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Comparative Studies of Fatty Acid Methyl, Ethyl and *i*-Propyl Esters of *Tamarindus indica* Seed Oil as Biodiesel Base-Stock

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The unsaturated fatty acids found in tamarind seed oil include oleic acid (16.0%), linoleic acid (56.0%), palmitic acid (8.0%) and stearic acid (4.0%). The free fatty acids (0.6%) present in the tamarind seed oil was converted to methyl, ethyl and isopropyl esters. Further, the base stocks were prepared by employing transesterification reaction catalyzed by a base. Biodiesel fuels thus prepared were evaluated for different parameters and methyl esters were found to show ester content (97.3%), density (0.86315 g/cm^3), acid value (0.42), oxidation stability (1.49 h), flash point (137.2 °C) and kinematic viscosity (5.09 cSt), ethyl esters have shown a kinematic viscosity (5.54 cSt), density (0.87030 g/cm^3), acid value (0.45), oxidation stability (2.16 h), flash point (141.2 ºC), ester content (97.7%) and isopropyl esters exhibited kinematic viscosity (20.05 cSt), density (0.9220 g/cm^3), acid value (0.58), oxidation stability (0.05 h) and flash point (145.3 ºC). The study involved investigation of effectiveness of four different antioxidants namely, butylated hydroxyl toluene (BHT), butylated hydroxyl anisole (BHA), *t*-butyl hydroxyl quinone (TBHQ) and diphenylamine (DPA) in different concentrations to the prepared methyl and ethyl biodiesels. BHA and BHT were observed to exhibit enhanced oxidation stability of produced biodiesel. The physical and chemical properties of methyl and ethyl esters were found to lie within EN and ASTM specifications.

Keywords: *Tamarindus indica* oil, Biodiesel, Antioxidant, Oxidative stability.

INTRODUCTION

One of the most important day-to-day requirement is energy, most critical aspects of daily life. The primary energy sources used by humans are non-renewable ones like coal, oil and natural gas. On the other hand, burning fossil fuel create lots of pollution. Finding sustainable alternative energy sources is the only practical solution to the current energy issue. Unseen alternate routes such as biodiesel has increased as a result of the search for ecofriendly fuels. Biodiesel is a type of fuel made by transesterifying animal or plant-derived oils to generate ethyl, methyl or propyl esters [1-7].

Utilizing waste products like tallow, pig fat, non-edible seed oils and waste cooking oil for energy production is sustainable and more environmentally sustainable. Consumption of organic waste is a method of managing solid wastes that also generates energy [8,9]. There are several advantages of using biodiesel, including its renewability, environment friendliness, greater combustion efficiency, high cetane number, biodegradability, higher flash point and good lubricity [10].

Vegetable oils are commonly transformed into biodiesel through the process of transesterification. *Tamarindus indica* is a dicotyledon belonging to Fabaceae (Leguminosae) family of plants. Tamarind tree grows abundantly in India and considering that tamarind trees can grow in poor soil and withstand prolonged drought, they are perfect raw material for low input farming. The seed oil resembles that of groundnut oil which is thrown as waste. Tamarind seed oil was found to contain carbohydrates (50-55%), tannins (20%), fiber (12-20%) and oil (4.5-16.2%) [11]. However, the seeds were found to be unsuitable for human consumption due to the presence of tannins and others toxic chemicals. The, the seed was found to be in use for making paper and as a sizing material in textile industries [12-14]. Tamarind seed oil is currently used for making soap,

lamp oil and varnishes [15]. As the fatty acid composition is rich in unsaturation, it can be used for the production of biodiesel. Major part of the studies was found to focus on the biofuels produced using jatropha, karanja, palm, waste cooking oil and some minor seed oils [16]. A few reports were observed taking tamarind seed oil for biodiesel conversion and no updated scenario except for emission characteristics of tamarind seed oil biodiesel and its blends [17-19] was observed. The current study reports the preparation of tamarind seed oil biodiesel using three different alcohols namely ethanol, methanol and isopropyl by base catalyzed transesterification and their physico-chemical characterization. As most of the biodiesels with unsaturated fatty acids exhibit poor-antioxidant behaviour, the biodiesel prepared in the present study was studied for their oxidation stabilities in the presence of commercial antioxidants. The efficacy of four different commercial antioxidants on methyl and ethyl esters of tamarind seed oil was also investigated at different concentrations.

EXPERIMENTAL

Tamarind seeds were procured from the Sanjeevani Herbal Health Care, Hyderabad, India while all the chemical (reagents and solvents) were procured from M/s. SD fine chemicals Co. Ltd. (Mumbai, India).

Extraction of tamarind seed oil: Dried tamarind seeds were powdered (750 g) and the oil was extracted using the Soxhlet extraction method with solvent hexane at around 80 ºC for 9 h and then the solvent was concentrated by rotary evaporator followed by drying under vaccum.

Characterization of extracted oil and biodiesel: AOCS Methods were employed to characterize *Tamarindus indica* seed oil (crude and refined) AOCS-Cd 3-25, iodine value; Cd 5a-40, acid value; Cd 8-53, peroxide value, Cd 2c-25, moisture and volatiles; Cd 6a-40, unsaponifiable matter; Cc 7-25, RI at 40 °C; Cc 13e-92, *p*-anisidine and Cc 13e-92, colour. Determination of phosphorous content was carried out by employing IUPAC method. Density (ASTM-D4052), kinematic viscosity (K.V., cSt) (ASTM-D445) of the biodiesels was determined as per ASTM protocols.

The biodiesels were also characterized for flash point, pour point following the ASTM methods. Methyl ester content and oxidation stability were determined by using EN methods. An analysis was carried out using three different values, and the average of the three values was determined.

Kinematic viscosity: Kinematic viscosity was determined employing cannon Fenske viscometer tube (calibrated) into a viscosity bath (Cannon Instrument Co., U.S.A) at 40 ºC as per ASTM D445-10 method. The result is reported as an average of duplicate independent measurement. The kinematic viscosity was calculated as:

$$\text{Kinematic viscosity} = \text{Viscometer constant} \times \text{time (s)} \quad (1)$$

Density: Density of the biodiesel at a certain temperature was measured by automatic density meter (Anton Parr, DMA 4500) at 15 ºC according to ASTM D4052 method. The instrument consists of sample tube, which is thoroughly cleaned by using *n*-hexane and air dried. Then the desired temperature 15 ºC is set and the sample (5 mL) is injected without any air gap. The specific gravity is also determined by using the same instrument.

Acid value: Number of mg of KOH required to neutralize 1 g of the sample. The acid value was determined by American Oil Chemist Society (AOCS) official method Ca 5a-40. The sample (2-5 g) was taken in a Erlenmeyer flask (250 mL) and 30 mL neutralized methanol was mixed under warm condition followed by the addition of few drops of phenolphthalein indicator (1% in ethyl alcohol). Resultant mixture was titrated against 0.1 N KOH solution till the light pink coloured appeared. Based on oleic acid molecular weight, acid value can be divided with two to obtain the free fatty acid (% FFA) value. Acid value is calculated using eqn. 2:

$$\text{Acid value} = \frac{\text{Titare value (mL)} \times N \times 56.1}{\text{Weight of the sample}} \quad (2)$$

where, $N = N_{KOH}$.

Oxidation stability: The parameter was determined employing European the rancidity in lipid. This process is called autoxidation, which result in a variety of decomposition products such as peroxides, alcohol, aldehydes ketones and carboxylic acids (short chain) such as formic acid and acetic acids [20]. The sample was exposed to hot air at a given or selected temperature. The volatile oxidation product (mainly formic acid) was transferred to the distilled water containing measuring vessel by the air stream and absorbed in the distilled water. The measurement of conductivity in distilled water, conducted in a continuous way, allows for the construction of an oxidation curve, with the point of interest being commonly referred to as the induction time. It provides a good indication time for measuring the oxidation stability. This test enables continuous monitoring of the process of oxidation.

The test was performed on a Rancimat apparatus (Metrohm Co.; Herisou, Switzerland). Oxidation stability index measurement was carried out at 110 ºC. A constant hot dry air (20 L/h) was blown through the sample (5 g) while heating to 110 ºC. The oxidative stability index (OSI) was obtained by induction period (IP), which were calculated automatically according to the method reported in the literature. The oxidation of volatile products produced during the reaction causes an increase in the electrical conductivity of water. The period (h) taken for a specific conductivity value, the inflection point of the curve is taken as the induction time.

Flash point: Flash point varies inversely with the fuel volatility. The value reflects the engine performance. This is important with the legal requirement and safety precaution involved in a fuel handling and storage. The value is determined using Pensky Martin Closed Cup. The flash point of the sample was determined according to the ASTM method using the instrument procured from Tanaka Scientific Ltd. Japan.

Pour point: The pour point of the sample was also determined according to the ASTM method. The pour point measurement was carried out (at ± 3 ºC) using Dott Scavini Apparatus & Co., Italy. The temperature of the sample was increased by 3 ºC at the top of sample, until it stopped pouring.

Ester content: Ester content of tamarind seed biodiesel samples was measured with a gas-liquid chromatograph equipped with flame ionization detector (FID), according to method EN 14103. HP-Innowax, 30 m × 0.3 mm × film thickness 0.25 µm column was used for the separation. The system was run using the split mode with a split ratio of 80:1. The carrier gas (N_2) flows was adjusted at 1.0 mL/min. The initial oven temperature was maintained at 210 ºC for 2 min, which was increased to 230 ºC at 20 ºC/min and finally kept at the final temperature for 10 min. The temperature of the system (inlet and detector) was kept at 250 ºC and 280 ºC, respectively. The estimation of ester content in biodiesel was conducted using the internal standard methyl heptadecanoate as outlined in the methodology specified in EN14103.

Partial and total glycerides: Determination of total mono, di and triglycerides and free and total glycerin in biodiesel methyl ester was determined by using gas chromatograph (GC) according to the ASTM 6584 method, silyating using N-methyl-N-trimethylsilytrifluoracetamide (MSTFA). Use of internal standard (1,2,4-butanetriol and tricaprin) and four reference materials. Monoolein, diolein and triolein standards were employed for determining mono-, di-, triglycerides taking respectively. Mono-, di-, triglycerides were calculated taking average conversion factor, the bond glycerine content of the sample.

Micro carbon residue: Micro carbon residue of biodiesel was calculated by following ASTM D4530 method. The test is intended to provide same indication of the carbon residue that result from the combustion of fuel. It is analyzed with automatically programmable micro carbon residue tester ACR-M3. The percentage of carbon residue calculated by the following formula:

$$\text{Micro-carbon residue (\%)} = \frac{C - A}{B - A} \times 100$$

where A = weight of the clean vial, B = vial with sample weight, C = vial with residue.

Composition of the extracted tamarind seed oil (fatty acid methyl ester): The oil was converted into fatty acid methyl esters (FAME) by acid-catalyzed methylation using 2% H_2SO_4 in methanol. The fatty acid composition of methyl ester was analyzed by GC-FID, Agilent 6890N GC. The column used was capillary fused silica, 30 m × 0.25 mm × 0.2 µm, DB-225 Agilent Technologies, USA). The programme at which run was carried out at 160 ºC for 2 min and then increased to 230 ºC at 5 ºC/min and finally holds for 20 min at 230 ºC. The inlet and detector temperatures were kept at 230 and 250 ºC, respectively. The nitrogen carrier gas was used at 1 mL/min. Fatty acids were confirmed by comparing with the retention times of Supelco reference standard (CRM47885). The fatty acid composition is reported in Table-1.

Biodiesel preparation: The transesterification process involved the addition of NaOH solution (5 g in 44.7 g methanol) in methanol to 500 g of purified oil, followed by mechanical stirring. All the contents with unconverted triglyceride and the ester produced were treated with NaOH in methanol (2.5 g NaOH in 59 g of methanol) again. Once the glycerol got separated after 1 h to ensure that the oil had completely converted to biodiesel. Then, to obtain the biodiesel, the crude biodiesel was vacuum-dried after being rinsed with water to eliminate any remaining traces of glycerol, soap or alkali. Ethyl ester and isopropyl esters were prepared by employing the above conditions.

TABLE-1
FATTY ACID COMPOSITION (wt.%) OF SEED OIL

Fatty acid	Weight (%)	Fatty acid	Weight (%)
C16:0	8.0	C20:1	1.2
C16:1	0.4	C20:2	0.6
C18:0	4.0	C22:0	4.5
C18:1	16.0	C22:1	0.1
C18:2	56.0	C24:0	6.9
C20:0	2.3		

Tamarind seed oil and biodiesel physico-chemical characterization: The flash point, pour point, kinematic viscosity, ester content and oxidation stability and the rest of the physico-chemical properties, mono-, di-, triglycerides, total glycerides, free glycerol, bound glycerol and total glycerol were also determined using standard ASTM and EN methods.

Refining of tamarind seed oil: Tamarind oil was refined using standard protocols such as degumming with water, alkali, phosphoric acid and the enzymatic degumming under varied circumstances during the degumming process. The degummed oils were utilized for further refining processes like bleaching after being dried at 90 ºC under high vacuum. The phosphorous content and bleached oil content was determined using the IUPAC method. The phosphorous content could not be reduced to less than 50 ppm, therefore an attempts were made to refine oil by employing enzymatic degumming and bleached process followed by alkali treatment to obtain refined tamarind seeds oil.

RESULTS AND DISCUSSION

The physico-chemical characteristics of seed kernel oil derived from *T. indicus* seeds were evaluated by following the established procedures and results are shown in Table-2. Following the extraction process, the crude oil underwent a refining procedure that comprised degumming and bleaching. The phosphorus content results of water degumming, acid and alkali degumming indicated the presence of phospholipids. The presence of phospholipids can damage the emission control system by hampering the catalytic convertor [21]. Therefore, further attempts were made to refine the oil employing enzymatic degumming and bleaching followed by alkali treatment, to obtain refined tamarind seed oil with low phosphorus content (12.7%) (Table-3). The physico-chemical properties of tamarind biodiesel is shown in Table-4. The results indicated that refining reduced the phosphorus, free fatty acid and peroxide value. The iodine value of the tamarind seed oil correlated well with unsaturation. All these properties are important for the good quality biodiesel prepared from vegetable oils.

The refined oil was converted into biodiesel using three different alcohols namely, methanol, ethanol and isopropyl alcohol by base catalyzed transesterification with more than 95% conversion, the physico-chemical parameters were compared to ASTM and EN specifications to access their biodiesel

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS OF REFINED TAMARIND SEED OIL

Characteristics	Crude oil	Refined tamarind oil
Phosphorous content (ppm)	703.0	12.7
Gum content (%)	2.11	0.04
Free fatty acid (wt.%)	1.8	0.6
Iodine value (g/100 g)	114.6	113.8
Saponification value (mg KOH/g)	188.2	188.1
Peroxide value (ppm)	14.0	1.8

TABLE-3
COMPARISON OF P CONTENT AND GUM CONTENT OBTAIN USING DIFFERENT DEGUMMING TECHNIQUE

Sample	Phosphorous content (ppm)	Gum content (%)
Crude tamarind seed oil	703.0	2.11
Water degummed oil	700.0	2.10
Acid degummed oil	336.1	1.0
Alkali refined oil	267.8	0.8
Enzymatic degummed oil	263.7	0.8
Enzymatic degummed, bleached oil	155.6	0.47
Enzymatic degummed, bleached and alkali refined oil (refined oil)	12.7	0.04

suitability. The fatty acid composition of the oil was determined by gas chromatography and the results indicated that linoleic acid was major followed by oleic acid and palmitic acid (Table-3). The methyl, ethyl and isopropyl ester's ester content was found to be 97.3, 97.7 and 96.9%, respectively. As per the European specification, ester content should be ≥ 96.5 for B100 biodiesel. Table-4 indicates that methyl, ethyl and *i*-propyl esters were within the range *i.e.*, ≥ 96.5. Tamarind seed oil rich in unsaturation, oleic and linoleic acids were in higher amounts. This related very well with the high iodine value of the tamarind seed oil.

The kinematic viscosity, which is an important property of fuels indicates the ability of a material to flow. The kinematic viscosity of biodiesel as per ASTM standard at 40 ºC should be between 1.9 to 6.0 cSt and 3.5 to 5.0 as per European specifications. The results show that both esters of methyl and ethyl matched with ASTM values, slightly higher as per European specifications. However, the viscosity value was higher for isopropyl esters (8.5 cSt) compared to methyl and ethyl esters which are 5.09 and 5.54 cSt, respectively. An increase in the viscosity correlated well with the density values of the three biodiesel samples. Isopropyl esters due to their high viscosity exhibited higher density value. Density values for methyl and ethyl esters were found to be well within the range as recommended by European specifications. The mono-, di-, tri- and total-glyceride contents of both the biodiesel samples tested were within the range of ASTM specifications. These values indicate that biodiesel samples of methyl and ethyl esters have negligible content of unconverted mono, di and tri glycerides in them. The glycerol in free form, bound glycerol, glycerol total of the methyl and ethyl esters were negligible and within ASTM specifications.

Flash point in case of three ester samples were above ASTM and EN specifications. The flash point of the products increases with their viscosity. Hence, ethyl esters exhibited higher flash point (141.2 ºC), compared to the methyl esters (137.2 ºC) and isopropyl esters exhibited elevated values (145.3 ºC) due to their higher viscosity. The biodiesel oxidatation stability index (OSI) depends on their composition. Due to high iodine value of tamarind oil (113.8 g/100 g), the oxidative stability index (OSI) was found to be 1.49 h for methyl; 2.16 h for ethyl and 0.5 h for isopropyl esters.

All the three ester samples were below ASTM specifications. To improve their oxidation stability, four different antioxidants in different concentrations were prepared methyl and ethyl biodiesel fuels namely, butylated hydroxyl toluene (BHT); butylated hydroxyl anisole (BHA); *t*-butyl hydroxyl quinone (TBHQ) and diphenylamine (DPA) were added at the percentage of 0.25%, 0.5% and 1.0% and their oxidation stabilities were evaluated.

Table-5 shows antioxidants effect on the oxidation stability of methyl esters of tamarind seed biodiesel. Antioxidants BHT and BHA were found to be better compared to DPA and TBHQ. With BHT and BHA methyl esters stability improved with the increase in their concentration (Fig. 1). At all the three levels, both BHT and BHA improved the stability of methyl esters beyond ASTM standard specifications. With the addition of DPA and TBHQ at all levels the oxidation stability improvement was little and could not improve further to meet ASTM specification. The efficacy of the antioxidants on methyl esters

TABLE-4
PHYSICO-CHEMICAL CHARACTERIZATION OF THE BIODIESEL WITH THREE DIFFERENT ALCOHOLS

Properties	Methanol	Ethanol	2-Propanol	EN specification	ASTM specification
Kinematic viscosity @40 °C (cSt)	5.09	5.54	7.5	3.5-5.0	1.9-6.0
Ester content (mass%)	97.3	97.7	96.9	96.5	–
Density at 15 °C (g/cm^3)	863.15	870.30	922.0	860-900	–
Acid value (mg/KOH/g)	0.42	0.45	0.58	0.5	0.5
Oxidation stability (h)	1.49	2.16	0.05	6.0 min	3.0 min
Flash point (°C)	137.2	141.2	145.3	≥ 101	≥ 130
Monoglycerides (mass %)	0.10568	0.10125	–	–	< 0.77860
Diglycerides (mass %)	0.02839	0.02276	–	–	< 0.54475
Triglycerides (mass %)	Nil	0.04703	–	–	< 1.3881
Total glycerides (mass %)	0.13408	0.17105	–	–	–
Free glycerol (mass %)	0.00393	Nil	–	–	< 0.019533
Bound glycerol (mass %)	0.03161	0.0345338	–	–	–
Total glycerol (mass %)	0.03554	0.0345338	–	–	< 0.42767

TABLE-5
OXIDATION STABILITY OF METHYL ESTERS WITH DIFFERENT ANTIOXIDANTS

Sample name	Oxidation stability (h)		
	0.25%	0.50%	1.00%
Methyl ester	1.49	1.49	1.49
Biodiesel + BHT	16.28	20.36	30.58
Biodiesel + BHA	13.56	14.92	19.09
Biodiesel + DPA	2.19	3.0	3.96
Biodiesel + TBHQ	1.68	1.96	2.12

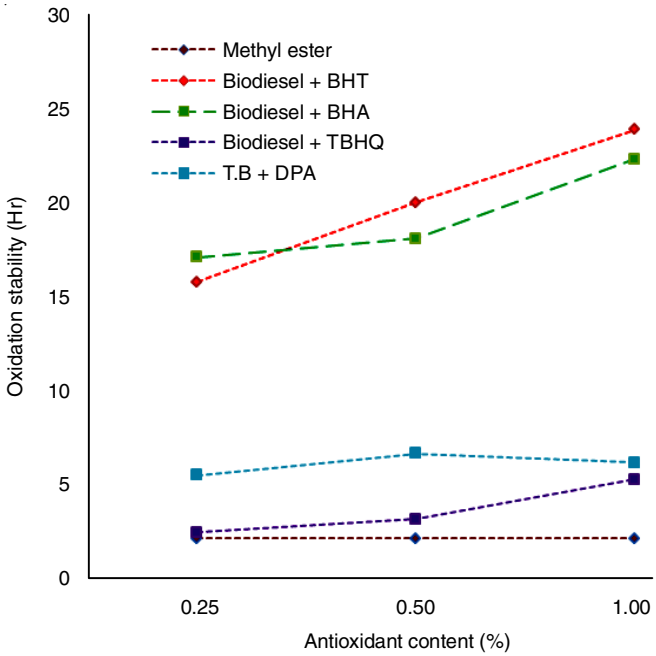

Fig. 1. Oxidative stability of methyl esters improved by adding antioxidants in different concentrations

stability was in the order of BHT > BHA > DPA > TBHQ. For ethyl esters (Fig. 2), similar pattern was observed. And in the case of methyl esters, BHT and BHA improved the oxidation stability with increase in their concentration, the oxidation stability at all three levels were above the ASTM standard. With DPA the increase in oxidation stability was negligible at 0.25 and 0.5% (Table-6). Maximum improvement was observed at 1% concentration with a value of 5.3 h. At 0.5% and 1% the oxidation stability value meets the ASTM standard (Table-6). Significant improvements in oxidation stability values were reported at all levels when TBHQ was utilized, exceeding the established ASTM standard value. The efficacy of the oxidation stability on the ethyl esters was in the order, BHT > BHA > TBHQ > DPA. The oxidation stability of ethyl esters upon the addition of commercial antioxidant is shown in Fig. 2.

Conclusion

In this work, the fuel competencies of methyl, ethyl and isopropyl esters derived from *Tamarindus indica* were found to be comparable as per ASTM and EN standards. All the physical and chemical properties of the esters of methyl and ethyl; ester content, viscosity, phosphorus content, acid value, flash point, mono-, di- and triglycerides and glycerol contents were well-matched with ASTM and EN standards. However,

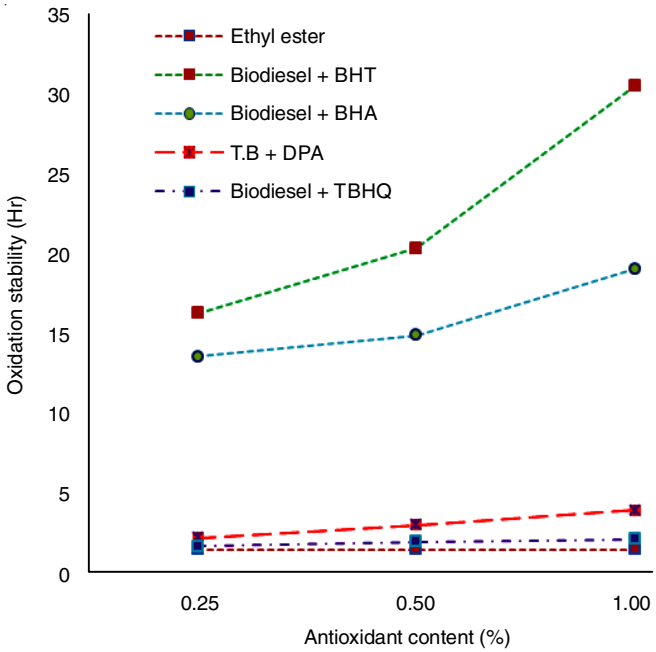

Fig. 2. Oxidative stability of ethyl esters improved by adding antioxidants in different concentrations

TABLE-6
OXIDATION STABILITY OF ETHYL ESTERS WITH DIFFERENT ANTIOXIDANTS

Sample name	Oxidation stability (h)		
	0.25%	0.50%	1.00%
Ethyl ester	2.16	2.16	2.16
Biodiesel + BHT	15.83	20.06	23.92
Biodiesel + BHA	17.12	18.13	22.34
Biodiesel + DPA	2.49	3.2	5.3
Biodiesel + TBHQ	5.53	6.69	6.22

their oxidation stabilities were found to be inferior due to the high amounts of unsaturation in the oil. Hence, four different antioxidants were used to improve their oxidation stability. The antioxidants BHT and BHA were found to be very efficient in improving oxidation stability of methyl and ethyl esters. Hence, *T. indicus* can be a renewable and sustainable raw material for biodiesel fuel preparation with the addition of antioxidant additives.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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