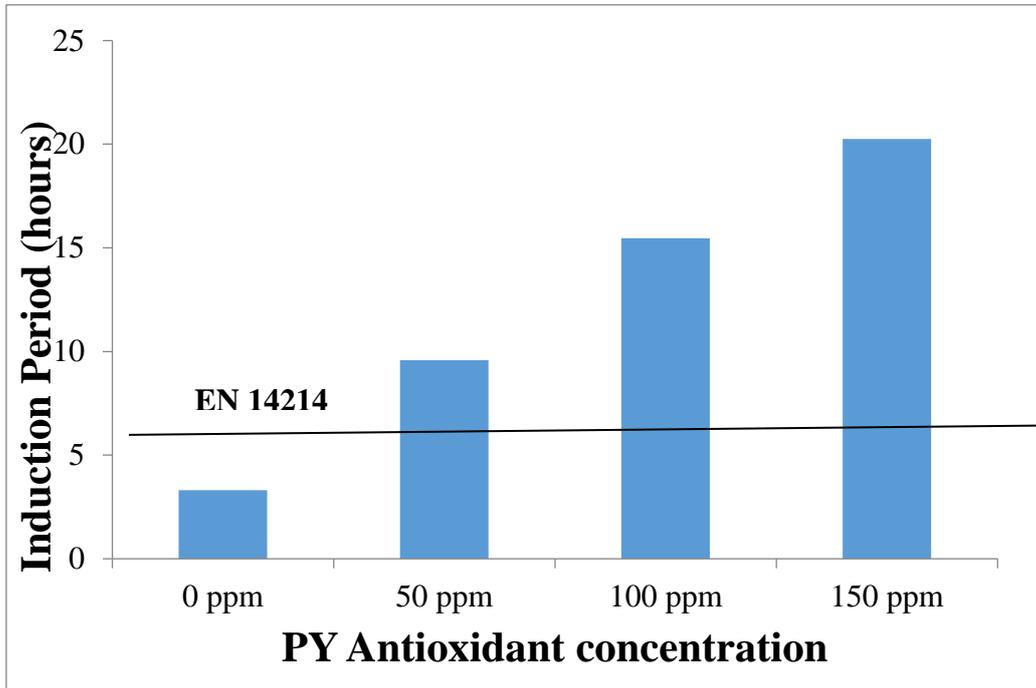
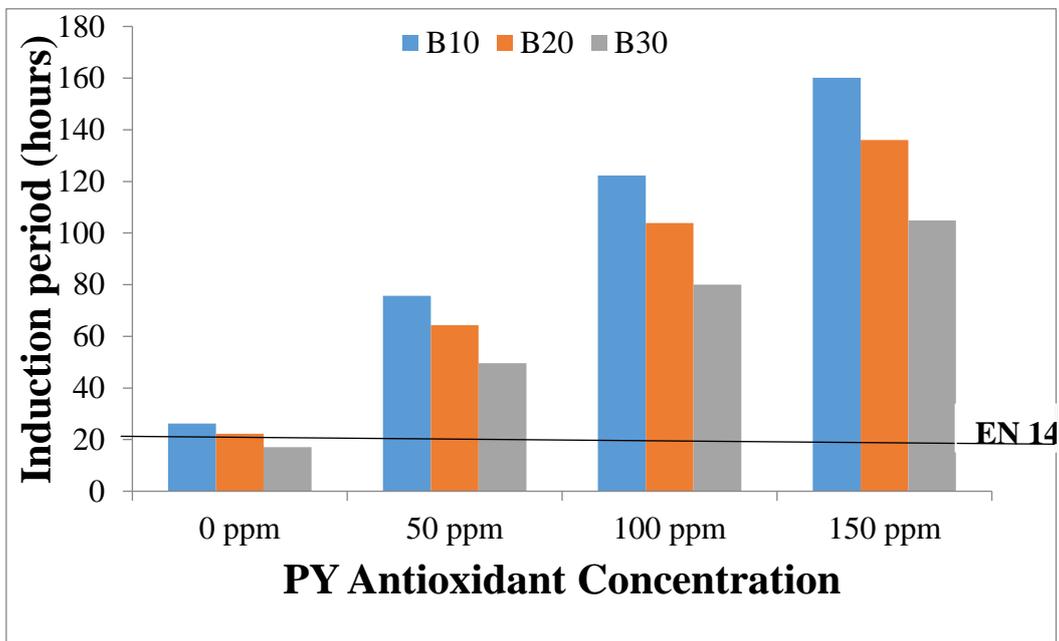*Fig. 3.7a Effect of PY antioxidant on the induction period of pure Jatropha biodiesel*

Fig. 3.7b Effect of PY antioxidant on the induction period of Jatropha biodiesel blends

Conclusions

The conclusions derived from this study are summarized as follows:

- The JCB produced fails to meet minimum oxidation stability limit (IP of 6 hours without addition of antioxidant.

- Oxidation indices acid and peroxide values increase with storage period for all the stored samples.

- Blending of JCB with less than 20% $^v/_v$ petro-diesel does not require any antioxidant up to 24 weeks storage period.

- Addition of PY antioxidant was effective in slowing down oxidation in all the samples. Rate of oxidation inhibition increased with increase in concentration of PY antioxidant.

- Less quantity of PY antioxidant is required for the blends B10, B20 and B30 compared to the pure biodiesel B100.

- The optimum blend is B30 while 100 ppm is the optimum PY antioxidant concentration.

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