Effect of Antioxidants on the Storage Stability of Biodiesel Produced from *Jatropha curcas*

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ABSTRACT: Biodiesel is ethyl or methyl ester of the long-chain fatty acids. It can be used along with the normal diesel as a blend or can replace the diesel as fuel. Biodiesel has many advantages over petroleum diesel but has some limitations too. One of the major challenges of biodiesel is that it is susceptible to oxidation during storage. Its quality degrades which can put the limit to its use as a diesel engine fuel. The purpose of the present research was to study the storage stability of biodiesel prepared from *Jatropha* oil. In this work, some of the properties that degrade with time were measured. These properties are density, kinematic viscosity, acid value, and peroxide value. These properties were measured using the standard procedures. It was observed that the quality of all the biodiesel samples degraded with time and samples which were exposed both light and air were the most affected. It was also observed that the antioxidants have a positive effect on the storage time. When antioxidants were in concentrations of 500 ppm the results were significantly improved.

Keywords: Acid Value, Jatropha biodiesel, Kinematic Viscosity, Oxidation Stability, Storage stability.

Abbreviations: KV, kinematic viscosity; AV, acid value; PY, pyrogallol; BHT, butylated hydroxytoluene; AO, antioxidant; PY100, biodiesel added with PY 100 ppm; PY300, biodiesel added with PY 300 ppm; PY500, biodiesel added with PY 500 ppm, BHT 100, biodiesel added with BHT 100 ppm, BHT300, biodiesel added with BHT 300 ppm, BHT 500, biodiesel added with BHT 500.

I. INTRODUCTION

Energy consumption is increasing as the population of the world is growing at an exponential rate. Most of the energy consumed in the transportation sector is derived from conventional fuels. The demand for the fuel keeps on growing at a much faster rate as compared to the supply of conventional fuels. This leads to an increase in the fuel prices and burden on the economy of most of the crude oil importing countries like India. The increase in conventional petrol and diesel consumption also causes the problem of global warming, air pollution which is causing serious health problems in densely populated cities. Therefore the alternative to conventional fuels has been the focus of research since the past few decades. Solar energy, Wind energy, hydraulic energy and energy from biofuels have attracted the attention of researchers from all over the world. Biofuels are being used as an alternative to petrol and diesel, where ethanol is a substitute for petrol and biodiesel is used as the replacement of conventional diesel. Biodiesel is a methyl or ethyl ester of long-chained fatty acids. Biodiesel has combustion properties viz. Calorific value, Cetane number and kinematic viscosity, almost similar to diesel [1-5]. It is renewable as it is derived from the plants [6], contains oxygen.

Another disadvantage of biodiesel is that it is prone to oxidation during its storage. Biodiesel is either ethyl or methyl esters of long-chained fatty acids made from vegetable oils. These fatty acids are polyunsaturated [13] and the double bond bis-allylic site is prone to the reaction with the available oxygen. The oxidation reaction breaks the biodiesel into peroxides and hydroperoxides and these oxides and peroxides further break into aldehydes, ketones and alcohols which are shorter chain compounds. These reactions also cause changes in the physical appearance of the biodiesel and also in the properties like density and viscosity [13-15]. The color of the biodiesel becomes darker and sediments form at the bottom. The smell also becomes like that of the paint.

The oxidation phenomenon is classified into two parts viz. primary and secondary oxidation [16]. During the primary oxidation, the carbon-free radicals are formed which lead to the formation of hydroperoxides and this keeps on going until the stable products of oxidation are formed. These are categorized as initiation, propagation and termination reactions [13, 17, 18]. The secondary oxidation reaction results into formation of aldehydes, small chain esters, and aliphatic alcohols, etc. [13].
Oxidation stability is very important characteristics of the biodiesel and is included in the American and European biodiesel standards ASTM D6751 and EN 14213 and EN 14214. Rancimat test is a common method used to find the oxidation stability which is measured by the parameter, induction period. Induction period, during the Rancimat test, is the time from the start of the test to the time the products of secondary combustion begin to form [21]. The induction period should be a minimum of 6 hrs as per EN14214 and 3 hrs as per ASTM 6751. The other indicators and parameters used for measuring storage stability are Kinematic viscosity, density, acid number and peroxide value [22-25]. These are also mentioned in various biodiesel standards including Indian biodiesel standards.

Since biodiesel oxidation stability is an important characteristic of the biodiesel, and the normally the biodiesel degrades during the long term storage, attempts have been made to find out the methods to improve the storage stability of the methyl esters. The biodiesel gets deprived of its natural antioxidants such as tocopherols and sterols etc. during the purification process done after transesterification [13]. Addition of antioxidants has found to improve the stability of biodiesel. Antioxidants used may be natural or synthetic. They are also classified as phenolic type or aminic type [13, 26, 27]. The phenolic antioxidants restrict chain reaction by stabilizing free radicals. The antioxidants may also be categorized as primary or secondary antioxidants [28].

Many studies have been performed [26-39] using several synthetic and natural antioxidants and favorable results have been observed where the stability of biodiesels have improved. Various natural and synthetic antioxidants are mentioned in Table 1.

Table 1: Some commonly used antioxidants for biodiesels [13, 27-41].

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Antioxidant</th>
<th>Chemical composition</th>
<th>Mol. mass (g/mol)</th>
<th>Density (g/cc)</th>
<th>Melt. pt. (ºC)</th>
<th>Boiling pt. (ºC)</th>
<th>Abbreviation</th>
<th>N/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Tert-butylhydroquinone</td>
<td>10 14 2 0</td>
<td>166.22</td>
<td>1.05</td>
<td>127-129</td>
<td>273</td>
<td>TBHQ</td>
<td>S</td>
</tr>
<tr>
<td>2.</td>
<td>2,5-Di-tert-butyldihydroquinone</td>
<td>14 22 2 0</td>
<td>222.33</td>
<td>—</td>
<td>215</td>
<td>321</td>
<td>DTBHQ</td>
<td>S</td>
</tr>
<tr>
<td>3.</td>
<td>Butylated hydroxytoluene</td>
<td>15 24 1 0</td>
<td>220.36</td>
<td>1.048</td>
<td>70</td>
<td>265</td>
<td>BHT</td>
<td>S</td>
</tr>
<tr>
<td>4.</td>
<td>Butylated hydroyxanisole</td>
<td>11 16 2 0</td>
<td>180.25</td>
<td>1.059</td>
<td>48-55</td>
<td>264-274</td>
<td>BHA</td>
<td>S</td>
</tr>
<tr>
<td>5.</td>
<td>4-tert-butylcatechol</td>
<td>10 14 2 0</td>
<td>166.22</td>
<td>—</td>
<td>50</td>
<td>285</td>
<td>TBC</td>
<td>S</td>
</tr>
<tr>
<td>6.</td>
<td>A-tocopherol</td>
<td>29 50 2 0</td>
<td>430.71</td>
<td>0.95</td>
<td>2.5-3.5</td>
<td>200-220</td>
<td>A-T</td>
<td>N</td>
</tr>
<tr>
<td>7.</td>
<td>S-Carvone</td>
<td>10 14 1 0</td>
<td>150.22</td>
<td>0.96</td>
<td>25.2</td>
<td>231</td>
<td>—</td>
<td>S</td>
</tr>
<tr>
<td>8.</td>
<td>B-cardene</td>
<td>40 56 0 0</td>
<td>536.89</td>
<td>0.941</td>
<td>176-184</td>
<td>654.7</td>
<td>B-C</td>
<td>N</td>
</tr>
<tr>
<td>9.</td>
<td>Propyl gallate</td>
<td>10 12 9 0</td>
<td>212.2</td>
<td>—</td>
<td>150</td>
<td>Decomposes</td>
<td>PG</td>
<td>S</td>
</tr>
<tr>
<td>10.</td>
<td>Pyrogalol</td>
<td>6 6 3 0</td>
<td>126.11</td>
<td>1.45</td>
<td>131-134</td>
<td>309</td>
<td>PY</td>
<td>S</td>
</tr>
<tr>
<td>11.</td>
<td>Gallic acid</td>
<td>7 6 5 0</td>
<td>170.12</td>
<td>1.694</td>
<td>260</td>
<td>—</td>
<td>GA</td>
<td>S</td>
</tr>
</tbody>
</table>

N = Natural  S= Synthetic

Sarin et al., [39] investigated the effect of five antioxidants on Jatropha biodiesel and reported that T BHQ was most efficient of the antioxidants used followed by BHT, TBP, OBPA and α-Tocopherol respectively. BHA, TBHQ, BHT, PG, and PY are the antioxidants which are used for biodiesel derived from cooking oil [40]. Fazal et al., [41] investigated the effect of metals and antioxidants on palm biodiesel. The antioxidants used were PY and BHT. They measured the properties of density, acid number, viscosity and induction period. They found that PY was more effective for suppressing the effect of metals as metals tend to increase the rate of oxidation. Singh et al., [42] have tested the storage stability of biodiesel from apricot kernel seed oil over a period of 6 months under various conditions using PY, PG, BHT, BHA and TBHQ. It was reported that 100 ppm of the biodiesel maintained the induction period of 6 hrs for the biodiesel up to 6 months. PY gave the best results as compared to other antioxidants tested and TBHQ was least effective.

From the already existing literature [13, 27-41], it was found that PY and BHT are the most effective antioxidants and there is always scope to improve storage stability of biodiesel under the storage conditions. Therefore the present research was carried out to investigate the effect of these two antioxidants on the storage stability of Jatropha biodiesel over a period of 6 months. Pyrogalol (1, 2, 3-trihydroxy benzene) is a phenolic compound which is commonly found in fruits like apricot and avocado [43]. It is used as a reagent for metallurgy of metals like gold and silver, in various pharmaceuticals and pesticides and also has application as a developer in photography. It has strong antioxidant properties and is also used as corrosion preventer in various boilers. Butylated hydroxytoluene (BHT) is also a phenolic antioxidant widely used as an antioxidant in food products that contain fats and oils [44]. In the past few years, it has become quite useful as an oxidation inhibitor in biodiesels as well. Fig. 1 and 2 shows the structure of PY and BHT respectively.
The density of biodiesel and its blends was measured using ASTM D 4052 test. In this test, the weight of the fixed volume of fuel sample was measured with the help of precision balance. The readings of weight were recorded as per ASTM D4052 at 15°C.

**Density:** The density of biodiesel and its blends increase with time and also on the storage conditions. Densities of the samples were measured using ASTM D4052 test. In this test, the weight of the fixed volume of fuel sample was measured with the help of precision balance. The readings of weight were recorded as per ASTM D4052 at 15°C.

**Kinematic Viscosity.** Viscosity is the major reason that vegetable oils cannot be used directly as fuels. They can be used only after the reduction in viscosity, by converting them into alkyl esters (biodiesel). Kinematic viscosity increases due to oxidation as the fuel quality degrades with increasing storage time. Therefore, it can be used as an indicator of Storage stability and quality of fuel. Kinematic viscosities of the stored fuel samples were measured using the U-tube viscometer at 40°C as per standard procedure mentioned in ASTM D445. The measurement was done using a capillary tube which was cleaned with the suitable solvents and thereafter dried using clean and filtered air. The biodiesel samples were poured carefully in the viscometer tube and efflux time was carefully noted using a stopwatch. Kinematic viscosity was measured using the following formula:

\[ \nu = k \times t \]  

where,  
\( \nu = \) Kinematic viscosity, cSt.  
\( k = \) constant, 0.00854  
\( t = \) time, seconds

**Acid Value:** The Acid Value (AV) is an indicator of the amount of free fatty acid in the oil. AV of any sample is the amount of potassium hydroxide (in mg) required for neutralizing 1 g of oil sample. AOCS Official method (Te TA-64, 1997) is used for to measure AV, in which the solution of fuel samples is titrated in neutral ethanol with 0.5 N KOH. Phenolphthalein solution was used as an indicator for titration. The following equation was used to calculate the AV of the fuel samples.

\[ \text{AV (mg KOH/g)} = \frac{\text{Volume of the titrant (in ml)}}{\text{Mass of sample in g}} \times N \times 56.10 \]  

where, N is the normality of accurately standardized sodium hydroxide solution.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Property</th>
<th>Units</th>
<th>ASTM D 6751 Test Method Limit</th>
<th>BIS: 15607 Test Method Limit</th>
<th>JB100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density @15°C</td>
<td>Kg/m³</td>
<td>ASTM D 4052 —</td>
<td>[P:16] of IS1448 860-900</td>
<td>865</td>
</tr>
<tr>
<td>2</td>
<td>Flash Point</td>
<td>ºC</td>
<td>D 93 130 sec</td>
<td>[P:21] of IS 1448 120</td>
<td>145</td>
</tr>
<tr>
<td>3</td>
<td>Acid Number</td>
<td>mg of KOH/g</td>
<td>D 664 0.5 max</td>
<td>[P:1/Sec1] of IS1448 0.5 max</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>Kinematic Viscosity @ 40ºC</td>
<td>CST</td>
<td>D 445 1.9-6</td>
<td>ISO3104, [P:25] of IS 1448 2.5-6</td>
<td>4.45</td>
</tr>
<tr>
<td>5</td>
<td>Cetane Number</td>
<td>—</td>
<td>D 613 47 min</td>
<td>ISO 5165, [P:9] of IS 1448 51 min</td>
<td>60</td>
</tr>
</tbody>
</table>

The analytical grade commercial antioxidants, Pyrogallol (PY) and Butylated hydroxytoluene (BHT) were procured from MedTek Pvt. Ltd., Ludhiana. The antioxidants were used in three concentrations viz. 100 ppm, 300 ppm, and 500 ppm. The samples were prepared and were stored in the containers under three different conditions and analyzed for a period of six months. One group of samples was stored in dark and sealed containers, one was stored in sealed but exposed to both light and air. The changes in its properties are shown in Table 2.
III. RESULTS AND DISCUSSION

The purpose of stability analysis was to find the shelf life of biodiesel and also to assess the effect of antioxidants on the measurable properties of biodiesel which are indicators of stability. For this, two liters each of the biodiesel and biodiesel blends fuel samples were taken and stored for a period of six months different storage conditions at room temperature. The stored biodiesel was designated as NAO (NO antioxidant), PY100 (100 ppm PY), PY300, PY500, BHT100, BHT300, BHT500 respectively.

The samples were stored under the following conditions:
(a) Samples in an airtight container in Cupboards where there was no light.
(b) Samples in airtight containers in the presence of daylight.
(c) Samples in open containers and in the presence of light.

The Physiochemical properties of density, kinematic viscosity and acid value, which are indicators of storage stability of the fuel samples, were measured every month as per BIS standard methods. The data for the period of six months was assessed to find out the degradation level of the biodiesel blends/pure biodiesel. The detailed explanations of these results and the changes in the density, Kinematic Viscosity and Acid value have been discussed below.

Density. Due to the Oxidation during the storage, the primary and secondary products are formed in the biodiesel and their corresponding blends. As a result of these reactions and the formation of the products of the oxidation, as discussed in the literature review, the increase in density was expected. The results showed that density for all the fuel samples increased with time. However, it was found that storage conditions had a lot of effect on the density variation. Also, the minimum variation was for the biodiesel samples using 500 ppm PY antioxidant as additive. Fig. 3 (a-c) reflect the changes in the density of the samples stored under sealed and dark conditions. The samples were sealed properly and were stored in dark in the cupboard where there was no chance of interaction of light.

Therefore the oxidation process was slowest in this case. The limit to the density of 900 kg/m$^3$ biodiesel blended diesel as per ASTM D 7467 and BIS: Doc: PCD 3(865) C is 820-860 kg/m$^3$ and for pure biodiesels is as per ASTM6751 BIS: 15607 is 860-900 kg/m$^3$.

The PY500 samples had the densities within the prescribed limits up to 20 weeks. In the 20th week the density was 895 kg/m$^3$, just marginally less than the standard limit, whereas for BHT500, the density was higher than the prescribed limit after 20 weeks (901 kg/m$^3$). The pure biodiesel, however, showed higher variation in densities and was within the standard limit up to 12 weeks.
Different concentrations of BHT.

Comparison of PY 500 and BHT 500.

Variation of Density of samples stored in sealed containers and in natural light.

The samples that were sealed but in light showed marginal higher density than the samples stored in sealed and dark in the corresponding weeks. This proved that the rate of oxidation increases when the samples are stored in the light as compared to the samples stored in dark. Fig. 4 (a-c) reflect the trends in density variation for the fuel samples in light but sealed properly. The samples were stored in the glass containers which were tightly sealed and were kept in the place where there was abundant natural light for maximum time. The density of biodiesel sample without antioxidant was above the prescribed limit after 8 weeks whereas using antioxidants reduced the rate of the increase in density. The density was within the range for up to 20 weeks and 16 weeks for PY500 and BHT500.

Variations in Density of samples stored in containers exposed to air and light.

The maximum change in density was recorded for the samples that were stored in open containers and natural light. The effect of the presence of air was even more prominent than the effect of light alone. All samples degraded prior to the ones kept sealed. Biodiesel sample without antioxidant had density above the maximum limit after 8 weeks itself whereas for samples with BHT and PY concentrations of 100 ppm and 300 ppm lasted within the standard range up to 12 weeks. The PY500 and BHT500 samples were within the limits up to 16 weeks. Fig. 5(a-c) show the variation of density for the samples stored in light and exposed to air. Increase in concentration of oxidants also affected the density variation. The rate of density increase reduced with a higher concentration of antioxidants and also PY was found to be slightly better than BHT in all respective concentrations.

Kinematic Viscosity. It has been concluded in many studies that kinematic viscosity is the good measure for storage stability of biodiesel. Kinematic viscosity (KV) increases with the storage time. Kinematic viscosity is one of the properties of the biodiesel that has been mentioned in Indian and American standards. For pure biodiesel, the standard value limits for Kinematic viscosity are 1.9 cSt- 6 cSt as per ASTM D6751 and 2.5-6 cSt as per Indian BIS 15607. During oxidation, increase in viscosity takes place only when the peroxides reach a particular value and there is the formation of oxidized polymeric compounds.
The peroxides formed are unstable and they break into lower molecular weight radicals that further form acids, aldehydes, ketones, alcohols, olefins, and alkanes. These products of oxidation reactions decrease the quality due to increased viscosity, and the formation of insoluble compounds.

Fig. 6 (a-c) shows the Kinematic viscosity variation for the biodiesel samples stored in sealed and dark conditions. All the samples were having the Kinematic viscosity less than the upper limit that is prescribed in the standards after six months. The antioxidants had positive effects and lowered the rate of oxidation. During six months, the maximum change of 36% in the Kinematic viscosity was detected for the samples using no antioxidants whereas the change in KV for PY500 and BHT500 during the same duration was 23% and 25% respectively.

Fig. 7 (a-c) shows the trends for the change of KV for the fuel samples sealed and stored in light. The rate of KV increase was higher than those samples that were stored in dark. During the six months, the KV of the samples without using antioxidants changed by 46% as compared to 36% change when the samples were stored under sealed and dark conditions. Addition of both PY and BHT had a positive effect on KV and it was found within the prescribed limits of various standards after 24 weeks. The minimum change of 23% was detected measured in KV of PY500 samples. Here again, the PY antioxidants samples had more resistance to oxidation as compared to the corresponding BHT samples of same concentrations. The pure biodiesel had higher KV than the upper limit of 6 cSt after 24th week.

![Graphs showing Kinematic viscosity variations](image1)

**Fig. 6.** Variations in Kinematic Viscosity of samples stored in sealed and dark.

![Graphs showing Kinematic viscosity variations](image2)

**Fig. 7.** Variations in Kinematic Viscosity of samples stored in sealed containers and in light.
Fig. 8 (a-c) discusses the variation for the KV change in the samples stored in light and open to air. The rate of change of KV is higher for these samples as air increases the oxidation rate. The KV approached the upper limit for PY100, BHT100 and without antioxidant samples in the 24th week with KV of 6.09 cSt, 6.12 cSt, and 6.23 cSt respectively.

![Fig. 8](image.png)

Fig. 8 Variations in Kinematic Viscosity of samples stored in containers exposed to air and light.

**Acid Value:** During oxidation, the fatty acid chain breaks into shorter chained molecules and as result the acid value increases. Therefore acid value becomes a good indicator of the extent of degradation of biodiesel. Acid number for pure biodiesel should be less than equal to 0.5 mg of KOH/kg as per American standard ASTM D 6751 and Indian standard BIS 15607.

Fig. 9 (a-c) shows that all samples those were stored in sealed and dark conditions had AV less than the standard upper limit except for the samples without antioxidants and PY100 and BHT samples the end of month.

![Fig. 9](image.png)

Fig. 9 Variations in Acid Value of samples stored in stored in sealed and dark.

The AV of PY500 and BHT500 was found to be marginally above that of the standard upper limit after 12th week. After six months the minimum AV was for PY500 samples, which was 1.25 mg of KOH per gram. For pure biodiesels without antioxidant, the AV after 6 months was 2.6 mg of KOH per gram.
The samples those were sealed and in the light as shown in Fig. 10 (a-c), degraded even quickly as the AV of all samples were found above the upper limit of standard value after the 12th week itself. The maximum change was for the samples that were open to air and in light. The results show that where AV of biodiesel without antioxidant crossed the standard limit after 1 month itself, PY500 and BHT500 samples had AV below the maximum limit even after 2 months of storage. This shows that the higher concentrations of antioxidant can further delay the degradation.

**IV. CONCLUSION**

One of the main drawbacks of the biodiesel is its degradation to oxidation when stored for a long period of time. The current study was conducted to test the storage stability of the biodiesel produced and also to find out the shelf life of the biodiesel under various conditions of storage under different conditions. Another objective of the study was to find the effect of two of the available antioxidants on the stability of the biodiesel. PY and BHT were selected based on the performance as discussed by various researches in the previous literature. The samples were stored under the three different conditions and the stability indicating quantities viz, density, kinematic viscosity and acid value were measured for six months. The following conclusions were drawn from the study.
Further scope of the study lies in investigating long term stability for the period of one year and above and using higher concentrations of antioxidants.

V. FUTURE SCOPE

The results of the study confirm that the presence of both, the light and air, affect the stability of biodiesel and increase the rate of oxidation which can be seen from the increased values of the measured parameters.

It was also observed that the antioxidants have a positive effect on the storage time. When antioxidants were in concentrations of 500 ppm the results were significantly improved.

The shelf life of the biodiesel with antioxidant showed significant improvement as compared to the shelf life of biodiesel without antioxidant. The results show that the shelf life is almost double when 500 ppm concentrations of BHT and PY were used as compared to biodiesel without antioxidant.

PY had a better effect on the storage stability as compared BHT in all concentration.

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Conflict of Interest. Authors hereby declare that there is no conflict of interest in this work.

REFERENCES

biodiesel produced from Karanja oil. Fuel, 88(11), 2315-2318.

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