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Effect of metal contents on oxidation stability of biodiesel/diesel blends

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HIGHLIGHTS

- Stability of metal contaminated biodiesel blend has been checked.
- Effectiveness of different antioxidants has also been checked.
- Biodiesel blends with diesel have shown the better oxidation stability.
- Effect of metals on the oxidation stability of biodiesel has found catalytic.

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ABSTRACT

Present paper deals with the evaluation of oxidation stability of metal contaminated biodiesel/diesel blend. Effectiveness of different antioxidants with respect to different biodiesel/diesel blends has also been checked. It is found that pyrogallol (PY) is the most effective antioxidant. As the % of diesel is increased in the blend, the oxidation stability of biodiesel/ diesel blend also increased. From the experiments it is found that B_{100} required large amount of antioxidant for maintaining the specification followed by B_{30}, B_{20}, B_{10} and B_7 samples with metal contents. Therefore it is possible to attain requisite oxidation stability of metal contaminated biodiesel by blending 70% petro-diesel in Jatropha curcas biodiesel (JCB). This optimum combination is expected to reduce the cost of biodiesel substantially and require lower quantity of antioxidant.

1. Introduction

Biodiesel is a fuel consisting of the alkyl monoesters of vegetable oils or animal fats. Biodiesel fueled engines produces less carbon monoxide, unburnt hydro carbons and particulate matters than diesel fueled engines. One drawback of biodiesel is that it is susceptible to oxidation which can induce polymerization of the ester and can form insoluble gums and sediments which are known to cause fuel filter plugging. Biodiesel, derived from vegetable oil and animal fats, is being used as engine fuel in USA and Europe to reduce air pollution and to reduce dependence on limited fossil fuel, localized to some specific regions. Because of the surplus availability of edible oils like soybean oil, sunflower oil and rapeseed oil, these countries are using edible oils as feedstocks for biodiesel production. On the other hand, the possibility of biodiesel production from edible oil resources in India is very less as the indigenous edible oil production is much less than the actual demand which is met by its import [1]. India accounts for 9.3% of world's total oil seed production and is the fourth largest edible oil producer in the world and still about 46% of total edible oil is imported to meet the domestic requirements and as such the question of diverting edible oil resources for biodiesel production in India does not arise. The only possibility seems to be the non-edible oil resources like Jatropha, pongamia, Mahua and sal, which can be commercially grown on waste lands and the oil resources can be used for biodiesel production. Jatropha curcas has been identified as one of the important source for biodiesel production in India.

Almost all the biodiesels have significant amounts of esters of oleic, linoleic or linolenic acids and the trend of increasing stability is linolenic < linoleic < oleic [2]. These esters undergo autooxidation with different rates depending upon the numbers and positions of the double bonds and result in the formation of a series of by-products like acids, esters, aldehydes, ketones, lactones, etc.

A number of reports have been found in the literature on the storage and oxidative stability of biodiesel synthesized from edible oils but only very few reports are available on the effect of blending of biodiesel with diesel on the oxidation stability of that blend. However, to the knowledge of the author of this work, no work has been reported on the effect of metal contaminants on non edible biodiesel/diesel blend oxidation stability.

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Sarin et al. [3] have used palm and Jatropha biodiesel blends to minimize the dosage of antioxidants and found an increase in the induction period of Jatropha biodiesel after it was blended with palm biodiesel.

Sarin et al. [4] investigated the Synergistic effect of metal deactivator and antioxidant on oxidation stability of metal contaminated Jatropha biodiesel. Research was conducted to increase the oxidation stability of metal contaminated Jatropha biodiesel by doping metal deactivator with antioxidant, with varying concentrations in order to meet the aforementioned standard required for oxidation stability. It was found that usage of antioxidant can be reduced by 30% to 50%, therefore the cost, even if very small amount of metal deactivator is doped in Jatropha biodiesel to meet EN-14112 specification.

Sarin et al. [5] analyzed the effect of blending of biodiesels synthesized from non-edible and edible oils on oxidation stability. Dependence of the OS on esters of fatty acid composition was also examined. Good correlation between the OS and PAME (palmitic acid methyl ester) was obtained.

Das et al. [6] have carried out long-term storage stability analysis of biodiesel produced from Karanja oil and reported that the oxidative stability of Karanja oil ME (KOME) decreased with increase in storage time of the biodiesel. Knothe and Dunn [7] indicated that presence of Cu, even in 70 ppm in rapeseed oil greatly increases the oxidizability of the fuel. Copper has also been found to reduce the Oxidation Stability Index (OSI) of methyl oleate more than either Fe or Ni. Karavalakis et al. [8] have evaluated the oxidation stability of biodiesel/diesel blend. They used animal fats and used frying oil for biodiesel. They examined the factors influencing the stability of several biodiesel blends with low and ultra low sulphur automotive diesel fuels.

Sarin et al. [9] have evaluated the oxidation stability of metal contaminated biodiesel and found that influence of metal was detrimental to oxidation stability and catalytic.

From the above literature, it can be concluded that oxidation cannot be entirely prevented but can be significantly slowed down by the use of antioxidants which are chemicals that inhibit the oxidation process. Two types of antioxidants are generally known: chain breakers and hydroperoxide decomposers [10]. Literature related to hydroperoxide decomposers is very scarce. The two most common types of chain breaking antioxidants are phenolic and amine-types. Almost all the work related to stability of fatty oil and ester applications is limited to the phenolic type of antioxidant. The mechanism of all chain breaking antioxidants is shown below in Fig. 1.

As can be seen, 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 which is further resistant to chain oxidation process. Thus the chain breaking antioxidants interrupt the oxidation chain reaction in order to enhance stability. The effectiveness of antioxidant is generally measured by stressing a fatty oil or ester molecule both with and without the antioxidant.

As per National Mission on Biodiesel in India, Jatropha biodiesel has undertaken for the present study in order to improve the stability of biodiesel and make it acceptable to oil marketing companies in India. The present paper aims to study the effect of metal contaminants on the stability of Jatropha biodiesel/diesel blend. Also the effectiveness of various antioxidants is checked in metal contaminated biodiesel and its blend with diesel.

$$ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$$

$$A^{\cdot} \rightarrow \textbf{stable product}$$

Fig. 1. Mechanism of all chain breaking antioxidants [2].

2. Materials

Butylated hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), propyl gallate (PG), and pyrogallol (PY) were the additives employed for their evaluation on diesel/biodiesel blends. All chemicals were of analytical grade and purchased from Sigma Aldrich, India. Different transition metals–iron (Fe), nickel (Ni), manganese (Mn), cobalt (Co), and copper (Cu) have also been purchased from Sigma Aldrich, India. Biodiesel is prepared in the laboratory and the procedure is discussed in the experimental section.

3. Experimental

3.1. Biodiesel preparation

Since the FFA contents of Jatropha curcas oil (JCO) were very high (15.4%), a two step acid–base catalyzed transesterification process is used to prepare biodiesel and the method is discussed in our previous publications [11,12]. After completion of the reaction, the reaction mixture was transferred to separating funnel and both the phases were separated. Upper phase was biodiesel and lower phase contained 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. Fatty acid composition of biodiesel was analyzed using Gas chromatograph [13] and is given in Table 1 which shows that the JCB is maximum composed of unsaturated fatty acids (75.3%) responsible for poor oxidation and thermal stability of biodiesel.

The biodiesel samples prepared above were tested for physico-chemical properties as per ASTM D-6751 and Indian IS-15607 specification given in Table 2 which shows that the biodiesel prepared from JCO meet most of the specifications except oxidation stability test.

As per National Mission on Biodiesel in India, the use of biodiesel should reach a minimum of 20% in 2012, while the revised European standard EN 590 already includes a provision for automotive diesel fuel to be blended with biodiesel up to 7% (v/v). According to European standard there is no specification beyond B_7 for oxidation stability. Therefore same oxidation stability specification requirement (20 h) is considered for oxidation stability for all biodiesel blends beyond B_7. As Indian standard follow the European standards for stability of biodiesel therefore basis of study is very correct.

3.2. Biodiesel/diesel blends preparation

For the purpose of experimentation, biodiesel is mixed with diesel in different proportions (B_{80}, B_{50}, B_{40}, B_{30}, B_{20}, B_{10} and B_7). Also to see the effect of metal contents on biodiesel, different metal contents (Fe, Ni, Mn, Co and Cu) are added in biodiesel in pre-decided concentrations with and without antioxidants.

3.3. Oxidation stability measurement

Oxidation stability of biodiesel from different feedstocks and their blends with automotive diesel was quantified by the induction period (IP). The IP was evaluated according to the Rancimat