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Full Length Article

Algal biodiesel stabilization with lower concentration of 1:3 ratios of binary antioxidants – Key factors to achieve the best synergy for maximum stabilization

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ABSTRACT

Poor storage stability of biodiesel is considered a major problem for its commercialization. The use of commercial antioxidants has been proven very effective for biodiesel stabilization; hence these are frequently being used for long term storage of biodiesel. Moreover, in comparison to individual antioxidants, use of their binary combinations with their optimized concentrations could be more economical and highly effective to improve the storage behavior of biodiesel. In present report the effectiveness of lower concentration of binary antioxidants on the oxidation stability of algal biodiesel was studied. The 500, 600 and 700 ppm concentrations of binary combinations of three antioxidants [*i.e.* Pyrogallol (PY); Propylgallate (PrG) and *tert*-butyl hydroquinone (TBHQ)], are prepared at weight ratios of 1:1, 1:2, 1:3 and 1:9 and vice-versa. Although, storage stability was increased with increase in antioxidant concentration; however, the best synergy was obtained with 1:3 ratios of binary antioxidants with 500 ppm concentration of binary antioxidants.

1. Introduction

Biodiesel is recognized as a potential alternate of conventional diesel fuel. It is a mixture of saturated and unsaturated fatty acids esters. In contrast to conventional diesel, biodiesel is renewable and biodegradable; it is obtained from the *trans*-esterification of both edible and non-edible vegetable oils [1]. Though, biodiesel has diesel like fuel characteristics, but the poor storage stability is the major restriction for its long term storage of. Oxidation of biodiesel leads the formation of oxidized by-products that causes the reduction in engine performance, and also its fuel characteristics get changed [2–4]. Therefore, auto oxidation becomes one of the most serious restrictions for it to be used as substitute of conventional diesel. Thus, lower oxidation rate is required not only for the fresh biodiesel, but also during its long term storage, handling and uses [1]. Higher oxidation susceptibility of biodiesel is related to its degree of unsaturation, configuration of double bonds, storage conditions, exposure to light and temperature, interaction with contaminants, construction material of the storage tank and presence of impurities in it [5–8]. 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 and purification by vacuum distillation. Oxidation of biodiesel results increase in acid value, density and viscosity, while, decrease in its induction period (IP) and iodine value. Formation of sediment and gum along with the fuel darkening are the major consequences of biodiesel oxidation which causes filter plugging, injector fouling, depositions in the engine combustion chamber and malfunctions in various components of the ignition system [9–11].

Thus, oxidation stability is considered a parameter of great importance for the long term storage of biodiesel and its quality control. Commercially available chemical additives (*i.e.* antioxidants) are frequently being used to prevent or retard the auto-oxidation of biodiesel. The addition of antioxidants not only slows down the rate of oxidation processes but also improves the fuel stability up to a maximum extent [12–14]. In comparison to individual antioxidant, it has been pointed out by the researcher's that the synergistic behavior of the mixture of antioxidants in defined proportions has shown better improvement in oxidation stability and long term storage of biodiesel as well [15–20]. During literature survey it is also observed that very limited reports are available on the study of effectiveness of binary combinations of antioxidants on oxidation stability of biodiesel produced from non-edible feedstock. However, the available reports mostly describe the effect of antioxidants on edible oil based biodiesels [16–19]. In previous efforts, the authors group has reported the effectiveness of binary antioxidants

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system for the improvement of oxidation stability of Jatropha and Karanja biodiesels [20]. Currently, global biodiesel research is mainly aligned towards the promotion and production of biodiesel from '*third generation feedstock (i.e. algae)*'[21–23]. The third generation biofuel feedstock is of low-cost, high-energy and entirely renewable. The third generation feedstock has the potential to produce more energy per acre than conventional crops. It can be grown using non-agricultural land and waste water. A further benefit of third generation biofuels is that it can be manufactured into a wide range of fuels such as diesel, petrol and jet fuel [21–23]. To align our research with current trends of biofuel production and processing, the present study focused on the evaluation of lower concentration of binary antioxidants to achieve the best antioxidant synergy for the maximum stabilization of algal biodiesel. Different binary combinations (9:1, 3:1, 2:1 and 1:1 wt ratios) of three phenolic antioxidants [*viz*. Pyrogallol (PY), Propyl-gallate (PrG) and *tert*-Butylhydroxyquinone (TBHQ)] were formulated to study their effectiveness on the oxidation stability of algal biodiesel along with other parameters like antioxidant synergy and stabilization factor. In previous observations these three antioxidants have found to be the most effective for biodiesel stabilization [23–28].

2. Experimental section

Pure cultures of *Chlorella vulgaris* was obtained from Vivekananda Institute of Algal Technology (VIAT), Chennai (India). The stock culture of microalgae strains was maintained regularly on agar slants and liquid medium using sterilized BBM (Bold's Basal Medium) medium (with initial pH of 6.8) under laboratory conditions (*i.e.* 24 °C (± 1 °C) under (~2500 lux) light intensity and 16/8 light dark cycle in a photo-bioreactor) [21,22]. Methanol and the base catalyst (KOH) were purchased from Sigma Aldrich India. Algal biodiesel was used as blending stock. Algal lipid was extracted from micro algae *Chlorella vulgaris* as per reported method [23,24]. Base catalyzed transesterification of algal lipid was performed under microwave irradiation according to the reported procedure [24]. Prior to transesterification the acid value of algal lipid was reduced by acid catalysed esterification processes (*i.e.* degumming). After the transesterification 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 was further purified by vacuum distillation to make it free from impurities and moisture. The main properties of algal biodiesel are listed in Table 1.

The fatty acid analysis of algal biodiesel was done using Gas chromatograph (Nucon 5700 series) equipped with Flame ionization detector (FID) using EOX column (serial no 5061; 30 m length, 0.25 mm ID and 0.25 mm outer dia).Pure nitrogen (99.999%) was used as carrier gas with a flow rate of 30 mL/min. The oven temperature was set at 160 °C for 2 minutes, followed by 4 °C/min ramp up to 240 °C and maintained for 40 min. The injector and FID detector temperature was set at 240 °C and 220 °C respectively. Supelco 37 component FAME mix (Sigma–Aldrich, USA) was used as standard. The fatty acid profile for algal biodiesels is given in Table 1.

The antioxidants Pyrogallol (PY, 98%), Propyl-gallate (PrG, 97%) and *tert*-Butyl hydroxyquinone (TBHQ, 97%) were procured from Sigma Aldrich, India and were used as received.

500 mL sample of algal biodiesel and its blends with antioxidants were stored in closed Borosil glass bottles of 1L capacity for 90 days and were kept indoors, at room temperature [Studies were carried out between January 2016 and August 2016 (average room temperature during the study period was 22 °C)]. Remaining 500 mL space in the bottle was occupied by air. Samples were taken out periodically at every 15 days to study the effects of added antioxidants.

The oxidation stability (induction period) of neat biodiesel and its additive blends was investigated by Petrotest "PetroOXY(e)-VERSION: 10.08.2011" instrument. 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. It is specified that the minimum IP for B100 should not be less than 6 h as per EN 14112 and *pr*EN16091 standard specifications. More details about the operating conditions of the instrument are mentioned in previous reports [20,23–28].

Table 1
Properties of Algal Biodiesel [23,24].

S. No	Properties	ABD
1	Density (g/cm^3) at 15 °C	0.881
2	Kinematic Viscosity (mm^2/s) at 40 °C	4.78
3	Calorific value (MJ/kg)	39455
4	Acid value (mg of KOH/g)	0.43
5	Moisture content (mg/kg)	300
6	Flash point (°C)	152
7	Cloud Point (°C)	−3
8	Pour point (°C)	−12
9	Oxidation stability (IP, at 110 °C, h)	5.0
10	**Free Fatty acid composition (%)**	
	Caprylic acid (C 8:0)	0.10
	Capricacid (C 10:0)	0.80
	Lauricacid (C12:0)	0.15
	Myrsticacid (C 14:0)	2.00
	Palmiticacid (C16:0)	26.12
	Palmitoleicacid (16:1)	0.50
	Stearic acid (C18:0)	6.12
	Oleic acid(C18:1)	22.45
	Linoleic acid (C18:2)	30.12
	Linoleic acid (C 18:3)	7.51
	Arachidic acid (C20:0)	0.22
	Erucic acid (C22:1)	3.81

Table 2
Formulation table for binary antioxidants.

	Antioxidant concentration					
	500 ppm		600 ppm		700 ppm	
Ratios	A (mg)	B (mg)	A (mg)	B (mg)	A (mg)	B (mg)
0:0	0	0	0	0	0	0
0:1	0	500	0	600	0	700
1:1	250	250	300	300	350	350
1:2	167	333	200	400	233	467
1:3	125	375	150	450	175	525
1:9	50	450	60	540	70	630

2.1. Sample preparation for induction period calculation

2.1.1. Individual antioxidants

Neat and single antioxidants blended samples of algal biodiesel (500 mL) were stored in a 1 L capacity Borosil glass bottles. Initially blending was done by adding individual antioxidants at concentrations of 500, 600 and 700 ppm. Samples were taken periodically from the stocks for testing under storage conditions.

2.1.2. Binary antioxidants

Previous observations confirmed PY as the best antioxidant for biodiesel stability followed by PrG and THBQ; therefore, in present study also PY is considered as primary antioxidant; and the antioxidant synergy is investigated between PY and other two best antioxidants [20].

Blends of algal biodiesel with binary antioxidants (PY:PrG and