Industrial Crops and Products 58 (2014) 8–14

Contents lists available at ScienceDirect

Industrial Crops and Products

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

# Effect of copper and mild steel on the stability of palm biodiesel properties: A comparative study

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ARTICLE INFO

*Article history:*
Received 26 October 2013
Received in revised form 13 March 2014
Accepted 19 March 2014

*Keywords:*
Copper
Mild steel
Palm biodiesel
Fuel properties
Compositional changes

ABSTRACT

The scarcity of fossil fuel has recently been introduced as a major concern to energy policy. This crisis has prompted the search for alternative energy sources. Biodiesel can be considered as one of the potential candidates of energy sources in order to resolve this problem. Most of the fuel properties of biodiesel are very close to that of petroleum diesel. However, commercial use of biodiesel in the automobile engine is being limited because of its unstable fuel properties. Instability of the fuel properties appears to be more aggravated when biodiesel comes in metal contact. The present study is intended to investigate the stability of different fuel properties and chemical composition of palm biodiesel upon exposure to copper and mild steel. Static immersion tests were performed by exposing metallic coupons in palm biodiesel at room temperature for different periods viz., 20, 40, 60 days. Compositional analysis of biodiesel was conducted by gas chromatography. Investigated fuel properties include induction period, total acid value, water content, calorific value, viscosity, density, cloud point, pour point, etc. Effect of biodiesel on metal surfaces was examined by measuring the corrosion rate and conducting SEM/EDS analysis. It is found that copper has strong influence in changing fuel properties especially for viscosity, water content, calorific value, density, etc. Compositional analysis of biodiesel showed that principal unsaturated constituent of palm biodiesel, methyl oleate reduced more in copper exposed biodiesel than that in mild steel exposed biodiesel. Formation of poly unsaturated methyl linoleate was observed in both metal exposed palm biodiesel.



## 1. Introduction

The scarcity of fossil fuel has increased the demand for alternative energy (Makareviciene et al., 2013). As a feasible solution of this energy scarcity, biodiesel can be considered as a potential candidate among the alternative energy sources. It is basically composed of mono-alkyl saturated/unsaturated esters of long chain fatty acids derived from vegetable oils or animal fats (Fazal et al., 2011a; Jain and Sharma, 2012). The principal factors that determine characteristics of biodiesel are, the chain length of fatty acid methyl esters, degree of unsaturation and concentration of different components (Wazilewski et al., 2013; Fazal et al., 2014). It has been noted that saturated and unsaturated components of biodiesel could be changed in the presence of metal surfaces (Jakeria et al., 2014). The factors that can degrade fuel properties of biodiesel are longtime storage (Jakeria et al., 2014), temperature fluctuation (Fazal et al., 2011b), absorption of moisture (McCormick et al., 2007), etc. Hydrolysis and oxidation are two major reactions that hinder the stability of biodiesel during longtime storage (Rodrigues et al., 2013). Presence of metal may accelerate those reactions.

It has been reported (Fernandes et al., 2013; Knothe and Dunn, 2003) that oxidation of FAME (fatty acid methyl ester) mostly initiated in the presence of oxygen. The initiator radical can be a metallic ion or can be an organic substance. The initiation process of oxidation reaction is rapidly forwarded due to the catalytic reaction of hydroperoxides inherited from FAME (Frankel, 1984). The products of primary oxidation result in secondary oxidation products. These secondary oxidation products mostly consist of acids, aldehydes, dimers and polymers (Knothe, 2005). Secondary oxidation products are prone to deteriorate the fuel properties (McCormick et al., 2007). Degradation of fuel properties can cause severe damage to the fuel system. These damages mostly include injector cooking, filter plugging, gumming, sedimentation, etc. (Jakeria et al., 2014). Presence of metallic surface can form corrosion products/debris that may also result in gumming and sedimentation. Previous studies (Fazal et al., 2012, 2013; Haseeb et al., 2010; Sarin et al., 2009) mostly focused on the corrosiveness of biodiesel for different

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http://dx.doi.org/10.1016/j.indcrop.2014.03.019
0926-6690/

metals and alloys. Compositional change may have a significant impact on fuel properties as well as it may change the corrosiveness of biodiesel. Some of the previous investigations (Fazal et al., 2010; Jakeria et al., 2014) showed that composition of biodiesel changes in the presence of metallic surface. Still there is a lack of adequate literatures to relate compositional change with fuel properties. This study aims to investigate the effect of copper and mild steel on compositional change of palm biodiesel and its consequences on different fuel properties.

## 2. Materials and methods

Palm biodiesel used in this study were supplied by Weshchem Technology Sdn Bhd Malaysia. Used copper samples in this study were made from 99.99% pure copper. Mild steel was composed of 0.2% C, 0.5% Mn, 0.5% Si and Fe (balanced). Static immersion tests of copper and mild steel coupons were conducted in palm biodiesel (B100) at room temperature (25 °C) for 20, 40 and 60 days by using a glass beaker. Each beaker contains 400 ml biodiesel. Two duplicate coupons of each metal were immersed in each beaker. Test coupons of Cu (19 mm diameter × 3 mm thickness) and mild steel (27 mm diameter × 2 mm thickness) were made from the respective round bar by machining and grinding. A hole of 2 mm diameter was drilled in each of the test coupons at the edge for hanging inside biodiesel in glass beaker. Each test coupon was polished by silicon carbide papers (grade 120–600) followed by washing and degreasing with acetone.

Before and after (20, 40, 60 days) immersion tests, palm biodiesel was analyzed by GC (gas chromatography) in order to determine the compositional changes. Prior to GC analysis. Biodiesel samples were diluted with *n*-Hexene at 2:1 ratio. For GC analysis, the used column was GC-2010. The GC oven temperature was 50 °C and the injection temperature were 250 °C oven temperature was increased at different stages from 50 °C to 250 °C. GC ion source temperature was 200 °C in full scan mode. The pressure was maintained at 55.30 kPa and high-pressure injection was switched off. To determine the oxidation stability of biodiesel before and after exposure to metal samples, Rancimet test was carried out according to EN14214 standard. This test was done by Metrochem Oxidation Stability Analyzer at 110 °C with 7.50 g biodiesel. Density and kinematic viscosity were determined periodically by Antonpar Digital Viscometer at 40 °C. Calorific value of biodiesel was determined in EKA 2000 Bomb Calorimter. Cloud point and pour point was investigated by EKA100 CPPP Tester. Standard 0.1 M KOH solution (potassium hydroxide) was used for titration to determine the Total Acid Number (TAN) of palm biodiesel samples. Karl Fischer water content measuring device was utilized to moisture content measurement. Before and after immersion, the weight loss of the test coupons was measured by a balance with four decimal accuracies. At the end of the test, corrosion was examined by the measurement of corrosion rate and changes in surface morphology. The obtained data from weight loss were converted into corrosion rate (mpy) using Eq. (1) (Fontana, 1987).

$$\text{Corrosion rate (mpy)} = \frac{W \cdot 534}{d \cdot t \cdot A} \quad (1)$$

Where corrosion rate "mpy" stands for mils (0.001 inch) per year is the weight loss (mg), $d$ is the density (g/cm$^3$), $A$ is the exposed surface area (square inch) and $t$ is the exposure time (h). Changes in surface morphology were characterized by HITACHI S-3400N scanning electron microscopy connected with energy dispersive X-ray spectroscopy (SEM/EDS).

## 3. Results and discussions

Table 1 shows the changes in chemical composition obtained by GC analysis of palm biodiesel before and after exposure to copper and mild steel for different times. It is observed that the major component of palm biodiesel is methyl oleate. It is a mono unsaturated molecule. In copper exposed palm biodiesel, methyl oleate has been decreased from 46.16% to 44.85% after 20 days. The reduction of methyl oleate persisted and it becomes 24.62% after 60 days exposure of copper. For mild steel exposed biodiesel, it was 45% after 20 days and followed by 42% for 60 days.

The second major constituent of palm biodiesel is palmitate and it is a saturated molecule (Table 1). It exhibited almost identical percentage upon exposure to both copper and mild steel for all sets of exposure time. Palmitate has been changed less than 5% for both metal-exposed fuels. This implies that palmitate is not so much reactive in the presence of metallic surfaces. It has been observed that methyl oleate (mono unsaturated) is reduced comparatively more in copper exposed biodiesel than that in mild steel exposed biodiesel (Fig. 1). This could be attributed to the more reactive nature of copper with unsaturated component methyl oleate. Methyl oleate is associated with double bonds and this particular structure offers more reaction sites for a metal ion to forward metal assisted oxidation of biodiesel. Copper seems to work as a suitable catalyst to reduce methyl oleate. Similar assumption was also observed in our previous study (Fazal et al., 2012). Palm biodiesel exposed to mild steel has not been observed with such a reduction in methyl oleate. It can be assumed that mild steel is less reactive with unsaturated components of palm biodiesel. Unsaturated molecules may form different acidic compounds and short chain molecules after several reactions in the presence of metal ions. In as received palm biodiesel poly unsaturated methyl linoleate was absent. Methyl linoleate was found to be formed after exposure of copper and mild steel in palm biodiesel. There lies a possibility that unsaturated compounds have gone through some reactions in the presence of metals that accelerated the formation of methyl

**Table 1**
GCMS analysis revealing the compositional differences of biodiesel before and after exposure to copper and mild steel at room temperature for 20, 40 and 60 days.

| Commercial name/formula | % of Area | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | MW | As received | Cu 20 d | MS 20 d | Cu 40 d | MS 40 d | Cu 60 d | MS 60 d |
| Methyl Laurate[a]/$C_{13}H_{26}O_2$ | 214 | 0.86 | 0.90 | 0.91 | 0.97 | 0.91 | 1.05 | 0.91 |
| Myristic acid, methyl ester[a]/$C_{15}H_{30}O_2$ | 242 | 2.53 | 2.660 | 2.69 | 2.83 | 2.68 | 2.95 | 2.71 |
| Palmitate[a]/$C_{17}H_{34}O_2$ | 270 | 36.14 | 36.06 | 34.88 | 36.08 | 35.82 | 36.22 | 35.44 |
| Methyl isoheptadecanoate[a]/$C_{18}H_{36}O_2$ | 284 | | 0.75 | 0.21 | 0.21 | 0.22 | 0.19 | 0.22 |
| Methyl linoleate[c]/$C_{18}H_{34}O_2$ | 294 | | 0.56 | 0.36 | 14.91 | 0.69 | 18.21 | 2.58 |
| Methyl oleate[b]/$C_{19}H_{36}O_2$ | 296 | 46.16 | 44.85 | 45.00 | 30.77 | 44.73 | 24.62 | 42 |
| Methyl stearate[a]/$C_{19}H_{38}O_2$ | 298 | 8.53 | 8.44 | 9.06 | 8.59 | 8.55 | 8.62 | 9.21 |
| Butyl palmitate[a]/$C_{20}H_{40}O_2$ | 312 | 0.59 | 0.59 | 0.65 | 0.65 | 0.62 | 0.68 | 0.62 |
| Eicosanoic acid, methyl ester[a]/$C_{21}H_{42}O_2$ | 326 | 0.84 | 0.91 | 0.88 | 0.96 | 0.97 | 0.96 | 0.97 |
| Squalene[c]/$C_{30}H_{50}$ | 410 | 1.57 | 1.39 | 1.39 | 1.62 | 1.48 | 1.62 | 1.48 |
| Oleic acid Butyl ester[b]/$C_{22}H_{42}O_2$ | 338 | | 0.56 | 0.52 | 0.54 | 0.59 | 0.55 | 0.59 |

a: Saturated; b: mono unsaturated; c: poly unsaturated; d: exposure time in days, MW: molecular weight.