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The effect of binary antioxidant proportions on antioxidant synergy and oxidation stability of Jatropha and Karanja biodiesels

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ABSTRACT

Oxidation has been measured a major problem for biodiesel commercialization. Auto-oxidation takes place when exposed to air, heat, light and metallic contaminants which affects adversely the fuel characteristics of biodiesel. Addition of synthetic antioxidants generally improves the oxidation stability of biodiesel; however the use of large concentration of additives makes the process uneconomical. This study investigates the effectiveness of individual as well as binary antioxidants to improve the oxidation stability of Jatropha and Karanja biodiesels. Antioxidant synergy was investigated using 500, 600 and 700 ppm of antioxidant combinations namly Pyrogallol:Propyl gallate (PY:PrG), Pyrogallol:tert-butyl hydroquinone (PY:TBHQ) and Pyrogallol:Butylated hydroxyanisole (PY:BHA) at weight ratios of 9:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:9, respectively. It was observed that higher blends of binary mixture produced negative synergy, however the best antioxidant synergy showed by the binary systems of PY:PrG, and PY:TBHQ, when the additives are mixed at 1:3 weight ratios; whereas binary mixture of PY:BHA resulted in complete antagonism. However, the effectiveness of the binary system on oxidation stability was found in order of 1:3/3:1 > 1:2/2:1 > 1:1 > 1:9/9:1. The efficacy of antioxidant combinations was evaluated by using pressurized PetroOXY method. Further the dependency of oxidation stability and antioxidant synergy on the fatty acid composition of biodiesel was also observed.

1. Introduction

Biodiesel is a renewable and biodegradable substance obtained from the transesterification of vegetable oils. It is a mixture of saturated and unsaturated fatty acids esters. Though biodiesel has diesel like fuel characteristics, but it is more prone to auto-oxidation than diesel because of unsaturation present in it. The oxidation of biodiesel results reduction in the fuel combustion efficiency [1–4]. Therefore oxidation is one of the most serious restrictions for biodiesel commercialization. Thus, minimum oxidation stability is required not only for the fresh biodiesel, but also during its long term storage, handling and uses [1]. Besides the degree of unsaturation in biodiesel, storage conditions and presence of impurities are also the determining factors for the oxidation of biodiesel. Exposure to light and temperature, types of storage tank material or presence of metal traces are some other factors that influence the stability of biodiesel [5,6]. In comparison to biodiesel, these oxidation processes are less pronounced in the parent oil due to the presence of natural antioxidants which get partially lost during refining [7].

Oxidation/degradation leads the increase the acid value, density and viscosity while decrease in IP (induction period) and iodine value of biodiesel. Because of the oxidation, thermal degradation and poor storage conditions, formation of sediment and gum along with the fuel darkening, cause filter plugging, injector fouling, depositions in the engine combustion chamber and malfunctions in various components of the ignition system [8–10]. Thus, oxidation stability is a parameter of great importance for the biodiesel quality control. Chemical additives (called antioxidants) are an alternative to prevent or retard the auto-oxidation of biodiesel. The addition of antioxidants not only slows down the oxidation processes but also improves the fuel stability up to a certain extent [11–15]. These additives can be classified as primary, synergists, oxygen removers, biological, chelating agents and mixed antioxidants. The primary

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antioxidants promote the exclusion or inactivate the free radicals formed during the initiation or propagation of the reaction, through donation of hydrogen atoms to these molecules, interrupting the chain reaction [16].

The synergistic behavior shown by these primary antioxidants has been studied for fatty acid derivatives and it is observed that the mixture of antioxidants is more efficient than that of individual antioxidant [17–25]. Antioxidants synergies not only provide the better oxidation stability but also make the process more economical and industrial viable [18]. During literature survey it is observed that very limited reports are available on the study of antioxidant synergy and oxidation stability of non-edible biodiesels. However, the available reports mostly describe the effect of antioxidants on edible oil based biodiesels [17–25]. Thus, there is an intense need to find out and optimize the best binary antioxidants combinations which could provide the maximum oxidation stability with minimum additive concentrations and could retain the fuel properties under the limits of prescribed fuel standards.

In extension of our ongoing research for the optimization of additive concentration for oxidation stability of biodiesel [26–28]; the aim of present study is to provide the experimental results for the synergistic effect of antioxidant and role of the additive proportions on antioxidant synergy and oxidation stability of Jatropha and Karanja biodiesels. In our previous reports [26–28] about the effects of antioxidants on oxidation stability of Jatropha and Karanja biodiesels and their diesel blends; where five phenolic antioxidants were used viz. PY (Pyrogallol), PrG (Propyl gallate), TBHQ (*tert*-Butylhydroxyquinone), BHA (Butylated hydroxy anisole) and BHT (Butylated hydroxy toluene); it was observed that the antioxidant effectiveness followed the order of PY > PrG > TBHQ > BHA > BHT for Jatropha biodiesel, whereas an order of PY > PrG > BHA > BHT > TBHQ for Karanja biodiesel. Based on our previous results, antioxidant synergy is investigated in present work among the best three antioxidants for Jatropha and Karanja biodiesel. A comparison is made between the effectiveness of individual and binary antioxidant system on the oxidation stability of Jatropha and Karanja biodiesels. Results obtained by this study will certainly help to support the sustainable development of biodiesel characteristics.

2. Experimental section

2.1. Material

Jatropha and Karanja biodiesel were used as blending stock and were prepared through base catalyzed transesterification of respective crude oils with Methanol. Jatropha curcas oil and Karanja (*Pongamia pinnata*) oil were purchased from Suahilodaya Inc. Meerut India and were used after vacuum distillation. Methanol and the catalyst (KOH) were purchased from Sigma Aldrich India.

Transesterification of 3000 mL Jatropha curcas oil using 600 mL methanol and 1 wt% KOH (w.r.t oil) was performed in a four neck round bottom flask (cap. 5 L) equipped with an overhead stirrer, PID controlled thermo-couple and water condenser. The reaction mixture was stirred at 300 rpm for 3 h at 60 °C temperature. After the reaction, the reaction mass was transferred to separating funnel and the biodiesel (upper layer) was separated from the glycerol (lower layer). Alcohol from both the phases was distilled off under reduced pressure. The biodiesel thus obtained was washed with the lukewarm distilled water to remove residual glycerol, unreacted catalyst and soap form during the transesterification. The biodiesel obtained was kept under reduced pressure to make it moisture free.

Similar procedure of adopted for the transesterification of Karanja (*P. pinnata*) oil. Prior the transesterification degumming experiment was done to reduce the high FFA value. Degumming of Karanja oil was done by using 0.5 wt% H_2SO_4 in methanol at 60 °C until the constant acid value was lowered and remained constant.

The main properties of *Jatropha* and Karanja biodiesel are listed in Table 1.

2.2. Fatty acid analysis

The GC–MS analysis of Jatropha and Karanja biodiesels were carried out on a QP-2010 gas chromatography mass spectrometer (GC-2010 coupled with GC–MS QP-2010) equipped with an auto sampler (AOC-5000) from Shimadzu (Japan) using an RTX-5 fused silica capillary column, 30 m × 0.25 mm × 0.25 μm (Rastek). 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 respectively and the split ratio was 1/30. The mass spectrometer was operated in electron compact mode with electron energy of 70 eV. Both the ion source temperature and the interface temperature were set at 200 °C. FAME peaks were identified by comparing their retention times with authentic standards by GC–MS post run analysis and quantified by area normalization. The fatty acid profile for Jatropha and Karanja biodiesels is given in Table 2.

The antioxidants (Fig. 1) Pyrogallol (PY, 98%), Propyl-gallate (PrG, 97%), TBHQ (tert-Butyl hydroxyquinone, 97%) and BHA (Butylated hydroxy anisole, 99%) were procured from Sigma Aldrich, India and were used as received.

2.3. Storage conditions

500 mL sample of biodiesel and its blends with antioxidants were stored in closed Borosil glass bottles of 1 L capacity for 90 days and were kept indoors, at room temperature [Studies were carried out between Oct. 2013 (average room temperature was 16 °C) to April 2014 (average room temperature was 24 °C)]. 500 mL space in the bottle was occupied by air. Samples were taken out periodically every 15 days to study the effects of added antioxidants.

2.4. Oxidation stability measurements

The oxidation stability (induction period) of neat biodiesel and its blends was investigated by Petrotest "PetroOXY(e)-VERSION: 10.08.2011" instrument. The IP of biodiesel and its blends was estimated according to the ASTM-D 7545-09 EN 14112 and prEN 16091 "Oxidation stability of fuel". IP was calculated for 5 ml fuel sample in hermetically sealed test chamber. The chamber was automatically pressurized with oxygen up to 700 kPa (~7 bar/101.5 psi) and heated up to 140 °C. This initiates a very fast oxidation process. As the fuel oxidizes, it consumes the oxygen in the sealed test chamber resulting in 10% pressure drop. The length of the induction period is a measure of how long the antioxidant protects the biodiesel and its blends from oxidation. The obtained IP values were converted to their corresponding Rancimat time by multiplying the obtained Petrotest time by a correction factor 20 (as recommended by the test method and was automatically suggested by the instrument). All experiments were performed in duplicate and the mean value is reported with an experimental error (SD) of 0.85%–0.95%. This experimental error (SD) was calculated for some initial observations particularly for the IP values obtained for tested ratios of binary mixtures of PY:PrG and PY:TBHQ with Jatropha