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Storage Stability of Biofuel


Centre for Energy Sciences, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

Abstract

Biofuel is one of the prime candidates to take over the role played by fossil fuel as the main source of energy in the future. Numerous studies have been done on the potential of biofuel to produce similar power output generated by the current petrol and diesel which are depleting without any drawbacks. The objective of this particular study is to investigate 4 of the more established vegetable oil in the energy industry namely jatropha, palm, coconut and canola oil in terms of storage stability of biofuel at room temperature and 80°C. The biofuels were tested in terms of density, kinematic viscosity, Total Acid Number (TAN), flash point and oxidation stability every 2 weeks for 10-12 weeks or 3 months at 2 different temperatures to obtain a conspicuous result. At the end of the experiment and test, it is found that palm oil is the biofuel with the best storage stability. The next biofuel that followed is jatropha oil, canola oil and finally coconut oil. Although palm oil showed poor kinematic viscosity, however it has good stability in terms of density, Total Acid Number (TAN) and also relatively stable oxidation and flash point in comparison with the 4 samples tested. The experiment result and data also showed that effect of continuous heating at 80°C promotes oxidation process, higher Total Acid Number (TAN), lower flash point as well as increase in density and kinematic viscosity.

Next, experimental investigations were carried out to evaluate the storage stabilities of various biodiesel fuels. The biodiesel fuels were palm methyl ester (PME), jatropha methyl ester (JME), coconut methyl ester (COME), 20% blends of PME with diesel fuel and 20% blends of JME with diesel fuel. The ordinary diesel fuel was used for comparison purposes. The biodiesels were tested in terms of density, kinematic viscosity, Total Acid Number (TAN), flash point and oxidation stability every week for 3 months. The results show that almost all fuel samples met the standard specifications regarding oxidation stability. The trends for density, viscosity and TAN increased due to oxidation. For the flash point, the trend also decreased, but the rate was very low. In overall consideration, among the biodiesel, COME was found to be better with respect to storage stabilities. The results of this investigation will be used for sustainable development of biodiesel fuel from various feedstocks.

Keywords: Biofuel, jatropha, palm, coconut, canola, storage stability, biodiesel
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Keywords: Biofuel, Jatropha, Palm, Coconut, Canola, Storage stability, Biodiesel.
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Utrecht University (Netherlands)
Storage Stability of Biofuel


Presenter: Mahendra Varman

Introduction

- **Biofuel?**
  Type of fuel whose energy is derived from biological carbon fixation – Vegetable oil, Bioalcohols, Biodiesel [Wikipedia, 2012]

- **Storage Stability?**
  In this study – oxidation stability, kinematic viscosity, density, flash point, total acid number (TAN)

Objectives

- Investigate the storage stability of different types of vegetable oil (biofuel) namely Jatropha, Palm, Coconut and Canola oil
- To study the effect of temperature (80 °C) on the storage stability of the vegetable oil (biofuel)
- Investigate the storage stability of different types of biodiesel namely Jatropha, Palm, Coconut methyl ester

Background

According to International Energy Agency (IEA):
Biofuels hold 1% of global road transportation consumption in 2006, could increase to 4% by year 2030

Biofuel development in Malaysia:
- Introduced National Biofuel Policy in 2006 by Ministry of Plantation Industries and Commodities
- Palm oil biodiesel (B5) program was officially launched on June 1st 2011
Methodology

- Vegetable oil samples stored in room temperature & heated 80°C for 10 weeks
- Biodiesel samples stored in room temperature for 10-12 weeks
- Every 2 weeks, these samples are tested for their storage stability

Terminology

<table>
<thead>
<tr>
<th>Properties</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Measure of mass per unit volume</td>
</tr>
<tr>
<td>Kinematic Viscosity</td>
<td>Measure of resistance of a fluid flow which is being deformed by either shear or tensile stress.</td>
</tr>
<tr>
<td>Total Acid Number</td>
<td>Amount of potassium hydroxide (KOH) in milligrams that is needed to neutralize the acids in one gram of oil. (Acidity)</td>
</tr>
<tr>
<td>Flash Point</td>
<td>Lowest temperature at which the vapour of a combustible liquid can be made to ignite momentarily in air. (Ignitability)</td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>Measure of an oil or fat's resistance to oxidation. (in terms of induction period)</td>
</tr>
</tbody>
</table>

Results: Density (Room Temp)

- Canola
- Coconut
- Palm Oil
- Jatropha

\[ y = 2 \times 10^{-0.05x} + 0.9085 \]
\[ y = 4 \times 10^{-0.05x} + 0.9048 \]
\[ y = 3 \times 10^{-0.05x} + 0.904 \]
\[ y = 3 \times 10^{-0.05x} + 0.8989 \]
**Results: Density (80°C)**

- $y = 0.0023x + 0.9066$
- $y = 0.001x + 0.8982$
- $y = 0.0003x + 0.905$
- $y = 0.003x + 0.905$

**Discussion**


**Results: Viscosity (Room Temp)**

- $y = 0.0372x + 47.949$
- $y = 0.0116x + 40.05$
- $y = 0.0189x + 34.929$
- $y = -0.0061x + 27.85$

**Results: Viscosity (80°C)**

- $y = 0.4839x + 36.166$
- $y = 0.5148x + 48.621$
- $y = 1.9033x + 26.264$
- $y = 1.9958x + 38.118$
- $y = 0.5148x + 48.621$
- $y = 1.9958x + 38.118$
Discussion

1. Heat accelerates the overall oxidation process. This leads to formation of Free Fatty Acid, therefore increasing the kinematic viscosity of oil

Results: TAN (Room Temp)

Results: TAN (80°C)

Discussion

1. Increase in acidity for oil samples is due to formation of peroxides which are the products of oxidation

2. Heating effect accelerates the formation of hydroperoxides which will later be oxidized into acid
Results: Flash Point (Room Temp)

\[
y = -1.2x + 244.67
\]

\[
y = -1.8x + 243.33
\]

\[
y = -0.8x + 237.33
\]

\[
y = -0.8143x + 260.57
\]

Results: Flash Point (80°C)

\[
y = -1.1143x + 260.57
\]

\[
y = -1.5714x + 244.86
\]

\[
y = -1.8x + 238.33
\]

\[
y = -1.1143x + 260.57
\]

Discussion

1. Factors that affect the flash point of biofuel are types of molecules;

   For e.g., weak dipole-dipole forces between molecules lowers the flash point of the oil sample when compared to strong hydrogen bonding interactions


2. By heating the oil, heat energy actually weakens the dipole-dipole forces between molecules of methyl ester. The end result of this is a lower flash point for oil samples heated at 80°C.

Results: Oxidation Stability (Room Temp)

\[
y = -0.2591x + 39.212
\]

\[
y = -0.3147x + 23.852
\]

\[
y = -0.1223x + 6.4014
\]

\[
y = -0.0146x + 0.1829
\]
Results: Oxidation Stability (80°C)

Discussion

1. Reason for decrease in oxidation time is due to formation of fatty acids and presence of double bond.

2. Heating decreases oxidation stability of biofuel

Experiment Summary Result for oil heated at 80°C for 10 weeks

<table>
<thead>
<tr>
<th></th>
<th>Density</th>
<th>Kinematic Viscosity</th>
<th>TAN</th>
<th>Rancimat Oxidation Test</th>
<th>Flash Point</th>
<th>Choice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola Oil</td>
<td>Excellent</td>
<td>Average</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
<td>3</td>
</tr>
<tr>
<td>Coconut Oil</td>
<td>Very Poor</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
<td>Very Poor</td>
<td>4</td>
</tr>
<tr>
<td>Jatropha Oil</td>
<td>Excellent</td>
<td>Average</td>
<td>Average</td>
<td>Very Poor</td>
<td>Average</td>
<td>2</td>
</tr>
<tr>
<td>Palm Oil</td>
<td>Good</td>
<td>Poor</td>
<td>Excellent</td>
<td>Average</td>
<td>Average</td>
<td>1</td>
</tr>
</tbody>
</table>

Effect of each property on Implications to the engine

1. Density- Affect the air-fuel ratio of the engine
2. Kinematic Viscosity- Fuel viscosity increases the fuel flow rate decreases
3. TAN- Accelerate the process of oxidation and will have an adverse effect to the engine - corrosion
4. Flash Point- Ensure ignition at the right timing and position of the piston.
5. Oxidation Stability- Oil samples that are easily oxidized promotes the formation of sediment
Objective 3: Biodiesel samples

<table>
<thead>
<tr>
<th>Fuel samples</th>
<th>Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME</td>
<td>100% Palm methyl ester</td>
</tr>
<tr>
<td>PME 20</td>
<td>20% PME and 80% Diesel</td>
</tr>
<tr>
<td>Diesel</td>
<td>100% Petroleum diesel</td>
</tr>
<tr>
<td>JME</td>
<td>100% Jatropha methyl ester</td>
</tr>
<tr>
<td>JME 20</td>
<td>20% JME and 80% Diesel</td>
</tr>
<tr>
<td>COME</td>
<td>100% Coconut oil methyl ester</td>
</tr>
</tbody>
</table>

Biodiesel properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>DIESEL</th>
<th>PME 100</th>
<th>PME 20</th>
<th>JME 100</th>
<th>JME 20</th>
<th>COME 100</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>816.18</td>
<td>843.96</td>
<td>839.15</td>
<td>864.02</td>
<td>847.32</td>
<td>843.11</td>
<td>ASTM D1298</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>cSt</td>
<td>3.63</td>
<td>4.92</td>
<td>4.61</td>
<td>4.81</td>
<td>4.49</td>
<td>3.68</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Acid value</td>
<td>mgKOH/gm</td>
<td>0.25</td>
<td>2.54</td>
<td>2.2</td>
<td>1.18</td>
<td>1.05</td>
<td>0.85</td>
<td>ASTM D664</td>
</tr>
<tr>
<td>Base value</td>
<td>mgKOH/gm</td>
<td>13.33</td>
<td>9.29</td>
<td>9.94</td>
<td>10.62</td>
<td>10.9</td>
<td>11.82</td>
<td>ASTM D2894</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>75</td>
<td>259</td>
<td>195</td>
<td>238</td>
<td>206</td>
<td>242</td>
<td>ASTM D93</td>
</tr>
</tbody>
</table>

Results: Oxidation stability

Discussion

> Among the biodiesel samples, all met with the standard specification of EN 14112 (min 6 h), except for JME and its blend
Results: Density

Discussion

1. Similar trend with increase in density

2. Increase in density is due to the formation of sediments, insolubles etc.


Results: Viscosity (40°C)

Discussion

1. Viscosity of PME increased from 4.92 to ~ 6 cSt (astm max limit = 6 cSt) after a storage time of 12 weeks (2160 h)

2. Prolonged storage leads to formation of Free Fatty Acid, therefore increasing the kinematic viscosity of oil
Results: Flash point

Discussion

1. The flash points for all biodiesel samples were adequate and above the limiting value (>93°C)

Conclusion

✓ Vegetable oil - Palm oil is the biofuel with the best storage stability
✓ Biodiesel - COME is the biofuel with the best storage stability
✓ Proper biodiesel production technology will further improve storage stability of PME, JME (e.g. acid catalyzed method)
✓ JME shows strong potential in terms of storage stability and considering its non-edible source