Jatropha–Palm biodiesel blends: An optimum mix for Asia

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Abstract

Biodiesel, an alternative renewable fuel made from transesterification of vegetable oil with alcohol, is becoming more readily available for use in blends with conventional diesel fuel for transportation applications. Soybean and Rapeseed are common feedstocks for Biodiesel production in USA and Europe, respectively. However, Asian countries are not self sufficient in edible oil and exploring non-edible seed oils, like Jatropha and Pongamia as biodiesel raw materials. However there is a gestation period of few years before these crops start yielding seeds and oil. On the other hand, South Eastern countries like Malaysia and Thailand have surplus Palm crops. But due to substantial amount of saturated fats in Palm, the Palm biodiesel has poor low temperature properties. In order to exploit the proximity of South Asian and South-East Asian countries, blends of Jatropha and Palm biodiesel have been examined to study their physico-chemical properties and to get an optimum mix of them to achieve better low temperature properties, with improved oxidation stability.

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1. Introduction

Biodiesel is an environment friendly liquid fuel similar to petro-diesel in combustion properties. Increasing environmental concern, diminishing petroleum reserves and agriculture-based economy of our country are the driving forces to promote biodiesel as an alternate renewable transportation fuel. Biodiesel derived from vegetable oil and animal fats is being used in USA and Europe to reduce air pollution, to reduce dependence on fossil fuel, whose resources are limited and localized to some specific regions. In USA and Europe, their surplus edible oils like soybean oil, sunflower oil and rapeseed oil are being used as feedstock for the production of biodiesel.

Since India is net importer of vegetable oils, therefore these oils cannot be used for the production of biodiesel. India has the potential to be a leading world producer of biodiesel, as biodiesel can be “harvested,” and sourced from non-edible oils like Jatropha Curcas, Pongamia Pin-...
parts. This is why the oxidation stability is an important criterion for biodiesel. Stability of biodiesel is inferior compared to petrodiesel and therefore doping of biodiesel in petrodiesel will affect the stability of fuel significantly [3]. The poor stability of biodiesel is also because of the double bonds in the fatty acids, which may lead to gum formation. In either of the cases the product will become off spec. Therefore, it was considered to include a limit for oxidation stability in the existing quality standard for biodiesel.

Almost in all biodiesel fuel significant amounts of esters of oleic, linoleic or linolenic acids are present and the trend of increasing stability was linolenic < linoleic < oleic. These esters undergo auto-oxidation with different rates depending upon the number and position of the double bonds and results in formation of a series of by-products, like acids, esters, aldehydes, ketones, lactones, etc.

During the oxidation process, the fatty acid methyl ester usually forms a radical next to the double bond. This radical quickly binds with the oxygen in the air, which is a biradical. This forms peroxide radical. The rapid radical destruction cycle begins after that. This peroxide radical immediately creates a new radical from the fatty acid methyl ester, which in turn binds with oxygen in the air. Then the destructive radical auto-oxidation cycle starts. During this process, up to 100 new radicals are created quickly from one single radical. The decomposition occurs at an exponentially rapid rate and results in formation of a series of by-products [4]. These species formed during the oxidation process cause the fuel to eventually deteriorate. Finally the oil spoils and became rancid very quickly.

Oxidative rancidity begins with an initial chain reaction:

\[ RH \rightarrow R^\cdot \]

followed by a propagating reaction that involves unstable peroxides and hydroperoxides:

\[ R^\cdot + O \rightarrow ROO^\cdot \]
\[ ROO^\cdot + RH \rightarrow R-OH + R^\cdot \]

followed by the termination reactions resulting in aldehydes, alcohols and carbonic acids:

\[ R^\cdot + R^\cdot \rightarrow R-R \]
\[ ROO^\cdot + R^\cdot \rightarrow R-OO-R \]

A number of reports has appeared on the storage and oxidative stability of biodiesel synthesized from edible oils. However no reports have been seen about oxidative stability of biodiesel from tree borne non-edible oil seeds. Dunn has studied the effect of oxidation under accelerated conditions on fuel properties on methyl soyate [5]. Knothe has reported the effect of structure of fatty compounds on stability of vegetable oil derived products [6]. Dunn has also studied the effect of different antioxidants on oxidation stability of biodiesel from soybean oil [7]. Ferrari et al. has compared the oxidative stability of neutralized, refined and frying oil waste soybean oil fatty acid ethyl ester [8]. It has also been reported that synthetic antioxidants are more effective than natural antioxidants [9]. Some stability studies were also carried out on methyl and ethyl fatty acid esters under different storage conditions [10]. Prankl studied the effect of storage conditions on stability of biodiesel and compared oxidation stability of biodiesel samples from different manufacturers [11]. Bondioli has also reported his findings on biodiesel stability kept under commercial storage conditions over one year [12]. From these literature reports and NREL survey report [13], it can be concluded that it will not be possible to use biodiesel without antioxidants. The two most common types of antioxidants are phenolic-types and amonic-types. As can be seen in Fig. 1 on mechanism of antioxidant action, 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 that does not contribute to the chain oxidation process. In this way chain breaking antioxidants interrupt the oxidation chain reaction.

As per proposed National Mission on biodiesel in India, we have undertaken studies on stability of biodiesel from tree borne oil seeds like Jatropha, Pongamia, etc. In order to improve the stability of biodiesel and make it acceptable to oil marketing companies, doping of antioxidant is required. Further studies were carried out to compare efficiency of various antioxidants, especially for Jatropha biodiesel and in comparison with other biodiesel. However in order to cut the cost and dosage of antioxidants, studies on blends of palm biodiesel with Jatropha biodiesel have been carried out.
2. Experimental

2.1. Biodiesel synthesis and testing

Fatty acid composition of vegetable oils were measured by GC (Model HR/GC/5300), using nitrogen as a carrier gas and di(ethylene glycol) succinate column (DEGS) by preparing the corresponding fatty acid esters and comparing them with the standard fatty acid ester samples. Detailed fatty acid composition is given in Table 1, which clearly indicates the predominance of saturated fatty acids in palm oil.

A series of biodiesel samples have been prepared using alkali catalyzed method. Methanol (1:3 molar oil: alcohol) was mixed with NaOH/KOH (1 wt.% of oil) added to the reactor containing oil slowly along with stirring. The reaction mixture was refluxed for 2-4 h. TLC monitored the progress of the reaction. After completion of the reaction the material was transferred to separating funnel and both the phases were separated. Upper phase was biodiesel and lower part was glycerin. 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. The residual product was kept under vacuum to get rid of residual moisture [14,15].

The synthesized biodiesel samples were tested for physico-chemical properties as per ASTM D-6751 and Indian IS-15607 specification (Table 2). It is clear from the data that although the biodiesel prepared from different oils meet most of the specifications, all biodiesel samples failed in oxidation stability test, with the exception of palm biodiesel.

The oxidation stability of palm oil is good due to presence of higher concentration of saturated fatty acids. The oxidation stability of Jatropha and Pongamia (Karanjia) was found to be close to soybean and rapeseed oil, which can be explained by their matching composition of unsaturated fatty acids (Table 2). The results are very much in line with biodiesel quality survey of 2004 and 2006, which indicate that majority of samples, failed in EN-14112 test [13].

Cloud point, pour point and cold filter plugging point (CFPP) are the major criteria for determining cold temperature properties of fuels, and were measured as per ASTM D2500, D97 and D6371 test methods respectively.

2.2. Biodiesel stability

Oxidation stability of biodiesel from different feedstock and their blends with different dosages of different antioxidants were studied in Rancimat equipment model 743. In the Rancimat Method, the oxidation is induced by passing a stream of purified air at the rate of 10 l/h. through the biodiesel sample (~5 ml), kept at constant temperature. The vapors released during the oxidation process, together with the air, are passed into the flask containing 60 ml of water, which has been demineralized or distilled and contains an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicates the end of the induction period when the conductivity begins 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 induction; this provides the good characteristic value for the oxidation stability.

3. Results and discussion

3.1. Stability study

As discussed earlier, biodiesel stability is a matter of concern as it cannot be stored beyond a period. In order to assure customer acceptance, standardization and quality assurance for the market introduction of biodiesel, certain
improvements should be made in its properties and analyze basic parameters needed to attain stability. As per EN 14112/IS 15602 test method, oxidation stability is measured by heating at 110 °C. In order to study the trend of oxidation stability of biodiesel from various resources, the oxidation stability is measured by heating them at 110 °C. It was found that the trend of induction period had direct correlation with the percentage of saturated fatty acids. For example, biodiesel from sunflower oil (BDSU) having only 11.6% saturates, showed induction period of 1.73 h. On the other hand, the palm oil biodiesel (BDP) having 43.4% saturates, exhibited induction period of 13.37 h (Fig. 2).

Another set of study was done to observe the effect of temperature on biodiesel stability. The oxidation stability tests were carried out at 100 °C and 120 °C. As anticipated, the oxidation process accelerated with increase of temperature. However, no difference in relative stability was noticed and biodiesel from the oil having large fraction of saturated fatty acids like palm was found to be still better than biodiesel from other oil sources like Jatropha, having larger fraction of unsaturated fatty acids (Fig. 2). The reason for good stability of palm oil biodiesel is due to the resistance to auto-oxidation of saturated fatty acids.

As given in Table 1, Palm oil has maximum proportion of saturates making it less susceptible towards oxidation. In Indian scenario, Jatropha is the main feedstock available for biodiesel production. So, further study has been concentrated on oxidation stability of Jatropha biodiesel.

Two pronged approach has been adopted for improving oxidation stability of Jatropha biodiesel. First route deals with the doping of Jatropha methyl esters with stabilizer or antioxidants. Among stabilizers utilized in this study were three phenolic antioxidants; 2,6–ditertiarybutyl hydroxytoluene (AO-1), bis–2,6-diteritarybutyl phenol derivative (AO-2), mixed butylated phenol (AO-3), and aminic antioxidant octylated butylated diphenyl amine (AO-4).

All four antioxidants were doped at 200 ppm dosage in Jatropha, Karanja, Sunflower and Soybean based biodiesel and tested in Rancimat to observe the effectiveness of different antioxidants. The results obtained are shown in Fig. 3. From these experiments, it is observed that the antioxidant AO-1 is most effective among all the antioxidants used. Therefore, it is decided to study the effect of dosage of antioxidant (AO-1) on oxidation stability of Jatropha biodiesel. The Fig. 4, shows the effect of phenolic antioxidant AO-1 from 25 ppm dosage to 400 ppm on 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 200 ppm of antioxidant is the minimum requirement to meet EN 14112 specification for biodiesel oxidative stability.

Although it is found possible to meet the desired EN specification by using antioxidant, it will have a cost implication, as antioxidants are costly chemicals. Therefore, another set of study was undertaken to blend Jatropha...
oil methyl ester with palm oil methyl ester, which is having good oxidation stability. The reason for good stability is the resistance to autoxidation, which was primarily due to the presence of saturated fatty acids. It has clearly

- BDSU (Sunflower Biodiesel), BDK (Karanjia Biodiesel), BDJ (Jatropha Biodiesel), BDS (Soybean Biodiesel), BDP (Palm Biodiesel)

Fig. 2. Biodiesel oxidation stability variation with feedstock.

Fig. 3. Selection of antioxidants for biodiesel oxidative stability.

Fig. 4. Antioxidant dose optimisation for Jatropha and Palm biodiesel.
shown in Table 1 (fatty acid comp.) that among all feedstocks, palm oil has maximum proportion of saturates making less susceptible towards oxidation and imparts better stability than other feedstock methyl esters. It was decided to blend palm methyl ester in different composition and observe its effect on induction period of Jatropha methyl ester, and the results are shown in Fig. 5.

It was observed from the Fig. 5, that as the proportion of palm was increasing, oxidation stability also increases (JBD = Jatropha biodiesel, PBD = palm biodiesel, JPBD-1(JB:PB::80:20), JPBD-2(JB:PB::60:40), JPBD-3(JB:PB::50:50), JPBD-4(JB:PB::40:60), JPBD-5(JB:JB::20:80). It is found from the experiments that minimum 60% palm biodiesel is required to be blended with Jatropha biodiesel to meet the specification of induction of 6 h by EN 14112 test.

As 60% palm biodiesel is quite high amount to blend, further study was initiated to blend jatropha biodiesel with palm biodiesel (80:20), along with antioxidant. The antioxidant dose was varied from 25 to 200 ppm dosages and oxidation stability of these blends was studied, in terms of induction period in Rancimat instrument. As per results shown in Fig. 4, approx. 150 ppm of antioxidant is required to achieve requisite oxidation stability norms.

So it was planned to increase palm biodiesel concentration to 40% (JPBD-2, JB:PB::60:40) and optimize dosage of antioxidant AO-1. As per results shown in Fig. 4, the induction period of >6 h was observed even at 25 ppm dosage of antioxidant. Thus it is possible to attain requisite oxidation stability of biodiesel by blending 40% Palm Oil in Jatropha oil and usage of only 25 ppm of antioxidant. This optimum combination reduces the cost of biodiesel substantially, by use of cheaper raw material Palm and requirement of substantially lower quantity of antioxidant.

3.2. Low temperature property study

One of the major problems associated with the use of biodiesel, especially prepared from Palm oil is its poor low temperature flow property, measured in terms of cloud point, pour point and CFPP. However Jatropha biodiesel has good low temperature property, comparable to conventional biodiesel feedstocks like soybean and rapeseed.

Jatropha–Palm biodiesel samples were therefore examined for their low temperature properties, to study the effect of palm biodiesel on Jatropha biodiesel properties. As per results shown in Fig. 6, the blending of 20% Palm biodiesel in Jatropha biodiesel increases cloud point by...
2 °C, pour point by 3 °C and CFPP by 1 °C. Jatropha–Palm (60:40) blend was tested for low temperature properties and found to exhibit cloud point of 10 °C, pour point of 12 °C and CFPP of 5 °C. Thus, the blending of Palm biodiesel in Jatropha biodiesel exhibits additive response in cloud and pour point properties. Though blending of Palm biodiesel with Jatropha biodiesel worsen the low temperature properties of Jatropha biodiesel, the achieved results are of limited concern in the temperate climate of Asia. In addition, these values of cloud point, pour point and CFPP are of little concern after blending at 5–20% biodiesel in diesel.

4. Conclusion

Jatropha biodiesel, when blended with palm methyl ester leads to a composition having efficient and improved low temperature property as well as good oxidation stability. The feedstock for the synthesis of biodiesel must have a suitable combination of saturated as well as unsaturated fatty compounds to achieve improved oxidation stability and low temperature properties. Jatropha biodiesel has poor oxidation stability with good low temperature properties. On the other hand, Palm biodiesel has good oxidative stability, but poor low temperature properties. The combinations of Jatropha and Palm give an additive effect on these two critical properties of biodiesel.

The stability of biodiesel is very critical and biodiesel requires antioxidant to meet storage requirements and to ensure fuel quality at all points along the distribution chain. In order to meet EN 14112 specification, ≈200 ppm concentration of antioxidant is required for biodiesel (except palm biodiesel), which is much higher than that required for petroleum diesel. In order to minimize the dosage of antioxidant, appropriate blends of Jatropha and palm biodiesel are made. It was found that antioxidant dosage could be reduced by 80–90%, if Palm oil biodiesel is blended with Jatropha biodiesel at around 20–40% concentration. Since palm biodiesel has poor low temperature properties like cloud point and pour point, the blending of Jatropha biodiesel improves the same. Therefore, optimum mixture of Jatropha biodiesel with palm biodiesel can lead to a synergistic combination with improved oxidation stability and low temperature property. This techno-economic combination of Jatropha and Palm biodiesel could be an optimum mix for Asian Energy Security.

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