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Effect of antioxidants on physico-chemical properties of EURO-III HSD (high speed diesel) and *Jatropha* biodiesel blends

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ABSTRACT

The stability of fuel during storage is an important consideration for bulk users. Storage instability leads to solids formation which can plug nozzles and filters. This work focuses on the effect of the addition of antioxidants on **EURO-III and *Jatropha* Biodiesel blends**. The changes in physico-chemical properties were observed for **these blends** after addition of antioxidants. BHA (butylated hydroxy anisole), BHT (butylatedhydroxy toluene), TBHQ (tert-butylhydroxyquinone) and DPA (diphenylamine) were the antioxidants used for this study. The rate of change in kinematic viscosity and density of **EURO-III-*Jatropha* Biodiesel blends** with antioxidants were found to be less as compared to the neat samples. The oxidation stability of the neat samples, after addition of antioxidants, was found to increase significantly. It was also observed that addition of antioxidant significantly improved the oxidation stability of biodiesel-diesel fuel blends however in some case may act as pro-oxidants. The results showed that the addition of an antioxidant to diesel fuel blends influenced beneficially most of the important fuel properties.

1. Introduction

Biodiesel an alternate environment friendly liquid biofuel has reached an important position in the global fuel market. Increased environmental concern brought the quality of biodiesel and its blends into focus. Also it is well accepted that clean combustion in diesel engines can be accomplished only by engine modification coupled with diesel fuel reformulation or additive introduction [1,2].

Biodiesel, is a mixture of methyl esters with long chain fatty acids derived from vegetable oil and animal fats, and is similar to the commercial diesel oil in terms of fuel quality and combustion properties [3,4]. When compared to petroleum diesel, it possesses a number of advantages such as biodegradability and non-toxicity [5]. Biodiesel also has a favourable combustion–emission profile, producing much less carbon monoxide, sulphur oxides, nitrogen hydride, particulate matter, and unburned hydrocarbons compared to the petroleum-base diesel [6]. Therefore, to reduce air pollution and minimize the emission of greenhouse gas, it is beneficial to use biodiesel as an alternative fuel to substitute the petroleum-based diesel [7].

However, a major drawback with biodiesel is that it is more susceptible to oxidation degradation. The oxidation stability depends on the fatty acid composition of the oil. The oil that contains more unsaturation is more prone to oxidation [8]. For example, it has been reported that the relative rate of oxidation of methyl ester of oleic acid (18:1) linoleic acid (18:2) & linolenic acid (18:3) is in the ratio of 1:12:25 [9], that results in the formation of by product that increases viscosity [10]. During the process of trans-esterification of vegetable oils, the basic fatty acid chain remain same [11]. It has also been reported that the rate of oxidation is directly proportional to the number of bisallylic carbons present [12]. Oxidation is a complex process and due to which the methyl ester gets converted into a variety of species including shorter chain fatty acid and aldehyde and also to high molecular weight species through oxidative polymerization. The first step is the formation of free radical adjacent to a double bond. Free radical being highly reactive reacts with atmospheric oxygen leading to formation of peroxy radical. This peroxy free radical gets stabilized by abstracting 'H' from new fatty acid methyl ester and thereby creating new free radical. The process continues resulting in the formation of aldehyde alcohol and carbonic acid [13]. These reactions are less pronounced in the parent oil due to the presence of natural antioxidants which get partially lost during refining thereby reducing

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the oxidation stability [14]. The use of antioxidant can improve the fuel stability to a certain extent. Several studies have reported the effect of various synthetic antioxidants on oxidation stability of biodiesel [15–22]. However, limited work has been carried out on the stability behaviour of biodiesel blends with EURO-III HSD (high speed diesel) as well as on impact of antioxidants on storage stability of biodiesel/diesel blends [16,18,23–29].

The aim of the present work is to investigate the potential of different concentrations of various antioxidants on JME EURO-III HSD blends concerning the improvement of the oxidation stability of low sulphur diesel/biodiesel blends. The goal was to identify suitable antioxidant that could significantly improve the stability of biodiesel and its blend with EURO-III HSD diesel.

2. Experimental section

2.1. Blending components

EURO-III HSD/Bharat Stage III, JME (*Jatropha curcus* methyl ester) and antioxidants.

2.2. EURO-III HSD/Bharat Stage III

EURO-III HSD (a 50 L lot) corresponding to Bharat Stage III, was obtained from the retail outlet and its key physicochemical characteristics were done. The results are presented in Table 1.

2.3. Jatropha curcus methyl ester (JME)

Bulk preparation of JME under optimized process conditions and its detailed characterization: both physicochemical and chemical have been carried out [30]. The complete details of JME are given below. Table 2 shows the physicochemical characterization results. The prepared biodiesel was used to constitute the biodiesel-diesel-blends containing 5%, 10%, 20% and 40% biodiesel (i.e.JB-5, JB-10, JB-20 and JB-40) volume/volume with base diesel fuel to study their physico-chemical behaviour during long term storage.

2.4. Jatropha curcus methyl ester (JME) profile & GC

The composition of prepared JME was analysed using a GC (gas chromatograph) supplied by Nucon 5700 series with EOX column (serial no 5061; 30 m length, 0.25 mm ID and 0.25 mm outer dia). Helium (99.9% purity) was used as the carrier gas with a column flow rate of 1 ml/min and a pre-column pressure of 49.7 kPa. The column temperature regime was 40 °C for 3 min, followed by a 5 °C/min ramp up to 230 °C, followed by 40 min at 230 °C. The injection volume and temperature were 0.2 μl and 240 °C and the split ratio was 1/30. FAME (Fatty acid methyl ester) peaks were identified by comparison of their retention times with authentic standards by GC and quantified by area normalization.

The GC of JME is shown in Fig. 1.

Analysis revealed that JME biodiesel contains mainly Palmitic (16:0), Palmitoleic (16:1), Steric (18:0), Oleic (18:1), Linoleic (18:2) and Linolenic (18:3) methyl esters. The detailed composition is given in Table 3. The numbers in parentheses show carbon number and number of double bond present e.g. oleic acid 18 carbon atom and one double bond. The results obtained in the study are in agreement with those reported by other workers [31,32].

2.5. AO (antioxidants) used

The antioxidants used in the present study are BHA (butylated hydroxy anisole), BHT (butylatedhydroxy toluene), TBHQ (tert-butylhydroxyquinone) and DPA (diphenylamine). These analytical grade antioxidants were procured from Sigma Aldrich, India. Fig. 2 shows structure of various antioxidants used in the present study.

2.6. Storage conditions

Biodiesel and its diesel blend samples of volume 500 mL were stored in closed Borosil glass bottles of 1 Lit capacity for 80 days and

Table 1
Physicochemical characterization of EURO-III high speed diesel.

S.NO	Characteristics	Unit	Expected value for HSD	EURO-III requirement	Test methods
1.	Specific gravity @ 15 °C	–	0.8243	0.820–0.8450	ASTM-D 4052
2.	API @ 15 °C		40.16	36–41	Using correlation
3.	Cetane index (CI)		51	46	ASTM D 4737
4.	Aniline point	°C, °F	53, 127	–	ASTM D611-07
5.	Kinematic viscosity @ 40 °C	cSt	2.74	2.0–4.5	ASTM-D 445
6.	Flash point	°C	62	66	ASTM D 93
7.	Pour point	°C	9	15 max	ASTM D 97

Table 2
Physico-chemical characterization of JME.

S.No	Property (unit)	Biodiesel (B-100)	Std. limits	Test methods
1	Flash point (°C)	161.5	Min 100	ASTM D 93
2	Moisture content	0.041%	Max. 0.05%	ASTM-D 2709
3	Cloud point (°C)	+12	–	ASTM D 2500
4	Pour point (°C)	+3	–	ASTM D 97
5	Calorific value (KJ/kg)	39071	–	–
6	Specific gravity	0.8811	0.820–0.845	ASTM-D 4052
7	Viscosity (cSt)	4.7138	1.9–6.0	ASTM-D 445
8	Acid value		0.5 max	ASTM-D 664
9	Oxidation stability (at 140 °C, h)	4.21	6 h min	ASTM-D 7545

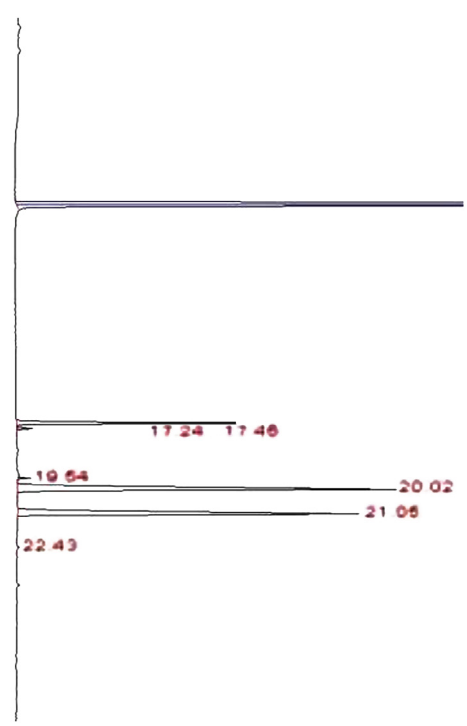

Fig. 1. Fatty acid profile of *Jatropha methyl ester.*