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Study of oxidation stability of *Jatropha curcas* biodiesel/ diesel blends

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Abstract
Biodiesel production is undergoing rapid technological reforms in industries and academia. This has become more obvious and relevant since the recent increase in the petroleum prices and the growing awareness relating to the environmental consequences of the fuel overdependency. However, the possibilities of production of biodiesel from edible oil resources in India is almost impossible, as primary need is to first meet the demand of edible oil that is already imported therefore it is essential to explore non-edible seed oils, like *Jatropha curcas* and *Pongamia* as biodiesel raw materials. The oxidation stability of biodiesel from *Jatropha curcas* oil is very poor. Therefore the aim of the present paper is to study the oxidation stability of Jatropha curcas biodiesel/ diesel blend. Also the effectiveness of various antioxidants is checked with respect to various blends of biodiesel with diesel.

Keywords: Jatropha curcas biodiesel, Oxidation stability, Antioxidants, Metal contaminants, Rancimat.

1. Introduction

Biodiesel is an environment friendly liquid biofuel similar to petro-diesel in terms of fuel quality and combustion characteristics. Increasing environmental concerns, fast depleting petroleum reserves and agriculture based economy of India are the driving forces to promote biodiesel as an alternative renewable fuel. Biodiesel, derived from vegetable oil and animal fats, is being used as engine fuel in USA and Europe to reduce air pollution and to reduce dependence on limited fossil fuel, localized to some specific regions. Because of the surplus availability of edible oils like soybean oil, sunflower oil and rapeseed oil, these countries are using edible oils as feedstocks for biodiesel production. On the other hand, the possibility of biodiesel production from edible oil resources in India is very less as the indigenous edible oil production is much less than the actual demand which is met by its import [1]. India accounts for 9.3% of world's total oil seed production and is the fourth largest edible oil producer in the world and still about 46% of total edible oil is imported to meet the domestic requirements and as such the question of diverting edible oil resources for biodiesel production in India does not arise. The only possibility seems to be the non-edible oil resources like Jatropha, pongamia, Mahua, sal etc., which can be commercially grown on waste lands and the oil resources can be used for biodiesel production. Jatropha curcas has been identified as one of the important source for biodiesel production in India.

As per the survey of Government of India, out of total land area, 60 Mha are classified as waste and degraded land. India has third largest road network in Asia having road length of about 3 million kms and the land area along the road can be used for growing the Jatropha and Pongamia crops and the

available oil can be converted into biodiesel. Similarly, the land along the track of Indian railway of about 63,140 km can also be easily used for cultivation of Jatropha curcas.

The fatty acid profile of biodiesel corresponds to that of parent oil or fat and is a major factor influencing its fuel properties. Due to the presence of significant amount of fatty acids with double bonds, oxidative stability has been found to be of significant concern when the biodiesel is stored over an extended period of time. This is why; the oxidation stability becomes an important criterion for biodiesel fuel quality [2, 3]. It is reported that stability of biodiesel is inferior to petro-diesel and therefore, the blending of biodiesel with petro-diesel will affect its fuel stability significantly [4]. The poor biodiesel stability is attributed to the presence of double bonds in the fatty acids that may ultimately lead to formation of gum and other oxidation byproducts.

Almost all the biodiesels have significant amounts of esters of oleic, linoleic or linolenic acids and the trend of increasing stability is linolenic < linoleic < oleic [2]. These esters undergo auto-oxidation with different rates depending upon the numbers and positions of the double bonds and result in the formation of a series of by-products like acids, esters, aldehydes, ketones, lactones, etc.

During oxidation process, the fatty acid methyl ester usually forms a radical next to the double bond. This radical quickly binds with the oxygen of the air, which is itself a biradical and forms peroxide radical (Figure 1). The rapid radical destruction cycle begins thereafter. This peroxide radical immediately creates a new radical from the fatty acid methyl ester, which in turn binds with oxygen of the air and in this way, the destructive radical auto-oxidation cycle starts. During this process, up to 100 new free radicals are created quickly from one single radical meaning thereby that decomposition occurs at an exponentially rapid rate resulting in the formation of a series of by-products [5]. These species so formed cause the fuel to eventually deteriorate. Finally, the oil spoils and become rancid very quickly. Oxidative rancidity begins with an initial chain reaction followed by propagation reaction that involves unstable peroxides and hydroperoxides followed by the termination reactions resulting in the formation of aldehydes, alcohols and carbonic acids (Figure 1).

Initiation: $RH + I \rightarrow R\cdot + IH$

Propagation: $R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

Termination: $R\cdot + R\cdot \rightarrow R\text{-}R$

$ROO\cdot + ROO\cdot \rightarrow$ Stable Products

Figure 1. Primary oxidation reaction

A number of reports have appeared in the literature on the storage and oxidative stability of biodiesel synthesized from edible oils but only very few reports are available on the effect of blending of different biodiesels on the oxidation stability of that blend. However, no work has been reported on the effect of blending of biodiesel from non- edible oils with petro diesel on their stability.

Sarin et al. [6] have used palm and Jatropha biodiesel blends to minimize the dosage of antioxidants and found an increase in the induction period of Jatropha biodiesel after it was blended with palm biodiesel. Dunn has studied the effect of oxidation under accelerated conditions on the fuel properties on methyl soyate [7]. The effect of different antioxidants on oxidation stability of biodiesel from soybean oil was studied by Dunn [8]. Knothe has reported the effect of structure of fatty compounds on the stability of vegetable oil derived products [9]. Ferrari et al. [10] have compared the oxidative stability of neutralized, refined and frying oil waste soybean oil fatty acid ethyl ester.

Park et al. [11] studied the blending effect of biodiesel on the oxidation stability of biodiesel and found a close relationship between the oxidation stability of the blended biodiesels with the fatty acid composition. Some stability studies were also carried out on methyl and ethyl fatty acid esters under different storage conditions [12]. Synthetic antioxidants were reported to be more effective than natural antioxidants [13]. Das et al. [14] have worked on long-term storage stability of biodiesel from Karanja oil and found that it is possible to increase the stability considerably by adding the antioxidants.

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From the above literature, it can be concluded that oxidation cannot be entirely prevented but can be significantly slowed down by the use of antioxidants which are chemicals that inhibit the oxidation process. Two types of antioxidants are generally known: chain breakers and hydroperoxide decomposers [2]. Literature related to hydroperoxide decomposers is very scarce. The two most common types of chain breaking antioxidants are phenolic and amine-types. Almost all the work related to stability of fatty oil and ester applications is limited to the phenolic type of antioxidants. The mechanism of all chain breaking antioxidants is shown in Figure 2.

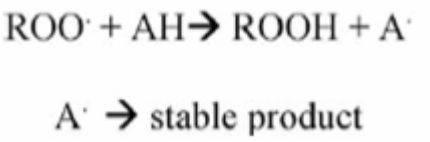

Figure 2. Mechanism of all chain breaking antioxidants

As can be seen, the antioxidant contains a highly labile hydrogen that is more easily abstracted by a peroxy radical than fatty oil or ester hydrogen. The resulting antioxidant free radical is either stable or further reacts to form a stable molecule which is further resistant to chain oxidation process. Thus, the chain breaking antioxidants interrupt the oxidation chain reaction in order to enhance the stability. The effectiveness of antioxidant is generally measured by stressing a fatty oil or ester molecule both with and without the antioxidant.

As per National Mission on Biodiesel in India, Jatropha biodiesel has undertaken in order to improve the stability of biodiesel and make it acceptable to oil marketing companies in India. The aim of the present paper is to study the effect of blending of biodiesel with petro diesel on its oxidation stability and to compare with the stability of pure biodiesel.

2. Materials

Butylated hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), propyl gallate (PG), and pyrogallol (PY) were the additives employed for their evaluation on diesel/biodiesel blends. All chemicals were of analytical grade and purchased from Naveen traders, India. Biodiesel from Jatropha curcas oil prepared in the laboratory as will be discussed in the experimental section.

3. Experimental

3.1 Synthesis of biodiesel and its testing

Since the initial FFA contents of Jatropha oil was very high (15.4%) therefore a two step acid- base catalyzed transesterification process is used to prepare biodiesel [15].Methanol (70:30% by volume oil: alcohol) was mixed with H_2SO_4 (1 wt.% of oil) and then added slowly to the reactor containing oil along with stirring. The reaction mixture was heated at 65^0C for 2–4 hrs and the resulting low FFA products of the reaction were subjected to base catalyzed transesterification. After completion of the reaction, the reaction mixture was transferred to separating funnel and both the phases were separated. Upper phase was biodiesel and lower phase contained glycerin. Alcohol from both the phases was distilled off under vacuum. The glycerin phase was neutralized with acid and stored as crude 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. Fatty acid composition of biodiesel was analyzed using gas chromatograph [16].

The synthesized biodiesel samples were tested for physico- chemical properties as per ASTM D-6751 and Indian IS-15607 specification as given in Table 1 which shows that although the biodiesel prepared from JCO meet most of the specifications but failed in oxidation stability test.

The results obtained were in good agreement with biodiesel quality survey of 2004 and 2006, which indicates that majority of samples, failed in EN-14112 test [17] due to presence of large amount of unsaturated fatty acids.

As per National Mission on Biodiesel in India, the use of biodiesel should reach a minimum of 20% in 2012, while the revised European standard EN 590 already includes a provision for automotive diesel fuel to be blended with biodiesel up to 7% (v/v). but at the same time there is no specification given for

biodiesel blends beyond B_7 for oxidation stability. Therefore same oxidation stability specification requirement (20 hrs) is considered for oxidation stability for all biodiesel blends beyond B_7.

Table 1. ASTM and IS specification of biodiesel

S.No.	Property (unit)	ASTM 6751	ASTM 6751 limits	IS 15607	IS 15607 limits	Jatropha ME
1	Flash point(^{0}C)	D-93	Min.130	IS 1448		172
2	Viscosity at 40^{0}C(cSt)	D-445	1.9-6.0	IS 1448		4.38
3	Water and sediment (vol%)	D-2709	Max.0.05	D-2709	Max.0.05	0.05
4	Free glycerin (% mass)	D-6584	Max.0.02	D-6584	Max.0.02	0.01
5	Total glycerin (% mass)	D-6584	Max.0.24	D-6584	Max.0.24	0.03
6	Oxidation stability of FAME, hrs		3	EN 14112	Min. 6	3.27
7	Oxidation stability of FAME blend, hrs			EN 590	Min. 20	

3.2 Blends preparation

Biodiesel prepared from Jatropha curcas oil is mixed with petro diesel in pre- decided amount to prepare various blends.

3.3 Stability measurement

Oxidation stability of biodiesel from different feedstocks and their blends with automotive diesel was quantified by the induction period (IP). The IP was evaluated according to the Rancimat method EN 14112 for pure biodiesel and the modified Rancimat method EN 15751 for the biodiesel blends with petro-diesel. In the modified Rancimat method, a number of parameters were changed, mainly because of the higher volatility of hydrocarbon fuels compared to methyl esters, which may lead to higher sample evaporation. All stability measurements were carried out on a Metrohm 873 Biodiesel Rancimat instrument. Samples of 3 g of pure biodiesel and 7.5 g of biodiesel blends were analyzed under a constant air flow of 10 L/h, passing through the fuel and into a vessel containing distilled water [high-performance liquid chromatography (HPLC) water]. The samples were held at 110^{0}C heating block temperature; with a temperature correction factor ΔT to be set to 1.5^{0}C (as recommended by the test method). The electrode is connected to a measuring and recording device. The end of the induction period is indicated when the conductivity starts to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. When the conductivity of this measuring solution is recorded continuously, an oxidation curve is obtained whose point of inflection is known as the IP. This provides the good characteristic value for the oxidation stability.

As discussed earlier, biodiesel stability is a matter of concern as it cannot be stored beyond a period. In order to ensure customer acceptance, standardization and quality assurance for introduction of biodiesel into market, there is need to improve the fuel and to carry out analysis to measure the stability. As per EN 14112/IS 15602 test method, oxidation stability is measured by heating at 110^{0}C.

Fatty acid composition of Jatropha biodiesel is given in Table 2. It is clear from table 1 and 2 that due to large amount of unsaturated fatty acids, oxidation stability of JCB is very poor. On the other hand, other properties are within range according to ASTM and Indian standards.

Biodiesel is supposed to be blended with diesel while using in diesel engine and accordingly, a set of study was undertaken to blend Jatropha oil methyl ester with petro diesel having good oxidation stability due to absence of unsaturated fatty acids. And then the effect of blending on oxidation stability is checked. Also relative effectiveness of various antioxidants is checked in its blends with petro-diesel.

Table 2. Fatty acid composition of Jatropha curcas oil

Fatty Acid	Molecular Formula	Structure	% Composition
Palmitic acid (P)	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$	16.8
Stearic acid (S)	$C_{18}H_{38}O_2$	$CH_3(CH_2)_{16}COOH$	7.7
Oleic acid (O)	$C_{18}H_{34}O_2$	$CH_3(CH_2)_7 - CH= CH - (CH_2)_7COOH$	39.1
Linoleic acid (L)	$C_{18}H_{32}O_2$	$CH_3(CH_2)_4 CH = CH - CH_2 - CH=CH - (CH_2)_7 COOH$	36.0
Linolenic acid (LL)	$C_{18}H_{30}O_2$	$CH_3(CH_2)_4CH = CH-CH_2-CH=CH-CH_2 - CH=CH - (CH_2)_4 COOH$	0.2

4.Results and discussion

4.1 Effect of antioxidants on the oxidation stability of pure biodiesel

All the 5 antioxidants were doped at different dosage (50, 100, 150, 200 and 300 ppm) in Jatropha biodiesel and Rancimat test was conducted to study the effectiveness of different antioxidants and the results are given in Figure 3.

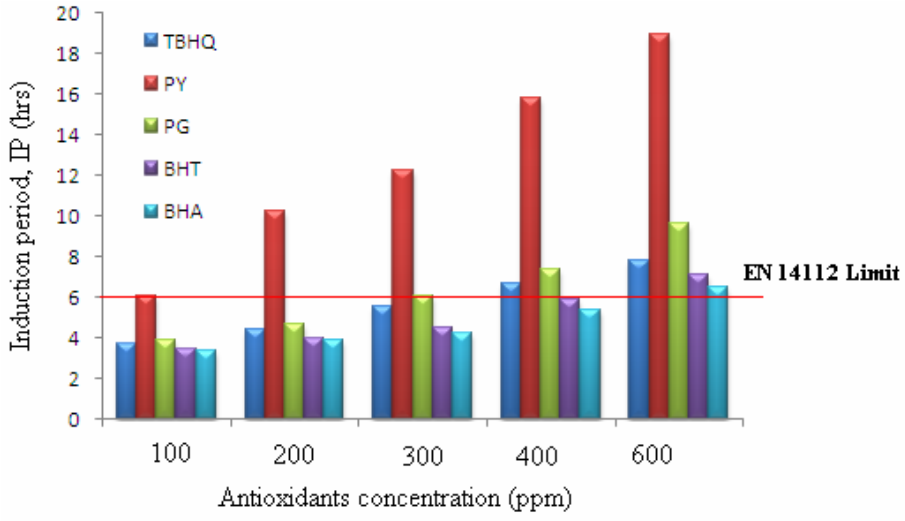

Figure 3. Relative effectiveness of antioxidants

Figure 3 shows the effect of all phenolic antioxidants from 100 ppm to 600 ppm dosage on the oxidation stability. The oxidation stability of Jatropha biodiesel has been found to increase with increase in dosage of antioxidant. Finally, it is found that dosing of 100 ppm of PY antioxidant is the minimum concentration required to meet EN 14112 specification for biodiesel oxidative stability.

4.2 Effect of blending of biodiesel with petro diesel on its oxidation stability

Although, it is possible to meet the desired EN specification by using antioxidant but there will be cost implications as antioxidants are costly chemicals. Also biodiesel is supposed to be blended with petro-diesel while using in diesel engine therefore the biodiesel blends with petro diesel in different composition (B_2, B_5, B_7, B_{10}, B_{20}, B_{30}, B_{40}, B_{50} and B_{80}) were prepared and then its effect on oxidation stability was studies and the results are shown in Figures 4 and 5.

It is clear from the Figure 4 that as the amount of diesel is increased in the blend, the IP increases indicating the improvement of oxidation stability that can be attributed to the reduction of unsaturated fatty acid in the blend. It has been found experimentally that minimum 80% diesel is required to be blended with Jatropha biodiesel (B_{20}) to meet the specification of induction of 20 h according to European standard EN 590. However if we go beyond B20, the IP will decrease below 20 hrs and it will

not be able to maintain the specification according to EN 590. Therefore the effect of various antioxidants on oxidation stability is required to be studied beyond B_{20}.

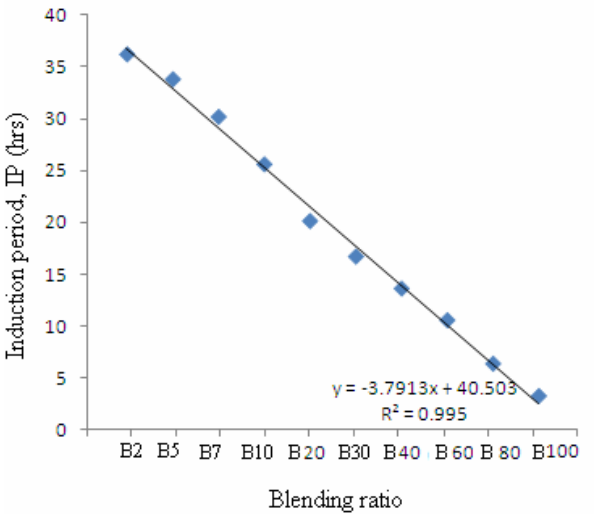

Figure 4. Variation of induction period with blending ratio

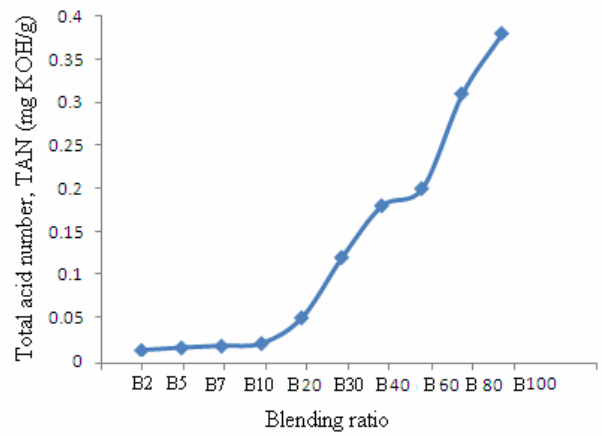

Figure 5. Variation of TAN with blending ratio

Figure 5 shows the decrease in total acid number (TAN) with the increasing % of petro-diesel in the blend. Due to lack of oxidation and lower TAN, the viscosity of biodiesel blends with petro-diesel will also decrease with the increasing % of petro-diesel (Figure 6).

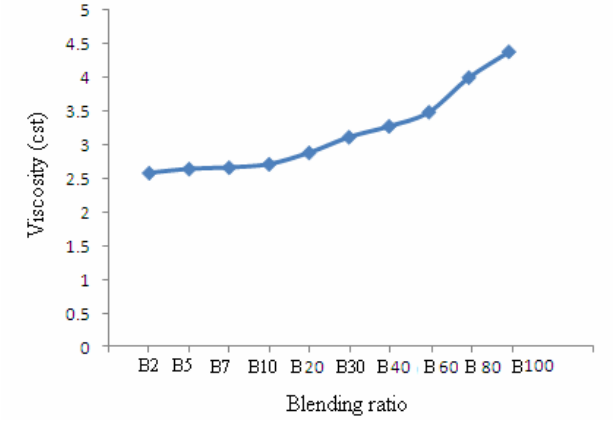

Figure 6. Variation of viscosity with in increasing proportion of blend

4.3 Effect of antioxidants on the oxidation stability of biodiesel blends with petro-diesel

Further study was initiated to blend Jatropha biodiesel with petro- diesel (B_{30}, B_{40}, B_{50} and B_{80}), along with antioxidant. The antioxidant dose was varied from 50 to 600 ppm dosages and oxidation stability of these blends was studied, in terms of induction period using Rancimat test. The results are shown in Figure 7, 8, 9 and 10.

Figure 7 indicated the effectiveness of various antioxidants in B_{80} blend. The result shows that to maintain the specification of 20 hrs induction period 400 ppm of PY or 600 ppm of PG is required to be dope in the blend which is a very large.

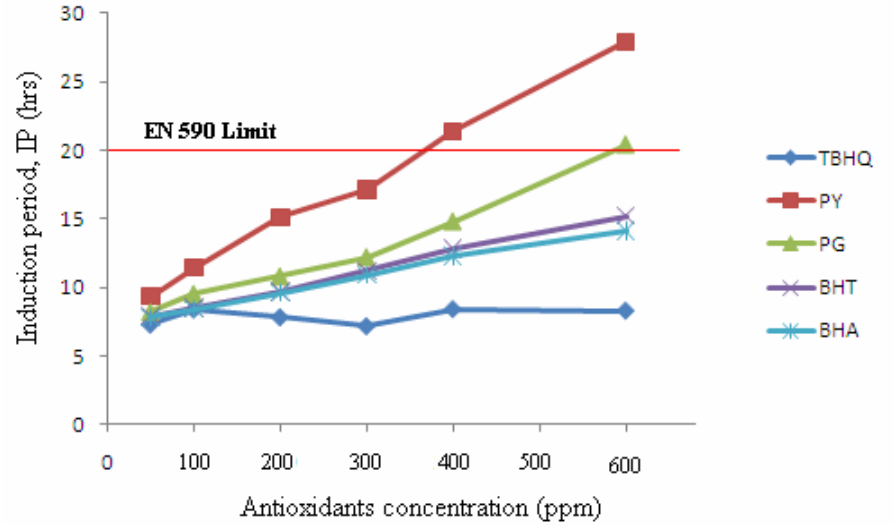

Figure 7. Effect of antioxidants on the stability of B80 blend

Figure 8 shows the effect of various antioxidants on the oxidation stability of B_{50} blend. It shows that to maintain the specification of 20 hrs induction period 300 ppm of PY or 400 ppm of PG is required to be dope in the blend which is again very large amount.

Figure 9 shows the effect of various antioxidants on the oxidation stability of B_{40} blend. Now it shows that to maintain the specification of 20 hrs induction period 200 ppm of PY or PG is required to be dope in the blend which is again very large amount.

In all the above three cases (B_{80}, B_{50} and B_{40}) the amount of antioxidants (PY and PG), required for increasing the IP up to 20hrs is very large as greater than the amount required in pure biodiesel to maintain the specification. However other 3 antioxidants are failed to increase the IP up to 20 hrs for B_{80}, B_{50} and B_{40}.

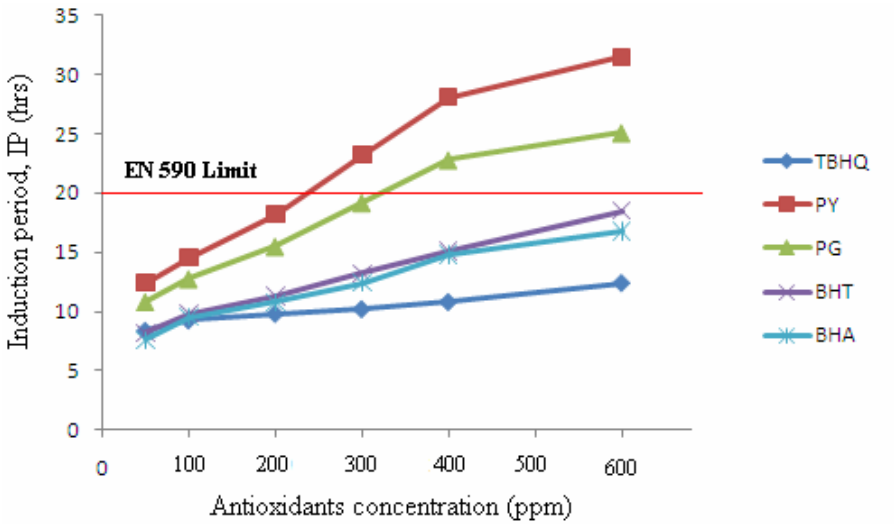

Figure 8. Effect of antioxidants on the stability of B50 blend

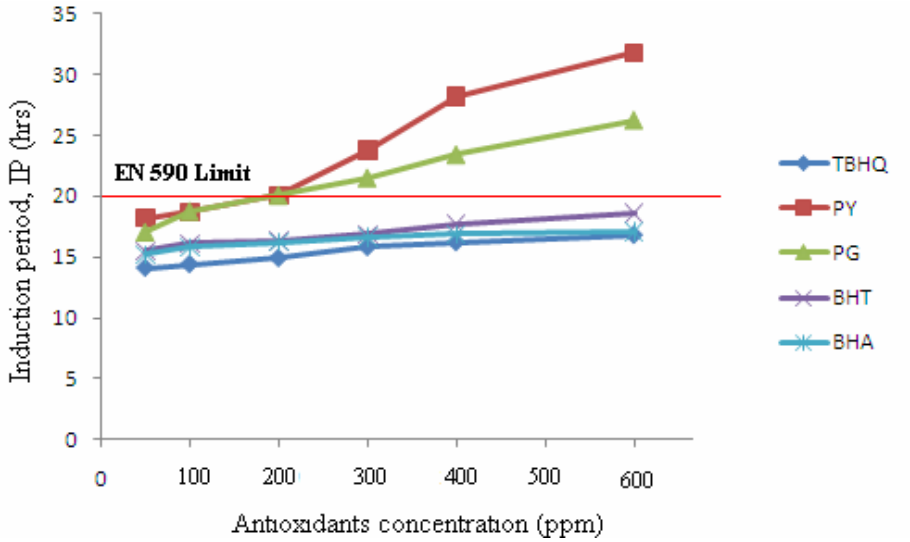

Figure 9. Effect of antioxidants on the stability of B40 blend

Figure 10 displays the effect of various antioxidants on B_{30} blend. From the results it may be concluded that to maintain the specification of 20 hrs induction period, 50 ppm of PY or PG is required to be dope in the blend which is lesser than that required by pure biodiesel to maintain the specification. On the other hand 200, 300 and 300 ppm concentration is required for TBHQ, BHT and BHA respectively to achieve the same oxidation stability specification.

Thus, it is possible to attain requisite oxidation stability of biodiesel by blending 70% petro-diesel in Jatropha biodiesel using only 50 ppm of antioxidant (PY and PG). This optimum combination is expected to reduce the cost of biodiesel substantially and require lower quantity of antioxidant. No antioxidant however is needed if the diesel proportion is beyond 80% in the blend.

Among all the antioxidants tested, PG and PY showed a greater effect on the stability of the biodiesel blend with diesel. This was as expected, because both of these additives presented an increased stability performance with pure methyl ester samples. The use of TBHQ showed an excellent performance in neat biodiesel however, an undesirable pro-oxidant interaction was found with the biodiesel blends. On the other hand, BHT and BHA were found to be the least effective antioxidants in the pure biodiesel. However, both additives resulted in higher stability for all biodiesel blends. The reason for this may be attributed to the greatly different structure of methyl esters compared to non polar hydrocarbons, which may interact with the highly hindered polar phenol group of BHT or BHA to reduce their antioxidant capability [18].

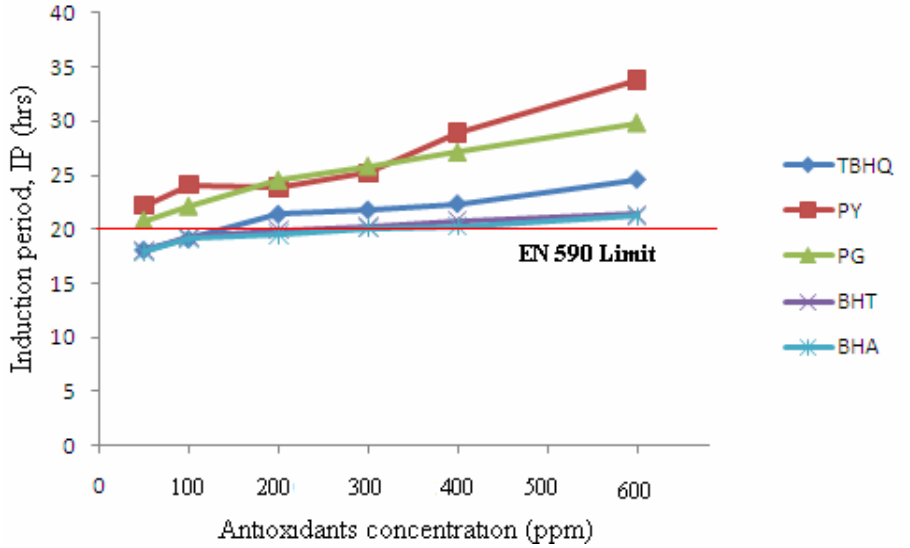

Figure 10. Effect of antioxidants on the stability of B30 blend

5. Conclusion

Biodiesel is supposed to be blended with petro- diesel while using in diesel engine therefore oxidation stability study has been carried out with respect to biodiesel/ diesel blend. Jatropha biodiesel, when blended with petro-diesel leads to a composition having efficient and improved oxidation stability. The results have shown that blending of biodiesel with diesel with less than 20 % (v/v) would not need any antioxidants but at the same time, need large storage capacity. Similarly, if the amount of diesel is decreased in the blend, it will require the addition of antioxidant but in lesser amount compared to pure biodiesel. A B_{30} blend has been tested for the same purpose. PY is found to be the best antioxidants among all 5 antioxidants used. The optimum amount of antioxidant (PY) for pure biodiesel is 100 ppm while it is 50 ppm for B_{30} blend to maintain the oxidation stability specification.

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