INVESTIGATION OF STORAGE STABILITY OF BIODIESELS

S. KOVÁCS, GY. PÓLCZMANN, J. HANCSÓK

University of Pannonia, Institute of Chemical and Process Engineering
MOL Department of Hydrocarbon and Coal Processing, Veszprém, H-8201, P.O.Box: 158, HUNGARY,
E-mail: kovacss@almos.uni-pannon.hu

The production and application of fuels from agricultural origin have emerged into focus in the last couple of years. A number of factors which affect the whole mankind has confirmed and strengthened this process, which are of environmental, political and economic nature [1].

The main reason of this tendency is the energy policy of the European Union, namely to reduce the green house gas emission of fuels, to decrease the significant dependence of EU on import energy and crude oil and to support rural development. To achieve these objectives, the European Union created the 2003/30/EC and 2009/28/EC directives, which regulate the application of biomass derived fuels. The main purpose is to promote the use of biofuels in transportation by recommending and specifying the share of the bio-components. This proposed value (10 energy % share of biofuels in the transport sector by 2020 in the EU) can be reached by the conversion of different triglyceride-containing biofeedstocks (e.g. vegetable oils, used frying oils, animal fats, algae oils, brown grease, etc.) to different biofuels or blending components. Nowadays FAME (Fatty Acid Methyl Esters), called as first generation biofuel, is mostly used as diesel bio blending component.

The chemical structure of these alternative fuels and the applied feeds determined its quality and performance properties. Due to the presence of significant amount of unsaturated fatty acids, the oxidation stability has high importance during long term storage. The amount and structure of the fatty acids and ester bonds are major factors influencing these properties outside the storage conditions [4-9].

The storage stability can be worsen due to storage conditions, such as light and air exposure, high temperature, different pollutants and the presence of water, which are catalyzing the harmful reactions. Hydroperoxides are formed during these oxidation reactions and they react with other free radicals. Insoluble deposits and gums are formed in these reactions too. These degradation products in engine causing operational problems; like fuel filter plugging, injector fouling and deposit formation in engine combustion chamber. This increase the kinematic viscosity of the degraded fatty acid methyl ester samples. The products of the primary oxidation reaction they can be further oxidised to form aldehydes, ketones and shorter chain fatty acids. These compounds cause corrossions in the injection system (Fig. 1).

Keywords: biodiesel, storage stability, oxidation stability, Rancimat method
Figure 1: Mechanism of the biodiesel oxidation process

However, the natural antioxidants can prevent or delay these reactions [4, 5]. Storage stability of biodiesel is its ability to resist degradation in contact with environment and storage conditions. The preservation of this during storage is an important issue for the viability and sustainability of the biodiesels [5, 10, 11].

Table 1: The main properties and the fatty acid composition of the biodiesel samples

<table>
<thead>
<tr>
<th>Property</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>EN 14214</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, 15 °C, kg/m³</td>
<td>883.2</td>
<td>884.9</td>
<td>883.7</td>
<td>860–900</td>
</tr>
<tr>
<td>Sulfur content, mg/kg</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>max. 10</td>
</tr>
<tr>
<td>Kinematic viscosity, 40°C, mm²/s</td>
<td>4.523</td>
<td>4.473</td>
<td>4.400</td>
<td>3.5–5.0</td>
</tr>
<tr>
<td>Acid value, mgKOH/g</td>
<td>0.09</td>
<td>0.08</td>
<td>0.35</td>
<td>max. 0.5</td>
</tr>
<tr>
<td>Iodine value, gl/100g</td>
<td>112</td>
<td>83</td>
<td>101</td>
<td>max. 120</td>
</tr>
<tr>
<td>Water content, mg/kg</td>
<td>101</td>
<td>256</td>
<td>420</td>
<td>max. 500</td>
</tr>
<tr>
<td>Fatty acid composition, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>palmitic acid C16:0</td>
<td>4.9</td>
<td>2.4</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>palmitoleic acid C16:1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>stearic acid C18:0</td>
<td>1.5</td>
<td>2.5</td>
<td>1.7</td>
<td>-</td>
</tr>
<tr>
<td>oleic acid C18:1</td>
<td>61.5</td>
<td>91.8</td>
<td>75.5</td>
<td>-</td>
</tr>
<tr>
<td>linoleic acid C18:2</td>
<td>21.2</td>
<td>1.2</td>
<td>12.3</td>
<td>-</td>
</tr>
<tr>
<td>linolenic acid C18:3</td>
<td>8.1</td>
<td>0.6</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>arachidic acid C20:0</td>
<td>0.6</td>
<td>0.8</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>gondoic acid C20:1</td>
<td>1.3</td>
<td>0.5</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>behenic acid C22:0</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>erucic acid C22:1</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>lignoceric acid C24:0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 2: Schematic of Rancimat test
Results and discussion

During our experimental work the effect of real storage conditions on the physical and chemical properties of the different biodiesels were investigated. The ambient temperature fluctuations and the contact with the air in case of sampling had effect to the samples. The analytical measurements were carried out in every second week.

Oxidation stability – induction period

The biodiesel samples originated from different sources showed different induction periods, but always decreased. The difference in the measurement results is due to the different fatty acid compositions (the different raw material). The sample A was found below the minimum induction period (6 h) after 25 weeks. The other two samples (B and C) satisfied the oxidation stability requirements of the valid standard after 30 weeks (Fig. 3).

Acid value

As expected, the experimental results showed an increasing trend in case of all samples but none of the samples exceeded the requirement of the standard 0.5 mg KOH/ g (Fig. 4).

Iodine value

The iodine value is in context with the number of the double bonds of the hydrocarbons. In case of biodiesels shows how the material is prone to polymerization and form deposits in the storage vessels and in the engines. The iodine value of the samples decreased gradually (Fig. 5). This indicates the decrease of the number of double bonds and the progress of the deterioration (the polymerization reaction). The reason of the iodine value differences was the different fatty acid composition. The observed slight decrease of iodine number in the case of biodiesel “B” due to the lower amount of polyunsaturated fatty acids (1.8%) (Table 1).
Water content

Water in biodiesel can initiate hydrolysis reactions, could increase the microbial contamination and the risk of emulsification. Based on the water content of the biodiesel samples it can be concluded that it showed increasing trend in all cases (Fig. 6).

Density

According to the literature the change of the density correlates well the changes during the storage. Based on the measurement results we did not find a clear trend. However in case of all sample the measured density satisfied the valid standard (Fig. 7).

The change of the density does not reflect the results of the Rancimat method. This measurement is not suitable for tracking the biodiesel degradation. But this is a standard property and it is important to do the test periodically.

Kinematic viscosity

Based on the results of the viscosity measurement we did not find clear tendency (Fig. 8). The values are satisfied the requirements of the valid standard in all cases. The change of the viscosity does not reflect the results of the Rancimat method. But this is a standard property and it is important to do the test periodically.

Summary

The main objections of our biodiesel long term storage stability experiments are the followings:

- The biodiesel samples originated from different sources showed different induction periods, but in every case it decreased. Based on the experimental results we concluded that the storage stability of the biodiesel samples largely dependent of the initial storage stability of the samples. It is no coincidence that the EN 14214 standard is recommended the addition of stabilizers to improve the oxidation stability of FAME immediately after production or before blending to fossil gas oils.
• The storage stability of samples the better their polyunsaturated fatty acids content are smaller.
• The acid value is an excellent feature of the biodiesel quality change because the formed acidic components gave information about the rate of hydrolysis and oxidation reaction. The experimental results are correlating with will the results of Rancimat test.
• The water content of the biodiesel samples showed increasing trend in all cases.
• In case of density and viscosity the measurement results did not show clear trends. The change of these properties does not reflect the results of the Rancimat method.

In case of the investigation of long term storage stability of biodiesel the history of the samples can be a important information.

ACKNOWLEDGMENTS

“This work was supported by the European Union and co-financed by the European Social Fund in the frame of the TAMOP-4.2.1/B-09/1/KONV-2010-0003 and TAMOP-4.2.2/B-10/1-2010-0025 projects.”

REFERENCES