Technical Note

Storage degradation of palm-derived biodiesels: Its effects on chemical properties and engine performance

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ARTICLE INFO

Article history:
Received 10 May 2010
Accepted 21 May 2011
Available online 28 June 2011

Keywords:
Palm
Palm stearin
Biodiesel
Degradation
Engine performance
Emission

ABSTRACT

Palm olein and palm stearin are co-products of palm oil refining processes having different melting point ranges. This study compares the storage degradation characteristics of biodiesels derived from these two palm products, which are palm olein and palm stearin, in terms of chemical properties, engine performance and exhaust emission. The degradation study was carried out by keeping biodiesels in dark closed-lid containers at room temperature for up to 6 months. It was found that the oxygen present in the container led to slow degradation of biodiesels through oxidative reaction with the double bonds in biodiesel. Within 6 months, the majority of oxidative products were composed of shorter hydroperoxide compounds and other short secondary products. These changes resulted in lower heating value and higher density of biodiesels, which in turn caused reductions in fuel combustion efficiency and fuel economy. In terms of emission, the degraded biodiesel produced more complete combustion as indicated by lower emissions of black smoke and carbon monoxide but with higher emission of NOx. In terms of palm oil type, even though palm olein biodiesel possessed higher degree of unsaturation and produced higher peroxide value and acid values from the degradation, its combustion efficiency and fuel economy were still superior to the biodiesel produced from palm stearin possibly due to its higher chain lengths.

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1. Introduction

Even though biodiesel is superior to petroleum diesel in terms of biodegradability, non-toxicity and low emission, the weak point of biodiesel for engine fuel is that it is sensitive to degradation. This is because the double bonds within the unsaturated components of methyl esters such as in methyl linoleate (C18:2) and methyl linolenate (C18:3) can be easily oxidized. The degraded products of biodiesel include insoluble gums, organic acids and aldehydes. These products were claimed to not only degrade the properties of biodiesel, but also build problems in engine operation [1]. In the past, several studies reported the effects of biodiesel degradation at different storage time and conditions on the changes in chemical properties of biodiesel [2–8]. It was found that storage time and conditions led to changes in oxidative stability, iodine, acid and peroxide values as well as the flash point and cetane index. However, these studies did not systematically cover the effects of biodiesel degradations on engine performance and exhaust emission. Furthermore, for palm biodiesel, the difference in degradation characteristics between palm stearin and palm olein biodiesels has never been investigated. On the other hand, the studies on engine performance and exhaust emissions still had no analysis on the correlation between the changes in chemical and engine properties. For example, Thompson et al. [9] studied the degradation of rapeseed biodiesel and found that the degradation led to changes of brake power by less than 2% and reduction of black smoke by 3.2%. Monyem et al. [10] reported that the exhaust emissions of oxidized soybean biodiesel contained less CO and hydrocarbon by 15% and 16%, respectively, with no significant changes in nitric oxide and black smoke emissions.

In Thailand and other tropical countries, the primary energy crop is palm. In crude palm oil refineries, after degumming, deodorizing, and removing fatty acids, the palm oil undergoes a crystallization process, where, the high-melting-point portion (palm stearin) is solidified and phase separated from the low-melting point product (palm olein). Therefore, a major difference between palm olein and palm stearin is the degree of unsaturation, where palm olein contains higher degree of unsaturation. When these oils are converted to biodiesels by transesterification, the chemical structures are modified into long-chain fatty acid alkyl esters, with the same degree of unsaturation as in the raw material. As both palm oil products have been used for biodiesel, it is of interest to
compare their properties, engine performance, and degradation characteristics.

In this study, the biodiesel storage degradation for palm olein biodiesel (POB) and palm stearin biodiesel (PSB) has been systematically investigated. The analysis was carried out in terms of changes in chemical properties and correlation with engine performance and exhaust emission after being stored in dark closed-lid containers.

2. Experimental

2.1. Raw materials

The biodiesels produced from palm stearin and palm olein used in this study were kindly supplied by Pathum Vegetable Oil Co., Ltd. (Thailand). Here, the abbreviations POB and PSB will be used for palm olein biodiesel and palm stearin biodiesel, respectively. The commercial petroleum-base diesel fuel used as a reference fuel was purchased from a gas station. This petroleum diesel was actually the blend of petroleum diesel with 2% of biodiesel as regulated by the Thai Ministry of Energy (2007).

2.2. Preparation of degraded biodiesels

The biodiesels were stored in dark closed containers at room temperature (temperature variation between 25 and 30 °C) for the period of 6 months, during which time the chemical properties were analyzed monthly. The biodiesels were also tested for engine performance and exhaust emissions initially and again after 3, 4, 5 and 6 months, respectively.

2.3. Analysis of chemical properties

The biodiesels were characterized for iodine value (IV), peroxide value (PV), acid value (AV), density, kinematic viscosity and heating value. The acid value was determined by titration method according to ASTM D 664. Viscosities of biodiesels were tested using Cannon Fensky Routine No. 75 P 573 viscometer at 40 °C according to ASTM D 445. The peroxide and iodine value were approximated by titrating with sodium thiosulfate solution following ISO 3960 and EN 14111 standards, respectively. The densities of biodiesels were measured at 15 °C and the heating values were recorded as high heating value (HHV) by the 1261 Isoperibol Bomb Calorimeter according to ASTM D 2015.

2.4. Engine performance and exhaust emission tests

The short-term engine test was carried out in a 4-cylinder, 4-stroke, direct injection Nissan BD-30 diesel engine. The engine maximum power was obtained at the speed of 3600 rpm and main specifications of the engine are given in Table 1. The engine performance test was measured by Eddy current dynamometer. In this work, the tests of diesel and biodiesel fuels were performed at variable loads and engine speeds. The engine was tested at speeds ranging from 1800 to 4000 rpm at full load. The performance parameters obtained from the engine test included brake power (P), brake specific fuel consumption (bsfc) and brake fuel conversion efficiency (ηbf). The bsfc indicates the fuel consumption rate per unit power by:

\[\text{bsfc} = \frac{\text{fuel mass flow rate} \left( m_f \right)}{P}\]

whereas the brake fuel conversion efficiency (ηbf) measures the efficiency in converting the heating value of fuel into engine power by:

\[\eta_{bf} = \frac{P}{m_f \times \text{Fuel Heating Value}}\]

where \(m_f\) is the mass flow rate of fuel injected. The exhaust emissions of engine measured here included CO and NOx by Madur GA-40T Plus fuel gas analyzer, and black smoke by KOEN DS-2000 smoke detector.

3. Results and discussion

The refined palm oil (palm olein) and palm stearin are triglyceride co-products obtained from the palm oil refining process. These co-products are separated by crystallization at low temperature, where the non-crystallized part is separated as cooking oil (palm olein) and the crystallized part is removed as palm stearin. Therefore, the triglycerides in palm stearin contain higher amounts of saturated triglycerides, where their compositions are shown in Table 2. In this study, the degradation characteristics of the two types of biodiesels were compared in terms of their chemical properties, engine performance, and exhaust emission.

Table 2

<table>
<thead>
<tr>
<th>Oil type</th>
<th>Iodine Value</th>
<th>C 12:0</th>
<th>C 14:0</th>
<th>C 16:0</th>
<th>C 18:0</th>
<th>C 18:1</th>
<th>C 18:2</th>
<th>C 18:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm Olein</td>
<td>≥ 56</td>
<td>0.1–0.5</td>
<td>0.5–1.5</td>
<td>38.0–43.5</td>
<td>3.5–5.0</td>
<td>39.8–46.0</td>
<td>10.0–13.5</td>
<td>ND–0.6</td>
</tr>
<tr>
<td>Palm Stearin</td>
<td>≤ 48</td>
<td>0.1–0.5</td>
<td>1.0–2.0</td>
<td>48.0–74.0</td>
<td>3.9–6.0</td>
<td>15.5–36.0</td>
<td>3.0–10.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.1. Chemical and physical properties

3.1.1. FTIR spectra

The changes in chemical structures of degraded palm olein and palm stearin biodiesels were compared and analyzed by using FTIR technique, as shown in Fig. 1. The spectra of the degraded biodiesel were obtained from 10-month old biodiesels. It was found that the chemical structure changes due to degradation of POB studied here possessed a similar characteristic to the degradation analysis of sunflower oil in the study of Guillén and Cabo (2002) [11]. In Fig. 1(a), the spectral changes of POB occurred at several wave numbers. The most significant ones were the drop in absorbance peaks of C–O stretching (several peaks in the range of...
1016–1466 cm⁻¹) and the monomer C=O (1744 cm⁻¹), indicating the break down of ester groups in POB. Moreover, the absorbance peaks of the C=C stretching (near 1656 cm⁻¹) and cis C=C (near 3005 cm⁻¹) of the degraded POB totally disappeared, agreeing with the significant drop in iodine number after a long storage time. In contrary, the broad peak of hydroperoxide near 3444 cm⁻¹ became noticeable for the degraded POB. This band should not be confused with another sharper peak near 3270 cm⁻¹, which was associated with the overtone of methyl ester carbonyl band [11]. These changes in FTIR absorbance peaks indicate that the degradation occurred both at the C=C bonds and at the carbonyl bonds of methyl ester, which were transformed at least into hydroperoxide.

While the FTIR spectrum of the degraded POB indicated significant structural changes, those of PSB was quite different as the change in the broad peroxide band (3444 cm⁻¹) was unobservable within the limit of this technique (Fig. 1(b)). There were only a slight decrease in the absorbance peak of C=C stretching (near 1656 cm⁻¹), and the reduction in the peaks of cis-alkene’s C–H out of plane bending (near 436, 586 and in the range of 850–880 cm⁻¹), indicating lower degree of structural changes in PSB. Even though the FTIR spectra could confirm some changes occurred in degraded biodiesels, it was not sensitive enough for detecting trace components and overlapping peaks. Therefore, other titration techniques were used here to quantify these chemical changes through iodine, peroxide, and acid values.

3.1.2. Iodine value: IV

Iodine value is a measure of the quantity of double bonds (unsaturation) in biodiesel. As expected, the initial iodine value of POB was higher than that of PSB due to higher degree of unsaturation. From Fig. 2, the iodine values of biodiesels produced from both types of biodiesel dropped gradually in the first 3 months and more sharply afterwards. It was found that the amount of double bonds in PSB dropped by 33.6% in 6 months, which was less than that of POB (47.5%). This difference indicates that the degree of unsaturation strongly affects the biodiesel degradation rate.

![Fig. 1. FTIR spectra of fresh and degraded (a) palm olein biodiesels and (b) palm stearin biodiesels.](image)
3.1.3. Peroxide value: PV

Peroxide value indicates the amount of peroxide in biodiesel; therefore, the changes in peroxide value can be used to indicate the initial oxidation of oil. Although peroxide value is not specified in the biodiesel fuel standard, this parameter may influence methyl ester content and cetane number, parameters that are specified in the fuel standard. Increasing peroxide value increases cetane number, an effect that may reduce ignition delay time [5]. Here, the changes in peroxide values of the biodiesels are shown in Fig. 3. As can be seen, the peroxide values of both types of biodiesels increased gradually in the first 3 months and more sharply afterwards consistent with the drops of iodine values. This result confirmed that the oxygen present in the biodiesel tank reacted with the double bonds of unsaturated methyl esters to form hydroperoxide compounds (ROOH) through an oxidation process. Hydro-peroxides are unstable and can easily form a variety of secondary oxidation products which can further undergo two major types of degradation. One is fission reaction to give shorter-chain compounds and another is polymerization to longer chain [1,12–16].

3.1.4. Acid value: AV

The acid value is a measure of the amount of acidic substances in fuel. During storage, the hydroperoxide produced from the oxidative degradation can undergo the complex secondary reactions including a split into more reactive aldehydes, which further oxidize into acids, leading to an increase in acid value [4]. Another reason for the increase in acid value is the hydrolysis of methyl ester by the reaction of moisture in the ambient air with methyl ester [3,16]. As can be seen in Fig. 4, the acid values of biodiesels increased with the same trend as the peroxide values. Moreover, the acid values of biodiesel derived from palm olein were higher and increased faster than those of palm stearin. This is consistent with the higher degree of unsaturation in palm olein, which leads to higher oxidation rate.

3.1.5. Density

The densities of biodiesels (Fig. 5) also increased with storage time by the same pattern as the peroxide values. Therefore, this increase was potentially due to the increase in molecular interaction of degraded biodiesels as peroxides were formed.

3.1.6. Kinematics viscosity

Kinematic viscosity is an important property of fuel as it indicates the ability of fuel to atomize into small droplets in the combustion chamber. At the molecular level, the increase in viscosity is also an indicator for the formation of larger molecules in biodiesel. From Fig. 6, the viscosity did not increase during the 6-month period. On the other hand, the viscosities of both types of biodiesels dropped steadily during the first 3 months and slowly rose afterwards indicating that, during the period of 6 months, the oxidative degradation of biodiesel possibly led to chain scission into smaller molecules rather than forming into polymers. It is also noticeable that the drop in viscosity of POB was sharper than that of...
palm stearin counterpart consistent with the higher degree of peroxide formation in POB.

### 3.1.7. Heating value

The heating value is higher for fuel with longer chain and higher degree of saturation [17]. From Fig. 7, the heating value of POB was higher than that of palm stearin counterpart, even though palm stearin contains higher degree of saturation. This is because the major component of palm stearin shown in Table 2 contains molecules with 16 carbon atoms (C16), whereas that of palm olein comprises molecules with mostly 18 carbon atoms. With longer storage time, the heating values of the biodiesels decreased steadily consistent with the degradation of biodiesels into shorter peroxide compounds. This change led to a reduction in the percentage of carbon and hydrogen in the fuel molecules and thus lowering the heating values. For both types of biodiesels, the rates of heating value reduction were similar, which were about 0.13 MJ/month.

### 3.2. Engine performance characteristics

The engine performances of the fresh and stored biodiesels were evaluated based on brake power, brake fuel conversion efficiency, and brake specific fuel consumption by comparing with petroleum diesel. All tests were performed at various engine speeds ranging from 1800 to 4000 rpm.

#### 3.2.1. Brake power: $P$

The effect of fuel types on brake power of a diesel engine depends on several factors, including the heating value, density and viscosity. The fuel with higher heating value and higher density (higher fuel input per stroke) will provide higher brake power.

#### 3.2.2. Brake specific fuel consumption: $bsfc$

The brake specific fuel consumption rate depends largely on the heating value of the fuel. For fresh fuels, the fuel consumption rates of the biodiesels were higher than that of the petroleum diesel (Fig. 9). Therefore, to produce the same power, higher amounts of biodiesels were needed, where the palm stearin and palm olein biodiesels consumed more fuel than petroleum diesel by 5% and 4% by weight, respectively. As the biodiesels degraded, their heating values dropped even more leading to an increase in $bsfc$ by approximately 1.2 weight % per month.

#### 3.2.3. Brake fuel conversion efficiency: $\eta_{bf}$

The brake fuel conversion efficiency ($\eta_{bf}$) indicates the engine’s ability to convert chemical energy of fuel into mechanical power. From the analysis of $\eta_{bf}$, Fig. 10 shows that both types of biodiesels possessed higher fuel conversion efficiency than petroleum diesel.
by about 11%. However, within the 6-month storage, the fuel conversion efficiency decreased only slightly for degraded biodiesel.

3.3. Exhaust emissions

It is well known that biodiesels are superior to petroleum diesel in terms of more complete combustion leading to lower smoke and carbon monoxide emission but with higher NOx emission [20–22]. Here, the emission tests were carried out at a constant engine speed of 3600 rpm and various loads ranging from 0 to 30 kg. As the biodiesels degraded, the emission quality changes were as follows:

3.3.1. Black smoke and CO emissions

Black smoke and CO emissions indicate the degree of incomplete combustion. In this study, the average values of these emissions are shown in Figs. 11 and 12, respectively. Here, the percentages of black smokes and CO emissions of biodiesels were found to be 2–3 folds lower than that of petroleum diesel. This result is expected as the molecular structure of biodiesel contains oxygen atoms leading to more complete combustion compared to petroleum diesel. Comparing the two types of biodiesels, PSB provided slightly lower black smoke and CO emission than POB due to the shorter molecules of the former. Moreover, the emissions tended to decrease with storage time due to the higher oxygen contents in the degraded biodiesels.

3.3.2. Oxides of nitrogen (NOx) emission

High NOx emission usually occurs when excessive amount of oxygen is used in the combustion engine at high temperature [23]. From Fig. 13, the average values of NOx emissions for fresh biodiesels were slightly higher than that of petroleum diesel due to higher excess oxygen content. Moreover, the NOx emission of POB was slightly higher than that of the palm stearin counterpart. This is because the higher degree of unsaturation in POB leads to lower cetane number and thus higher combustion temperature and more NOx formation [20]. As the biodiesels degraded, the NOx emissions of biodiesels were increasingly higher, where the emission for POB was even higher than that for PSB. This can be explained by the higher degree of oxidation and thus higher content of oxygenated products in POB.

4. Conclusion

This study investigated the degradation effect of biodiesels in closed-lid containers at room temperature to the changes in chemical properties, engine performance, and exhaust emissions for two different types of biodiesels. From the analysis of results, the chemical properties, engine performance, and exhaust emissions were all found to be inter-related. Within the 6-month storage, the longer storage of biodiesels led to a higher degree of oxidative reaction at the double bonds of biodiesel molecules. This reaction produced shorter hydroperoxide compounds as indicated by the drop in iodine value and viscosity and the increase in peroxide and acid values leading to the drop in heating values and the increase in fuel densities. These changes in chemical properties directly affected the engine performance in that, even though the brake powers of degraded biodiesels were higher than those of fresh biodiesels, the overall fuel conversion efficiency dropped slightly together with an increase in fuel consumption rate. In terms of emissions, it was found that oxidative degradation led to a more complete combustion as the oxygen contents in the fuel molecules were higher. As a result, the black smoke and CO emissions were lower with longer storage time. However, the higher amount of excess oxygen led to the increase in NOx emission. By
comparing the two types of biodiesels, the biodiesel with longer chains provided higher fuel economy but slightly lower fuel conversion efficiency. Moreover, the biodiesels with higher degree of unsaturation will produce higher NOx emission as it degrades. It was also found that the storage time of more than 10 months for biodiesel with higher degree of unsaturation, especially with the presence of air inside the container, would create particles of potentially insoluble polymers, which could be detrimental to the fuel filtering system.

Acknowledgements

The authors would like to thank the National Research University Project of Thailand, Office of the Higher Education Commission for financial support and Pathum Oil Co. Ltd. for the biodiesels used in this study.

References