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Full Length Article

FTIR assessment and investigation of synthetic antioxidant on the fuel stability of *Calophyllum inophyllum* biodiesel

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ABSTRACT

'Fuel Stability' is one of the most significant properties of biodiesel, which insists the biodiesel stability during prolonged storage period. Poor resistance to oxidation process is the main hurdle for biodiesel commercialization in the global fuel market. Biodiesel degradation by the products yielded from oxidation process may deprive the fuel properties and obviously engine performance. Dosage of synthetic antioxidants is an appropriate method for improving the fuel stability of biodiesel. The present research work investigates the effects of *tert*-butyl hydroquinone (TBHQ) antioxidant additive concentrations on the oxidation stability, long-term storage stability and thermal stability of Calophyllum inophyllum biodiesel. Fourier Transform Infra-red (FTIR) spectroscopy was used to characterize the oxidation variability of biodiesel, following the FTIR spectrum regions of C—H and O—H bonds for various concentrations of TBHQ. Dosage of TBHQ at 1000 ppm concentration (B100A3) with pure biodiesel enhances the oxidation stability by 94.658%, storage stability by 14.466% and thermal stability by 37.269%; meanwhile further dosage of antioxidant deteriorates the formation of hydrophobic and hydrophilic clusters between antioxidant and biodiesel compounds, which is characterized through FTIR spectrum. It is concluded that by dosing 1000 ppm of TBHQ antioxidant with Calophyllum inophyllum biodiesel could enhance the storage period.

1. Introduction

US and India recorded 1.2% and 7.1% higher fossil fuel (oil) consumption than the level of year 2013 respectively. In the year 2014, the global utilization of fossil fuel has been amplified by 0.8 million barrels per day [1]. To overcome this fossil fuel usage augmentation, the biofuel execution got its attention. Biofuel production has been escalated by 0.9% globally in the year 2015, among which India displayed the biodiesel production of about 13.1% higher level than the previous year [2]. The increment in energy utilization in Asia will be escalated about 1.5% by the year 2030 [3]. The major global energy crisis leads to implementation of biofuel in transportation sector. Degradation of biodiesel due to oxidation products leads to the spoilage of fuel quality, properties and its performance while fueling in diesel engines. This deprived oxidation stability of biodiesel curbs its commercialization, as it is less resistant to oxidation reaction. Hence fuel stability is an important issue that must be focused in biodiesel research. 'Fuel stability' is the term deals with the resistance to degradation process of a fuel. The degradation may be due to various factors like oxidation, thermal-oxidative decomposition, hydrolysis and foreign particles contamination. Fuel stability is conversed individually into three properties as storage stability, thermal stability and oxidation stability [4]. Antioxidants interact with the peroxide (oxidation product) radicals and lead to the formation of antioxidant free radical which stabilize the oxidation reaction and thereby inhibit the oxidation process of biodiesel [2,5].

Calophyllum inophyllum (C.I) biodiesel has been proposed as a superior source due to its higher oil yield and heating value than other biodiesel sources like karanja, neem and jatropha [6]. Also in our previous work it was found that C.I biodiesel possess higher oxidation stability (OS) with Induction Period (I.P) of 8.47 h at 110 °C than other biodiesel, which is depicted by using Rancimat instrument [7]. C.I biodiesel has been investigated and found to have improvement in oxidation stability by adding butylated hydroxytoluene (BHT) and 4-methyl-6-*tert*-butyphenol (MBEBP) with 30% biodiesel/diesel blend [8]. By adding 15% antioxidant extracted from pongamia leaf with 20% C.I biodiesel, I.P was found to increase from 5 h to 14 h at 110 °C [9]. C.I biodiesel shows 44.57% higher OS when 20% biodiesel added with 10% pentanol in our previous oxidation stability analysis [7]. C.I biodiesel was studied for oxidation stability variation with three different

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additives like 2-ethylhexyl nitrate (EHN), *N*-phenyl-1, 4-phenylenediamine (NPPD) and *N*,*N*-diphenyl-1, 4-phenylenediamine (DPPD) at 1000 ppm concentration and found that DPPD was effective among the other additives [10].

Previous studies concluded that the synthetic antioxidant *tert*-butyl hydroquinone (TBHQ) at 300–1000 ppm concentration is very effective in improving the oxidation stability of biodiesel extracted from soybean oil [11,12], palm oil [13], cottonseed oil [14,15], karanja oil [16], Terminalia belerica [17], linseed oil [18] and used cooking oil [19]. Also TBHQ has been proposed as the best additive for superior results in storage stability of biodiesel derived from soybean oil [20], jatropha oil [21], palm oil [22] and karanja oil [16]. Storage stability and thermal stability of Calophyllum inophyllum biodiesel with antioxidant have not been reached by previous researchers. Due to superior results of TBHQ and fewer studies on fuel stability of C.I biodiesel, this paper focuses its light over oxidation, storage and thermal stability variation on addition of TBHQ with Calophyllum inophyllum biodiesel.

Fourier Transform Infra-red (FTIR) spectroscopy has been proposed as a quick, reliable and efficient method for evaluating the fuel stability and also an efficient correlating tool for the analyzed results from Rancimat [23]. Oxidation-induced breakage of waste cooking oil methyl ester (biodiesel) linkages was explained using FTIR spectrum results [24]. FTIR has been used in our previous work of oxidation stability analysis of C.I biodiesel with pentanol addition [7]. Similarly FTIR is used in this study to characterize the effects of TBHQ at various concentrations.

2. Materials and methodology

2.1. Test fuels

General process for production of biodiesel is transesterification process (alcoholysis) [1–3]. As Calophyllum inophyllum (C.I) oil is highly acidic, two step of acid-base catalyzed transesterification has been used to extract biodiesel [6,25]. Initially the oil was taken to esterification process, which is heated at about 95 °C for 1 h to remove moisture prevailing in it. Then methanol (50% v/v oil) and Sulfuric acid (1% v/v oil) were added to the oil at 55–60 °C for 2.5 h accompanied by 350 rpm stirring speed. After reaction completion, the oil was poured into separation funnel to remove the excess impurities, sulfuric acid and methanol in the upper layer of the oil. Then the lower layer of the esterified oil was removed and heated at 95 °C for 1 h to remove the water and methanol. By repeating this process the acid value of esterified oil has been reduced to less than 4 mg KOH/g oil. Then the esterified oil has been involved in transesterification or alcoholysis process, in which the obtained oil was added with methanol (25% v/v oil) along with catalyst potassium hydroxide (1% w/v oil) and heated at 66 °C for 2 h stirred at 350 rpm [6]. In this transesterification process, triglyceride molecules of oil have been converted to methyl ester (biodiesel) and glycerol (by-product). The glycerol has been removed from the lower layer of separation funnel after 12 h of settling. Then the upper layer methyl ester has been involved in post-treatment process as washing, by which the biodiesel added with distilled water (50% v/v oil) and maintained at 60 °C [6]. Distilled water was sprayed over biodiesel surface and stirred softly. By discarding the lower layer, the pure biodiesel has been obtained, which is dried using rotary evaporator to free from methanol and water [6]. Antioxidant tert- butyl hydroquinone (TBHQ) was dosed with pure C.I biodiesel in different concentrations ranging from 375, 750, 1000, 1125, 1500 ppm. TBHQ was found to be completely soluble in C.I biodiesel at all concentrations. The following six test fuel blends were prepared and evaluated: (i) Pure biodiesel (B100), (ii) 100% biodiesel + 375 ppm TBHQ (B100A1), (iii) 100% biodiesel + 750 ppm TBHQ (B100A2), (iv) 100% biodiesel + 1000 ppm TBHQ (B100A3), (v) 100% biodiesel + 1125 ppm TBHQ (B100A4), (vi) 100% biodiesel + 1500 ppm TBHQ (B100A5). The properties of test fuels were determined (Table 1) by using equipments provided by Thermal Laboratory, Government College of Technology, Coimbatore, India.

2.2. Rancimat instrument

Oxidation stability (OS) is the tendency of fuel to resist the degradation of its physical and chemical properties by the presence of products like peroxides and hydroperoxides due to oxidation reaction [4]. OS is determined by using 873 Biodiesel Rancimat instrument (Metrohm manufacturer) based on the test method EN14214, which is also followed by Indian standard IS15607. Oxidation stability is depicted from 'Induction Period (I.P)' parameter, which was measured at temperature range from 140 °C to 155 °C at an equal interval of 5 °C. As per EN14214 standard, the biodiesel should display 6 h of I.P at 110 °C.

2.3. Aluminium containers

Storage stability (SS) addresses the relative susceptibility of a fuel to resist the oxidative degradation due to microbial growth and water contagion during long-term storage. Storage stability is evaluated using standard ASTM D4625, by which the fuel is to be stored in a closed aluminium container for a period of 100 days in an incubator at 40 °C [4,26]. Aluminium containers are used in this study, as it resist the catalytic effect on oxidation of biodiesel [5]. Regular monitoring of kinematic viscosity and acid value was done for every 10 days.

2.4. Thermo-gravimetric analyzer

Thermal stability (TS) term used to refer the fuel resistance to degradation attributed to elevated temperature higher than atmospheric condition. Generally biodiesel exhibits higher temperature during combustion inside engine cylinder, which is also evident from higher NOx (Oxides of Nitrogen) emission [27,28]. This elevated engine cylinder temperature influences the biodiesel getting re-circulated back to the fuel tank through the fuel injection system, which may lead to degradation of fuel physio-chemical properties [4]. Hence the biodiesel should also been analyzed for its thermal stability. Thermal stability was measured by thermo-gravimetric analyzer (TGA 2050). The standard for thermal stability analysis is not yet specified in any fuel quality specifications for biodiesel, but the effect of antioxidants on TS could be evaluated by using onset temperature parameter [29]. The effect of antioxidants on thermal stability of biodiesel samples has been investigated using onset temperature (T_{ON}). The fuel samples of quantity 8 mg were purged with oxygen and were heated to 500 °C at a rate of 10 °C/min.

2.5. FTIR spectroscopy

As mentioned earlier, FTIR is an effective tool for correlating the oxidation stability results by characterizing the absorption frequency (600–4000 cm^{-1}) of specific molecular compounds in the sample using FTIR spectrum data. In this study, the fuel blends were evaluated at wave number range 3000–3700 cm^{-1} and 2700–3000 cm^{-1}, which corresponds to the presence of O—H and C—H bonds respectively in the fuel samples.

3. Results and discussion

3.1. Oxidation stability analysis

All samples have been tested initially at 110 °C for assuring the induction period of above 6 h (Table 1). B100A3 shows the highest I.P of about 27.98 h at 110 °C (Fig. 1). The deviation of induction periods for pure Calophyllum inophyllum biodiesel and the consequences of TBHQ addition were investigated by testing the fuel samples at four temperatures as 140 °C, 145 °C, 150 °C and 155 °C (Fig. 2). The