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ORIGINAL PAPER

Effect of Metal Contaminants and Antioxidants on the Oxidation Stability of the Methyl Ester of Pongamia

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Abstract According to the proposed National Mission on biodiesel in India, we have undertaken studies on the stability of biodiesel from tree-borne non-edible oil seeds like *Pongamia pinnata*. Neat Pongamia methyl ester (PoME) exhibited an oxidation stability (OS) of 2.54 h and research was conducted to investigate the effect of the presence of transition metals likely to be present in the metallurgy of storage tanks and barrels, on the OS of PoME. It was found that the influence of metal was detrimental to OS and was catalytic, as even small concentrations of metal contaminants showed nearly the same influence on OS as large amounts. Copper showed the strongest detrimental and catalytic effect on OS. The OS of metal-contaminated PoME was found to increase with an increase in the dosage of antioxidant but the dosage required for copper-contaminated PoME became approximately four times than required for neat PoME. The dependence of the OS on the type of metal showed that long-term storage tests in different types of metal containers for examining the influence of container material on OS of biodiesel may be replaced by the significantly faster Rancimat test serving as an accelerated storage test.

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Introduction

Soybean oil and rapeseed are common feedstocks used for biodiesel production in the USA and Europe. The majority of Asian countries are net importers of edible oils, therefore these oils cannot be used for the production of biodiesel. In South Asian countries like India, biodiesel can be harvested and sourced from non-edible seed oils like *Pongamia pinnata*. *P. pinnata* commonly known as karanja, pongam, and honge belongs to the family Leguminaceae. *P. pinnata* is a fast-growing medium-size leguminous tree having the ability to grow on marginal land and this tree has been successfully introduced to humid tropical regions of the world as well as parts of Australia, New Zealand, China, and USA [1, 2]. *P. pinnata* bears flat to elliptically shaped 5–7 cm long green pods which contain 1–2 kidney shaped brownish red kernels and the yield of kernels per tree is between 8 and 24 kg, therefore, the tree has the potential for high oil seed production of about 25–40% [3]. Table 1 summarizes the biological features of *P. pinnata* that characterize the suitability of this crop for biodiesel production [1]. Researchers have investigated the performance of CI diesel engines with Pongamia biodiesel and concluded that Pongamia biodiesel can be used as an alternative fuel [4, 5]. Therefore, the sustainable production of vegetable oil for biodiesel production from a tree crop such as *P. pinnata,* which can be cultivated on marginal land, has the potential to not only provide a renewable energy resource but in addition will alleviate the competitive situation that exists due to food versus fuel issue.

Table 1 Agronomic predictions for Pongamia biodiesel production [1]

Agronomic predictions
Biological
~40% seed oil content
~50% $C_{18:1}$ contents
~20,000 seeds per year (10 year old tree)
~1.8 g per seed
~1.8 g pod wall (for biomass applications)
~25% protein/starch meal (for biomass or animal feed supplement)
~20 tons CO_2 sequestered per hectare
~5 m tall trees within 5–7 years

The quality of biodiesel is designated by several standards like EN-14214 and ASTM D-6751 and the OS is among the monitored parameters as EN-14214 calls for determining oxidative stability at 110 °C with a minimum induction period (IP) of 6 h by the Rancimat method (EN-14112) and ASTM standard D-6751 has recently introduced a minimum IP of 3 h by same method [6–8]. The oxidation process is reported in the literature and relative rates of oxidation are 1 for oleates, 41 for linoleates, and 98 for linolenates [9, 10]. The oxidation chain reaction is usually initiated at the positions allylic to double bonds. Therefore, fatty acids with methylene-interrupted double bonds, for example, linoleic acid [(9Z, 12Z)-octadecadienoic acid], are more susceptible to oxidation because they contain methylene groups that are allylic to two double bonds. Fatty acids with two such methylene groups, for example, linoleic acid [(9Z, 12Z, 15Z)-octadecatrienoic acid], are even more susceptible to oxidation.

Recently, the surrogate molecules i.e. methyl, ethyl, isopropyl, and butyl esters of β-branched fatty acid were synthesized having substantially better OS, low temperature flow properties and cetane number [11]. Although there are numerous publications on the storage, the OS of biodiesel, and the effect of antioxidants on the stability of biodiesel synthesized from edible oils, little is available on OS of biodiesel from tree-borne non-edible oil seeds [12–16]. The influence of the presence of three metals: copper, iron, and nickel on 5-g samples of methyl oleate on the oil stability index (OSI) at 90 °C is reported in the literature but with the AOCS OSI method, not with the Rancimat test method [17]. No paper is available on the influence of the presence of five metals: iron, nickel, manganese, cobalt, and copper, commonly found in the metallurgy of storage tanks and barrels; on the OS of biodiesel synthesized from non-edible oil seeds from *P. pinnata* with the Rancimat test method. From these literature reports and quality survey reports [18–20], it can be concluded that it will not be possible to use the biodiesel without antioxidants.

Therefore, according to the proposed National Mission on biodiesel in India, we have undertaken studies on the stability of biodiesel from tree-borne non-edible oil seeds of *P. pinnata*. The objective of this study was to investigate the influence of the presence of metals, doped as metal naphthenates, on the OS of PoME and then to improve the OS by doping with antioxidants. Different transition metals: iron, nickel, manganese, cobalt, and copper commonly found in the metallurgy of storage tanks and barrels, were blended with varying concentrations (ppm) in PoME samples.

Experimental Procedures

Materials

Pongamia pinnata seed kernels were collected in the Rajasthan state in India. Methanol of 99.8% purity was purchased from Ranbaxy Fine Chemicals Ltd (New Delhi, India), *n*-hexane and MeOH/KOH were of analytical grade and procured from Merck Specialties Pvt. Ltd (New Delhi, India) and Sigma-Aldrich Chemical Company (New Delhi, India), respectively. Antioxidants namely *tert*-butylated hydroxytoluene (BHT), *tert*-butylated phenol derivative (TBP), and aminic antioxidant octylated butylated diphenyl amine (OBPA) were of analytical grade and purchased from the Sigma-Aldrich Chemical Company (New Delhi, India). Various metal naphthenates were procured from M/s Notional Chemicals & Dyes Co. (Varanasi, India).

Methods

The *Pongamia pinnata* seed kernels were dried and crushed for better oil extraction and placed in a soxhlet apparatus. The soxhlet apparatus was fitted onto a round-bottomed flask containing hexane (250 mL). The hexane was refluxed at 65–70 °C and extraction was monitored by thin layer chromatography (TLC). After 16–18 h, the hexane was distilled off and brownish Pongamia seed oil was recovered for further studies.

Refining of Pongamia oil involving bleaching and deodorization was performed, and Pongamia methyl ester (PoME) was synthesized from refined Pongamia oil in the laboratory according to methodology described in the literature [3, 21–24]. Hexane extracted crude Pongamia oil had free fatty acids (FFA), 3 wt%; moisture content, 0.15%; OS, 1.36 h; unsaponifiable matter (UM), 2.3%, w/w; and peroxide value (PV), 46.3 mequiv/kg. Results of UM and PV are almost identical to previous results mentioned in literature [24]. Crude oil was refined to improve aforementioned properties. To a well-stirred mixture of orthophosphoric acid (0.5 g) and crude Pongamia oil

(1,000 g), KOH (4.36 g in 30 mL distilled water) was added at 35–40 °C over 15 min. Later, the temperature was raised to 65 °C, while stirring for the next 30 min. The reaction mixture was kept overnight to settle the flocculent particles. The refined oil (930 g) was decanted and dried in a rotary evaporator at 65 °C under reduced pressure. The oil was deodorized in a batch laboratory deodorizer at 235 °C under 2–4 mmHg pressure. The Pongamia oil was then analyzed and found to have a 0.03% moisture content and a 0.05% FFA. Other characteristics of Pongamia oil are given in Table 2 and results are almost identical to results previously mentioned in the literature [24, 25]. Pongamia seed kernels were found to contain 35% oil, which makes it suitable for commercial production of biodiesel.

For the synthesis of biodiesel from refined Pongamia oil, reactions were carried out in a batch reactor with a 500-cm^3 volume. This reactor was equipped with a reflux condenser, a thermometer and a mechanical stirrer. The reactor was immersed in a constant temperature bath and the stirring speed of the reaction mixture was fixed to 500 rpm to maintain uniform mixing, as the oil and solvent have density differences.

Biodiesel from crude *P. pinnata* was prepared by a transesterification process, involving the reaction of oil with methanol under reflux conditions. A series of experiments were designed to determine the optimal reaction conditions to get maximum conversion. Methanol (8:1 M ratio to oil) was added to the reactor followed by slow addition of catalyst (0.6 wt% of oil) with stirring. The stirring was continued until the complete dissolution of catalyst (15 min). To the above stirred solution, Pongamia oil was added and the reaction temperature was set at 65 °C for the experiment. After completion of the reaction, the material was transferred to a separating funnel and both phases were separated. The upper phase was methyl ester (biodiesel) and the 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. The methyl ester was washed with water twice to remove the traces of glycerin, unreacted catalyst, and soap formed during the transesterification. The residual product was kept under a vacuum to get rid of residual moisture. The product obtained (>98%) was sufficiently pure for testing.

Table 2 Characteristics of Pongamia oil

Characteristics	Value
Acid value (mg KOH/g)	5.06
Peroxide value (mequiv/kg)	8.3
Iodine value (g/100 g)	88.5
Viscosity (40 °C) (mm^2/s)	38.3
Saponification value (mg KOH/g)	185
Unsaponifiable matter (w/w)	0.8
Density (15 °C) (g/mL)	0.924
Tocopherols and other natural antioxidants (ppm)	<50

The PoME purity and product conversion (%) was determined by a gel permeation chromatography (GPC) technique which consists of a PL gel column (50 Å diameter of 600 × 7.5 mm dimensions) and a refractive index detector operated with a 1 mL/min flow rate of THF as the carrier solvent. The GPC technique provides separation of components on the basis of molecular weight/size and is helpful in monitoring the conversion of the oil into biodiesel. The synthesized PoME was tested for physicochemical properties as per ASTM D-6751 and EN-14214 specifications (Table 3). It is clear from the data that PoME meets all the specifications, except for the OS. Results obtained are almost similar to the results of mainstream biodiesel like Jatropha, Sunflower, and Soybean with exception of Palm [26]. The concentration of the contents of tocopherols and other natural antioxidants was practically none (<50 ppm).

The fatty acid methyl ester composition of PoME was determined by gas chromatography on a gas chromatograph (GC) (PerkinElmer, Clarus 500, New Delhi, India, located at IOC, R&D Centre, Faridabad), using nitrogen as the carrier gas and diethylene glycol succinate column (DEGS) by preparing the corresponding fatty acid esters and comparing them with standard fatty acid ester samples. The GC was equipped with a flame ionization detector (FID) and a glass column 3.1 m × 2.1 mm i.d. with a temperature program of 150–250 °C (6 °C/min, hold 20 min). The oven temperature was kept at 200 °C; the injector temperatures were 230 and 250 °C, respectively. Detailed fatty acid methyl ester composition (wt%) is given in Table 4. The overall proportions of unsaturated fatty acids present are almost identical to Jatropha, Sunflower, and Soybean with exception of Palm [26].

Metal naphthenates were selected being highly soluble in biodiesel. The metal concentration in metal naphthenates was checked by the ASTM D4951 test method, using inductively coupled plasma atomic emission spectroscopy. The concentration of cobalt, manganese, iron, copper, and nickel in their naphthenates is 5.21, 5.20, 3.91, 6.80, and 4.99%, respectively. The samples were further diluted in PoME, as per desired concentration.

The OS of methyl ester in the presence of metal contaminants and their blends with different dosages of different antioxidants were studied in Rancimat equipment model 743 (Metrohm, Switzerland). Data for all analytical measurements are means of triplicate values. Subsequent analysis showed no statistically significant difference between the measurements.

Table 3 Physico-chemical properties of Pongamia methyl ester

Property (units)	ASTM D 6751-08 test method	ASTM D 6751-08 limits	EN 14214 test method	EN 14214 limits	Mean	Standard Deviation
Flash point (°C)	D-93	Min.130	EN ISO 3679	Min. 120	141.67	1.53
Viscosity at 40 °C (cSt)	D-445	1.9–6.0	EN ISO 3104	3.5–5.0	4.23	0.015
Sulphated ash (% mass)	D-874	Max. 0.02	EN ISO 3987	Max. 0.02	0.002	0.0
Sulphur (% mass)	D-5453/ D-4294	Max. 0.0015 (S 15)	EN ISO 20846/20884	Max. 0.0010	0.0043	0.0012
		Max. 0.05 (S 500)				
Copper corrosion	D-130	Max. 3	EN ISO 2160	Max. 1	1	0.0
Cetane number	D-613	Min. 47	EN ISO 5165	Min. 51	55.27	0.15
Water and sediment (vol.%)	D-2709	Max. 0.05	–	–	0.033	0.0058
Conradson carbon residue (CCR) 100% (% mass)	D-4530	Max. 0.05	EN ISO 10370	Max. 0.3	0.037	0.0058
Neutralization value (mg KOH/g)	D-664	Max. 0.50	EN ISO 14104	Max. 0.5	0.42	0.025
Free glycerin (% mass)	D-6584	Max. 0.02	EN ISO 14105/14106	Max. 0.02	0.01	0.0
Total glycerin (% mass)	D-6584	Max. 0.24	EN ISO 14105	Max. 0.25	0.15	0.0057
Phosphorus (% mass)	D-4951	Max. 0.0010	EN 14107	Max. 0.0010	<0.001	0.0
Distillation temperature (°C)	D-1160	90% at 360 °C	–	–	90% at 360 °C	0.0
Oxidation stability at 110 °C (h)	EN 14112	Min. 3 h	EN ISO 14112	Min. 6	2.54	0.017
Ester content % (m/m)	–	–	EN 14103	Min. 96.5	99.6	0.057
Monoglycerides content % (m/m)	–	–	EN ISO 14105	Max. 0.8	0.01	0.00058
Diglycerides content % (m/m)	–	–	EN ISO 14105	Max. 0.2	0.024	0.00029
Triglycerides content % (m/m)	–	–	EN ISO 14105	Max. 0.2	Not Detectable	0.0
Sodium and potassium (mg/kg)	EN 14538	Max. 5	EN 14108/14109	Max. 5	<1	0.0
Calcium and magnesium (mg/kg)	EN 14538	Max. 5	EN 14538	Max. 5	<1	0.0

Table 4 Fatty acid composition of Pongamia methyl ester

Fatty acid methyl ester	Pongamia methyl ester (wt%)
Palmitic (C16:0)	9.8
Stearic (C18:0)	6.2
Oleic (C18:1)	72.2
Linoleic (C18:2)	11.8
Saturated	16.0
Unsaturated	84.0

Results and Discussion

The fatty acid methyl ester composition of PoME samples given in Table 4 show that PoME mainly consisted of oleic fatty acid methyl esters. The saturated and unsaturated fatty acid methyl esters in PoME were 16.0 and 84.0%, respectively.

Neat PoME showed an IP of 2.54 h so did not meet the minimum limit of 3 h IP in accordance with the recent ASTM D-6751 and minimum limit of 6 h IP as required by EN-14112. Previous literature reports mentioned an IP of 2.24 and 2.35 h for Pongamia biodiesel at 110 °C, so the present result was very much comparable with the previous work done [25, 26]. Previous literature reports also mentioned that oils with high oleic acids like olive, almond, corn, and peanut can have a lower OS [27]. Low OS of PoME can be attributed to the practical absence of tocopherols and other natural antioxidants. In the present study, two phenolic antioxidants namely BHT, TBP, and aminic antioxidant OBPA were used. All three antioxidants were doped to the PoME samples with varying concentrations of 50, 100, 150, 200, 250 and 300 ppm, and the corresponding IPs were measured with the Rancimat test method to observe the effectiveness of different antioxidants.

Figure 1 shows the IP of neat PoME and the effect of antioxidants on the IP of biodiesel. The OS of PoME has been found to increase with increases in the dosage of antioxidants. Finally it was found that antioxidant BHT is most effective among all the antioxidants used and results matched the behavior and effectiveness of these antioxidants studied earlier [26]. It is found that the minimum dosing of 250 ppm and 50 ppm, respectively, of BHT was needed to improve the IP of neat PoME from 2.54 to above 6 h as required by the EN-14112 specification and 3 h as required by ASTM D-6751 for biodiesel OS.

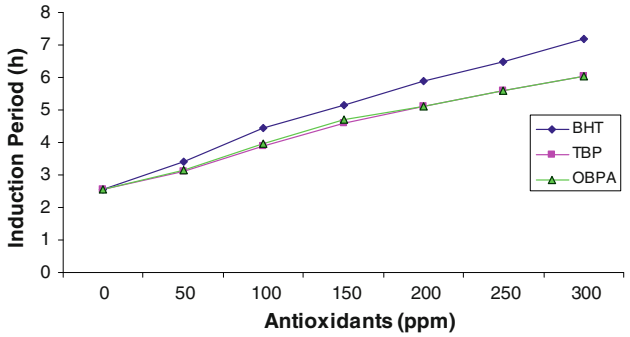

Fig. 1 Effect of antioxidant concentration on the oxidation stability of Pongamia methyl ester

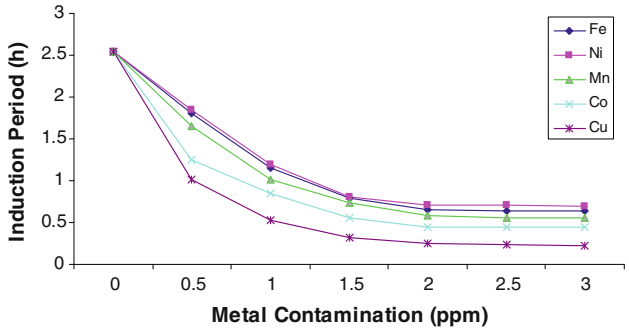

Fig. 2 Effect of metal contamination on oxidation stability

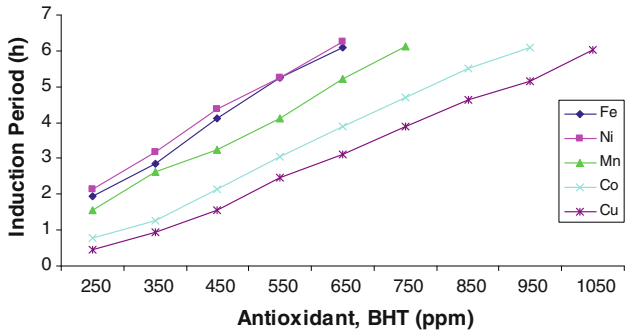

Fig. 3 Effect of antioxidant concentration on the oxidation stability of metal-contaminated (2 ppm) Pongamia methyl ester

Effect of Metal Contaminants on OS

Different transition metals: iron, nickel, manganese, cobalt, and copper commonly found in metal containers were blended, as metal naphthenates, with varying concentrations (ppm) with PoME samples. Figure 2 showed that the presence of these metals depressed the OS of biodiesel, as measured by the IP. The presence of metals in biodiesel resulted in acceleration of free radical oxidation due to a metal-mediated initiation reaction.

Copper had the strongest catalytic effect and other metals, namely iron, nickel, manganese, and cobalt also had a strong negative influence on OS (Fig. 2). The strongest catalytic effect of copper is due to its relative higher pro-oxidant effect. The strong catalytic effect of copper has also been reported in literature [17, 28]. For all the metal contaminants, IP values became almost constant as the concentration of metal is increased. This showed that the influence of metals was catalytic, as even small concentrations of the metals had nearly the same effect on OS as large amounts. The dependence of the OS on the type of metal confirms that Rancimat is a suitable lab test for correlating long-term stability.

Improvement of OS of Metal-Contaminated PoME

It had already been observed that the phenolic 2,6-ditertiarybutyl hydroxytoluene antioxidant BHT is the most effective among all the antioxidants used and a minimum dosage of 250 ppm of BHT was needed to improve the IP of neat PoME from 2.54 to above 6 h as required by the EN-14112 specification for biodiesel OS (Fig. 1). Therefore, it was decided to study the effect of the dosage of the antioxidant BHT on OS of metal-contaminated PoME. BHT was doped to the metal-contaminated PoME samples with varying concentrations (ppm), and the corresponding IPs were measured with the Rancimat test method.

As metallic impurities have a catalytic effect, a 2-ppm metal concentration was selected for antioxidant dose optimization. Figure 3 shows the variation of IP of 2 ppm metal-contaminated PoME with varying concentrations of BHT.

The OS of metal-contaminated PoME has been found to increase with an increase in the dosage of antioxidant BHT. Finally was is found that a minimum dosage of BHT (650 ppm) was needed to improve the IP of iron- and nickel-contaminated PoME and minimum dosage of 750 ppm of BHT in manganese-contaminated PoME was needed to meet the EN-14112 specification for biodiesel OS (Fig. 3). Figure 3 also shows that for cobalt and copper-contaminated PoME, a minimum dosage of 950 and 1,050 ppm, respectively, was required to meet the EN-14112 specifications.

Conclusion

PoME used in this work was found to exhibit an OS of 2.54 h in the Rancimat test. In order to meet the EN-14112 specification, a minimum dosage of 250 ppm concentration of antioxidant BHT is required for PoME. The IP of PoME decreased drastically even with small concentrations (ppm) of metal contaminants and influence of metals on IP is found to be catalytic as even small concentrations of metals had the nearly the same effect on OS as large amounts. Of

the five metals investigated, copper appears to have the strongest detrimental and catalytic effect. The dependence of the OS on the type of metal showed that long-term storage tests in different types of metal containers for examining the influence of container material on OS of biodiesel may be replaced by the significantly faster Rancimat test serving as an accelerated storage test.

The OS of metal-contaminated PoME was found to increase with increases in dosage of antioxidant BHT. It was found that a minimum dosage of 650 ppm BHT is needed to improve the IP of iron- and nickel-contaminated PoME and a minimum dosage of 750 ppm BHT in manganese-contaminated PoME is needed to meet EN-14112 specification for biodiesel OS. For cobalt and copper-contaminated PoME, minimum dosing of 950 and 1,050 ppm, respectively, is required to meet EN-14112 specifications.

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