Energy 135 (2017) 220–226

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Effect of antioxidants on the stability and corrosiveness of palm biodiesel upon exposure of different metals

M.A. Fazal [a, b, *], M.R. Jakeria [a], A.S.M.A. Haseeb [a], Saeed Rubaiee [b, c]

[a] Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Mechanical Engineering, University of Jeddah, Saudi Arabia
[c] Department of Industrial Engineering, University of Jeddah, Saudi Arabia

ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form
13 May 2017
Accepted 21 June 2017
Available online 22 June 2017

Keywords:
Palm biodiesel
Copper
Mild steel
Antioxidant

ABSTRACT

The properties of biodiesel get aggravated when metals are exposed into it. The present study aims to investigate the effect of antioxidants on the fuel properties of palm biodiesel upon exposure to copper and mild steel. The used antioxidants include pyrogallol (PY) and butylated hydro-oxy toluene (BHT). Static immersion tests of metal coupons in palm biodiesel in the absence and presence (500 ppm) of antioxidants were conducted at room temperature (25Ċ-27 °C) for 60 days. The investigated fuel properties include induction period, density, viscosity, acid number and calorific values. Results showed that pyrogallol was more effective to suppress the degradation of metal surface, fuel composition and fuel properties.

1. Introduction

Use of biodeisel as a promising alternative fuel is getting more acceptance in automobile [1]. However, few characteristics of biodiesel such as hygroscopic nature [2–4], affinity for metals and alloys [5,6], tribological degradation [7], auto-oxidation [8–10], compositional degradations [11,12], instability of fuel properties [13] are the major concerns related to its applicability in automotive engine. The most commonly affected fuel properties include induction period, total acid number, water content, viscosity, density, cold flow properties, calorific value etc. [3,14].

Compositionally, biodiesel is mono-alkyl saturated/unsaturated esters of long chain fatty acids derived from vegetable oils or animal fats [15]. Saturated fatty acids contain maximum number of hydrogen atoms possible per carbon atom having no double bonds. On the other hand, unsaturated fatty acid chains do not contain maximum number of hydrogen atoms due to the presence of double bond(s). Concentration of saturated and unsaturated components could be changed when biodiesel comes in contact with metal surfaces [16,17]. In addition to this, compositional and structural changes also occur. All these phenomena may directly influence the stability of different fuel properties of biodiesel. In our recent study [11], we have found that exposure of metal surface in biodiesel changes its unsaturated molecules and, therefore, the related fuel properties also change. The use of different antioxidants can inhibit degradation of biodiesel at different level [8,17]. It has been reported that pyrogallol (PY) and butylated hydro-oxy toluene (BHT) antioxidants are comparatively more effective in improving the fuel properties of biodiesel [18–22]. Effectiveness of these antioxidants was examined without exposing metal surface in biodiesel. But exposure of metals in biodiesel can influence the action of added antioxidants. Several studies have reported that antioxidants can suppress the corrosiveness of biodiesel [23,24]. However, in-depth studies on the effect of antioxidants on biodiesel composition and related fuel properties are rare. The aim of this study is to investigate the effect of different additives on the stability of biodiesel composition and related fuel properties upon exposure to copper and mild steel.

2. Materials and methods

Investigated palm biodiesel was supplied by Weshchem Technology SdnBhd, Malaysia. Antioxidants PY (98% pure) and BHT (99% pure) were obtained commercially from Sigma Aldrich Sdn Bhd.

* Corresponding author. Department of Mechanical Engineering, University of Jeddah, Saudi Arabia
E-mail addresses: fazal@uj.edu.sa, jewel_mme.buet@yahoo.com (M.A. Fazal), rafi_jk1987@yahoo.com (M.R. Jakeria), haseeb@um.edu.my (A.S.M.A. Haseeb), salrubaiee@uj.edu.sa (S. Rubaiee).

http://dx.doi.org/10.1016/j.energy.2017.06.128
0360-5442/

The antioxidants are used for controlling the oxidation of biodiesel by de-protonation (removal of H^+) from its molecular structure [25]. The chemical structure of the used antioxidants, PY and BHT are shown in Fig. 1. The test coupons of copper (19 mm diameter × 3 mm thickness) and mild steel (27 mm diameter × 2 mm thickness) were made from respective round bar. Used copper bar was 99.99% pure while the composition of mild steel was: 0.2% C, 0.5% Mn, 0.5% Si and Fe (balance). At the edge of each specimen, a hole of diameter 2 mm was drilled for hanging into the fuels. The coupons were then abraded with 400 to 1200-grit silicon carbide papers, washed by deionised water and degreased with acetone. Static immersion tests in the absence and presence (500 ppm) of antioxidants were conducted in palm biodiesel (B100) at room temperature (25 °C - 27 °C) for 60 days. The tests were carried out in glass beakers (500 ml each). Each beaker contained 400 ml biodiesel. Two duplicate coupons of each metal were individually immersed into the beakers. Biodiesel was kept exposing to the light and air during immersion period. The relative humidity during this test varied within 81–83%.

At the end of immersion test, the samples were cleaned carefully in a water stream by using a polymer brush in order to remove the loosely bonded corrosion products. The weight of each sample was recorded prior to and after immersion test by using a balance with a four decimal accuracy. The obtained data from weight loss measurement were converted into corrosion rate (μm/y) by using equation (1).

$$Corrosion\ rate = \frac{8.76 \times 10^9\, w}{D\, t\, A} \ldots \ldots \qquad (1)$$

where corrosion rate is in micrometer per year (μm/y), w is the weight loss (kg), D is the density (kg/m^3), A is the exposed surface area (m^2) and t is the exposure time (h).

Degradation of biodiesel properties and its remedial measures were examined and compared after the immersion tests. Gas chromatography mass spectroscopy (GCMS-QP 2010 Plus, Shimadzu) was used to conduct compositional analysis of biodiesel before and after the immersion test. Before GCMS analysis, calibration curves were obtained from standard solution to verify the traceability of different components of palm biodiesel. Palm biodiesel samples were diluted by *n*-hexane to make it compatible for GCMS analysis. The used column for GCMS analysis was TG-5MS VB-5 BPX 5, Shimadzu. Nitrogen was used as carrier gas. The GCMS column oven temperature was 50 °C and the injection temperature was 250 °C. The total flow was 514.0 mL/min. The pressure was kept at 55.3 KPa. GC ion source temperature was 200 °C with 300 °C interface temperature.

The oxidative induction period (IP) of each investigated fuel was determined by using Rancimat instrument (873 Biodiesel Rancimat Oxidation Stability Analyzer, Metrohm). Density and kinematic viscosity were determined by Anton-Paar Digital Viscometer (SVM 3000) at 40 °C. Calorific values of biodiesel samples were determined by using automatic calorimeter (C2000, IKA) according to ASTM D240 standard. Standard 0.1 M KOH solution (potassium hydroxide) was used during titration in order to determine the Total Acid Number (TAN) of palm biodiesel. This titration was conducted by using automated titration system (G-20 Rondolino, Mettler Toled) as per ASTM D664 standard. Water content in biodiesel was measured by using Karl Fischer water analyzer (V30 Compact Volumetric KF Titrator, Mettler Toled). At the end of the test, metal corrosion was investigated by the measurement of corrosion rate and changes in surface morphology. Changes in surface morphology were characterized by HITACHI S-3400 N scanning electron microscopy connected with energy dispersive X-ray spectroscopy (SEM/EDS).

3. Results and discussions

Table 1 shows the compositional analysis of biodiesel before and after 60 days of exposure to copper and mild steel coupons. Effect of different additives (e.g. PY and BHT) on biodiesel composition has also been presented. It is seen that the principal constituents of used palm biodiesel were methyl oleate (46%) and methyl palmitate (36%). After 60 days of exposure to copper and mild steel, the content of methyl oleate (mono-unsaturated) drops from 46% to 25% and 42% respectively while methyl palmitate (saturated) did not change significantly. This demonstrates that unsaturated ester molecules reacted with metals comparatively more than the saturated ester molecules. It is also evident from Table 1 that copper is more effective than mild steel in reducing methyl oleate. Antioxidant PY seems to be much better than BHT in reducing such changes.

Unsaturated ester molecules may easily be oxidized or changed to other components in the presence of metals. In this case, copper is found to be more aggressive than mild steel. In our recent study [3], it has been found that aggressiveness of copper increases with the increase of exposure time. It has been reported that copper can act as strong catalyst to oxidize biodiesel [26]. Oxidation of biodiesel in the presence of metals could be related to biodiesel composition as well as types of exposed metals. It is also seen from Table 1 that compositions of as-received biodiesel (B100) and copper exposed biodiesel in the presence of PY (B100/Cu/PY) are almost similar. Particularly in copper exposed biodiesel, BHT was

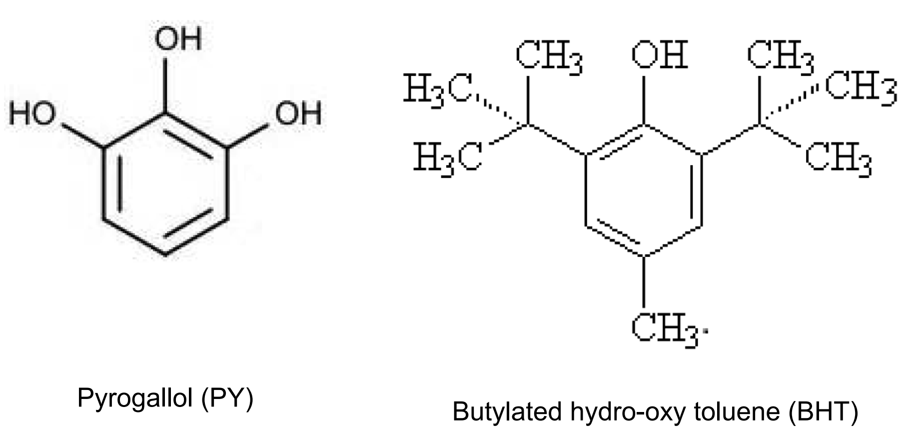

Fig. 1. Chemical structures of Pyrogallol (PY) and Butylated hydro-oxy toluene (BHT).