Corrosion Characteristics of Carbon Steel upon Exposure to Biodiesel Synthesized from Used Frying Oil

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Abstract

The use of biodiesel leads to corrosion of automotive material, which can potentially shorten engine lifetime. The study aims to investigate the effect of temperature and contact time on the corrosion characteristics of carbon steel upon exposure to biodiesel synthesized from used frying oil. The corrosion rate of carbon steel was analyzed based on weight loss measurement according to the standard of ASTM G31 as affected by temperature and contact time. The immersion temperatures used in this study were 30°C, 40°C, and 70°C, respectively. The contact times studied were 30 days, 40 days, and 50 days respectively. The results show that the increase of temperature and contact time of biodiesel on carbon steel surface speeds up the corrosion rate. Maximum corrosion rate (0.083 mmy) was observed on the carbon steel contacted to biodiesel at 70°C for 50 days. The SEM results showed an irregular shape of the corroded carbon steel surface. XRD / FTIR analysis of carbon steel samples show the presence of peaks, detected as Fe2O3, FeO(OH) and Fe2O3CO3, as the corrosion products.

Keywords: biodiesel; carbon steel; corrosion; FAME; used frying oil

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INTRODUCTION

The advances of technology in industrial and transportation activities lead to the rapid increase of fossil fuel consumption so that its supply will decrease rapidly. Because fossil fuels are not renewable, this situation may lead to the crisis of energy in the future (Jin et al., 2015). Nowadays, the world main issue in transportation is dominated by the use of petroleum based fuels, such as gasoline and diesel. Globally, the average energy consumption in transportation increases as much as 1.1% each year as the result of automotive industries development. The transportation sector has been estimated to contribute about 63% in liquid fuel consumption since 2010 until 2040 (Mahmudul et al., 2017). In addition, burning of fossil fuel causes environmental problem, especially in the form of air pollution (Thangavelu et al., 2016). Various efforts have been made to find alternative renewable energies as substitute to fossil fuels so that the fossil fuel consumption rate in the future can be
reduced. One of the renewable energy is biodiesel, can be used as a substitute for petroleum diesel fuel in many sectors including light vehicle, heavy vehicle, and marine sectors (Charpe and Rathod, 2011). Biodiesel has similar physical properties as conventional diesel fuel in many ways including viscosity, flash point, and cetane number (Nioroj et al., 2009). It is considered as an environmentally friendly fuel due to its low hazardous gasses emission upon combustion. With those advantages, biodiesel has been used as alternative fuel in many countries such as Europe, Australia and America (Mabus, 2010).

Basically, biodiesel is fatty acid methyl esters (FAMEs). Biodiesel can be synthesized through free fatty acid esterification or triglycerides transesterification contained in the vegetable oils (Leung et al., 2010). Biodiesel can be produced from many materials, such as used frying oil, edible oil, non-edible oil, and animal fat. From economical perspective, used frying oil is the best alternative as a raw material of biodiesel compared to other raw materials such as edible oil, non-edible oil, and animal fat, which are relatively more expensive. Used frying oil is also considered as a waste, which may potentially cause environmental problems. Utilization of used frying oil as an alternative source of biodiesel energy is expected to solve the problem of environmental pollution (Charpe and Rathod, 2011). Thus, biodiesel production from used frying oil is considered as an efficient and economical way.

Biodiesel contains saturated ester and unsaturated ester components, which are unstable, sensitive to light, temperature and metal ions (Jain and Sharma, 2011). Biodiesel also contains moisture, organic acids, aldehydes, peroxides, ketones, and ester, which cause corrosion in the fuel system (Fazal et al., 2014). Biodiesel is more susceptible to oxidation reaction and more corrosive than conventional diesel fuel unless modified or treated by adding additive (Haseeb et al., 2010; McCormick et al., 2007). Biodiesel oxidation leads to the formation of oxidation products, such as peroxide and hydroperoxide compounds. During the degradation process, those compounds are converted into aldehydes, ketones, and acids, which are volatile (Karavalakis et al., 2010). Besides, high molecular weight compounds can be formed through oxidation polymerization process. Oxidation mechanism can increase corrosion characteristics and change the fuel properties (Karavalakis et al., 2010). The presents of impurities such as water, alcohol, free fatty acids, glycerol, and residual catalyst from the production process may trigger the corrosion properties of biodiesel (Haseeb et al., 2011).

In automobile application, biodiesel can be in contact with some material that divided in three categories: ferrous alloys, non-ferrous alloys, and elastomer. Metal materials can be corroded and worn out in biodiesel (Haseeb et al., 2011). Several parts of diesel engine are made from carbon steel, such as fuel tank, fuel channel, and injection system so that potentially attacked by corrosion if the impurities contents of biodiesel are high (Haseeb et al., 2011).

Some studies have shown that biodiesel is more corrosive than conventional fuel diesel, but provides better lubrication than conventional fuel diesel (Haseeb et al., 2011). Kaul et al. (2007) studied corrosive properties of biodiesel made from Mahua, Karanja, and Salvador seeds in India. The results show that biodiesel made from Mahua and Karanja did not cause corrosion of piston, whereas biodiesel from Salvadoria had corrosion effect due to its high sulfur content. Fazal et al. (2014) studied that copper and aluminum showed low corrosion resistance compared to stainless steel in biodiesel. The result showed that corrosion rate increased along with the rising temperature. Even in high temperature when engine operates can accelerate the rate of corrosion in metal alloy (Park et al., 2014). Fazal et al. (2010) compared corrosion characteristic between biodiesel and petroleum diesel in automotive materials. The result shows that corrosion rate of metals and variation of fuel properties when exposed to metals are more pronounced in biodiesel than petroleum diesel. Copper and aluminum are susceptible to corrosion attack in biodiesel whereas stainless steel metals are more resistance to corrosion in biodiesel. Aquino et al. (2012) studied the effects of light, temperature, and metal ions on degradation process and corrosivity in copper and brass metal. The results showed that the presence of light in biodiesel kept at room temperature could accelerate corrosion on both metals. Copper metal alloys are susceptible to corrosion in biodiesel compared to aluminum alloys. Pitting corrosion had been observed in brass filter after 10 hours operated with biodiesel at 70°C (Sgroi et al., 2005; Kaul et al., 2007). Polymers, such as plastics and elastomers, can be degraded if they are in contact with biodiesel (Haseeb et al., 2011). This study focuses on the investigation of the effects of temperature and contact time of biodiesel synthesized from used frying oil on carbon steel corrosion.

METHOD
Materials and Apparatus

The biodiesel used in this study was made from used frying oil. Pretreatment of frying oil was done by filtration method using filter paper to separate the suspended impurities and followed by dehydration at 100°C to obtain transparent frying oil. The chemicals used in this biodiesel production were methanol (99.99% of weight, Meck KGaA, Germany), H2SO4 (Merck, 99%), and natrium hydroxide (99.99% weight Meck KGaA, Germany). Frying oil characteristics used in biodiesel production are shown in Table 1.
Biodiesel Production

Biodiesel production was done through two stages, they are esterification and transesterification. Esterification reaction was carried out at 60°C using H₂SO₄ catalyst at concentration of 0.5% of oil weight. Molar ratio of methanol and oil used in reaction was 6:1. Esterification reaction was carried out in 3 hours with continuous stirring at 200 rpm. After the time was reached, the mixture was separated in separation funnel in order to separate its oil layer. The process was followed by oil transesterification in a three-necked flask. As much as 500 g of esterified frying oil was heated to 60°C. The frying oil then reacted with methanol solution in molar ratio of methanol and oil is 6:1. The catalyst used for transesterification was 0.5% NaOH solution in methanol. The reaction process was carried out at 60°C for 3 hours. The reaction mixture was then cooled to form two layers, top layer and bottom layer. The top layer was biodiesel and the bottom layer was the mixture of glycerol, residual methanol, and catalyst. Biodiesel then washed as much as three times using aquadest. The residual water in biodiesel then separated through heating at 105°C.

FAME contents were analyzed using GC-MS (Gas Chromatography-Mass Spectrometry) TQ 8030 Shimadzu. Column temperature was set at 65°C (held in 8 minutes) then raised until 250°C (held in 20 minutes). The injector and detector temperatures were set at 250°C and 200°C, respectively.

Corrosion Testing

The corrosion was determined using the immersion method test, based on standard ASTM G-31. Plate steel dimensions as immersion testing are 15x5x1 mm. Prior to the immersion test, the steel pieces were scraped using 320, 400, and 600 grit of scrubbing papers respectively, in order to clean the dirt and corrosion crust. The test metal was then washed using water and followed by further washing using acetone and ethanol. Then the test metal was dried in oven then its mass was weighed. The corrosion rate was measured using following function:

\[
CR (\text{mmy}) = \frac{\Delta m}{\rho T S}
\]

CR is stated in mmy, ∆m is the weight loss (g), D is density of steel (g/cc), T is immersion time (hours), and A is the area of test metal (m²).

RESULTS AND DISCUSSION

Figure 1 shows that biodiesel contains fatty acid methyl ester (FAME) components, which are marked by the peak appearance at retention time of 39.78, 43.41, 43.8, and 44.32 minutes.

In addition, analysis result using mass spectrophotometry shows that FAME of the biodiesel components consists of methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate in compositions as showed in Table 2. The total FAME content in the biodiesel synthesized for 3 hours of reaction time was 98.41%, with the largest constituent component was methyl oleate.

Table 2. FAME components in biodiesel

<table>
<thead>
<tr>
<th>FAME components</th>
<th>Contents (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl palmitate</td>
<td>31.3</td>
</tr>
<tr>
<td>Methyl linoleate</td>
<td>14.3</td>
</tr>
<tr>
<td>Methyl oleate</td>
<td>45.54</td>
</tr>
<tr>
<td>Methyl stearate</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Figure 2 shows the corrosion rate of carbon steel in biodiesel at various temperature and immersion time. The results show that the higher biodiesel temperature will increase the corrosion rate of carbon steel. Corrosion rate in the immersion time of 30 days at biodiesel temperature of 30°C is 0.018.
mmy, while the corrosion rate at the immersion time of 30 days at biodiesel temperature of 70°C is 0.033 mmy. The maximum corrosion rate (0.079 mmy) was achieved at 70°C with immersion time for 40 days. The test result shows that the higher the biodiesel temperature will speed up the corrosion rate. It is due to the high temperature in oxidation process of FAME components in biodiesel increases rapidly so that it leads to the formation of metal oxide (Liu and Fang, 2009). Biodiesel contains unsaturated fatty acids with more carbon double bond and less hydrogen, which make them more susceptible to the oxidation. Biodiesel oxidation can decrease its quality due to the formation of aldehydes, alcohols, short chain carboxylic acids, and sediments (Jin et al., 2015). Those oxidation products are corrosive to the engine. Zuleta et al. (2012) stated that the presence of moisture content and free fatty acids may increase the corrosivity of biodiesel. Hydrolysis reaction of methyl ester by water absorbed from the air or residual water from the process of biodiesel production causes the formation of free fatty acids, which are corrosive (Haseeb et al., 2010). Methyl esters present in biodiesel are hygroscopic so that it can increase the moisture content. The water tends to be condensed on the metal surface causing metal corrosion. Iron metals are reactive metals that can react with fatty acids produces fatty acid salts and hydrogen in the following reaction (Hu et al., 2012):

$$\text{Fe} + 2\text{RCOOH} \rightarrow \text{Fe(R'COO)}_2 + \text{H}_2 \quad (2)$$

Salts formed from the reaction of iron metal and fatty acids cause the metal to be dissolved into biodiesel so that it potentially accelerates the formation of free radicals, which decrease the biodiesel stability (Sarin et al., 2009).

Choe and Min (2006) reported that metals could accelerate the oxidation reaction rate of fatty acids by reducing activation energy at the autooxidation initiation stage to be 63-104 kJ/mol. Metal can directly react with fatty acids producing alkyl radicals of fatty acids. This reaction can also produce reactive oxygen, such as $^{1}\text{O}_2$, radical hydroxy $^{\cdot}\text{O}_2$, and hydrogen peroxides. The presence of those species can accelerate fat oxidation process. Copper is predicted to accelerate the decomposition of hydrogen peroxides as much as 50 times faster than ion Fe$^{2+}$. Meanwhile, ion Fe$^{3+}$ accelerates the decomposition 100 times faster than Fe$^{3+}$. The reactions can be expressed as the following reactions:

$$\text{Fe}^{3+} + \text{RH} \rightarrow \text{Fe}^{2+} + \text{R}^{+} + \text{H}^+ \quad (3)$$

$$\text{Fe}^{2+} + \cdot\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{O}_2^{-} \quad (4)$$

$$\text{O}_2^{-} + \cdot\text{O}_2^{-} + 2\text{H}^{+} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (5)$$

$$\text{H}_2\text{O}_2 + \cdot\text{O}_2^{-} \rightarrow \text{HO}^{+} + \text{OH}^{-} + \cdot\text{O}_2 \quad (6)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{HO}^{+} \quad (7)$$

Fe metal can accelerate the autooxidation of fatty acids by decomposing the hydroperoxides

$$\text{ROOH} + \text{Fe}^{2+} \rightarrow \text{RO}, + \text{Fe}^{3+} + \text{OH}^{-} \quad (8)$$

$$\text{ROOH} + \text{Fe}^{3+} \rightarrow \text{ROO}, + \text{Fe}^{2+} + \text{H}^{+} \quad (9)$$

In the biodiesel oxidation process by oxygen from the air, methyl ester contained in biodiesel will form free radicals beside the double bond. Biodiesel oxidation increases along with the increasing of dissolved oxygen amount as the result of absorption process. Oxygen solubility in biodiesel is greater than the oxygen solubility in water (Choe and Min, 2006). Those free radicals are rapidly bonded with oxygen in the air to form peroxy radicals. Peroxide radicals then bond the methyl esters forming new radicals, which will bond the oxygen in the air. During the process there will be nearly 100 new radicals formed from one single radical. It indicates that the decomposition of radicals occurs at a very rapid rate and produces a series of byproducts such as aldehydes, ketones, lactones, formic acid, acetic acid, and propionic acid (Sarin et al., 2009; Tsuchiya et al., 2006).

Figure 2 shows that the increase of contact time from 30 days to 50 days at the same temperature of biodiesel towards carbon steel tends to increase the corrosion rate. The fastest corrosion rate occurs at the contact time of 50 days with the temperature of biodiesel is 70°C. This is because biodiesel tends to be oxidized as storage time increases and its hygroscopic properties. The results are supported by the study of Ashraful et al. (2014), who reported that total acid number (TAN) number increased along with the storage time of biodiesel. The high TAN contents in biodiesel are potential to accelerate the formation of crust, rust, and oxidation. Based on the results of study, biodiesel synthesized from coconut oil has the greatest TAN contents compared to the jatropha biodiesel, PME (palm oil methyl ester), COME (coconut oil methyl ester), and diesel. Acid contents can be formed when the residual water in biodiesel hydrolyzes ester to form alcohol and acids (Bouaid et al., 2007). The presence of acid components, which is formed, causes biodiesel become more corrosive.
large range of oxidation stability. Generally, the oxidation rate of biodiesel is affected by the concentration of methyl linoleate, methyl oleate, and methyl linolenate (polyunsaturated alkyl esters). Oxidation of biodiesel is due to the presence of unsaturated fatty acid chains or double bonds, which have high reactivity to oxygen, especially when in contact with air/water. The main products of the oxidation process are hydroperoxide compounds, which easily form secondary oxidation products. Oxidation reactivity of the C=C bonds amount in fuel and the increase number of C=C bonds correlates to the decrease in fuel oxidation stability. The increase in instability of biodiesel fuel is generally proportional to the number of C=C bonds in molecule (a molecule contains two C=C bonds has a half of stability compared to the molecule which has one C=C bond) (Berman, et al., 2011).

Methyl linoleate, methyl oleate, and methyl linolenate components are components of methyl ester, which have induction time less than 3 hours at 110°C. Table 2 shows that biodiesel produced from used frying oil contains methyl oleate and methyl linoleate, which are easily oxidized by temperature and air to form organic acids. These acids have the potential to cause corrosion of metals. This finding is supported by a study of Park et al. (2008) who reported that the stability rate of biodiesel will decrease if the linoleic acid contents in biodiesel increase.

Figure 3 is the results of SEM analysis of the surface of carbon steel. The steel surface corroded as the result of contacting with biodiesel. Corrosion on carbon steel spreads on the surface of steel is marked with the formation of dark colored pit as the result of corrosion.

The level of surface metal damage as the result of corrosion is significant, especially in a contact time of 40 days at biodiesel temperature of 70°C. The increase of biodiesel temperature leads to the increase of pit size on carbon steel. It occurs because if the temperature is raised the corrosion rate of carbon steel will increase. The high corrosivity of biodiesel can be attributed to the high concentrations of unsaturated acids (Kaul et al., 2007). Some oxidation products, Fe ions may dissolve into biodiesel or being deposited on the metal surface. Then they will react with free fatty acids form fatty acid salts on the carbon steel surface by the following reaction:

\[ \text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \]  \hspace{1cm} (10)
\[ \text{Fe}_2\text{O}_3 + 6\text{R’COOH} \rightarrow 2\text{Fe}(\text{R’COO})_3 + 3\text{H}_2\text{O} \]  \hspace{1cm} (11)
\[ 2\text{R’COOH} + \text{Fe} \rightarrow \text{Fe}(\text{R’COO})_2 + \text{H}_2 \]  \hspace{1cm} (12)

![Figure 3. SEM morphologies of carbon steel surfaces in condition of a) before contact, (b) 30D-30C, (c) 30D-70C, (d) 40D-30C, (e) 40D-70C, (f) 50D-70C](image-url)
Those reactions allow the weight of the metals to decrease after immersion test. It occurs since some of metal ions will dissolve in biodiesel so that the color of biodiesel will change from clear yellow into brownish, shown in Figure 4.

The formation of FeO(OH) is as the result of the decomposition reaction of Fe(OH)₃, which produces H₂O molecule and FeO(OH). Whereas H₂CO₃ is produced from the reaction between water and CO₂ absorbed from the air.

The presence of oxide compounds formed from the corrosion can be shown in XRD diffractogram in Figure 5. It shows that the presence of Fe₂O₃, Fe(OH)₃, Fe₂O₂CO₃ is as the result of corrosion. The presence of corrosion product, Fe₂O₂CO₃, may caused by the reaction with moisture content, oxygen, and CO₂ absorbed from the air. Fe₂O₂CO₃ is product of the reaction between H₂CO₃ and FeO(OH) with the following reaction mechanism (Marco et al., 2007):

$$2\text{FeO(OH)} + \text{H}_2\text{CO}_3 \rightarrow \text{Fe}_2\text{O}_2\text{CO}_3 + 2\text{H}_2\text{O} \quad (13)$$

CONCLUSION

Biodiesel contains fatty acid methyl ester (FAME) components, which are potentially causing the corrosion on carbon steels. Corrosion rate of carbon steel in biodiesel is mostly affected by the factors of temperature and contact time between biodiesel and carbon steel. The increase of temperature and contact time of biodiesel also increases the corrosion rate of carbon steels. The minimum corrosion rate, occurred at the carbon steel immersed in biodiesel in 30 days at contact temperature of 30°C, is as much as 0.018 mny. Meanwhile, the maximum corrosion rate occurred at the carbon steel immersed in biodiesel in 50 days at 70°C, is as much as 0.083 mny. The results of XRD/FTIR shows that products of carbon steel corrosion were Fe₂O₃, FeO(OH), and Fe₂O₂CO₃.
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