Thermal Analysis of Biodiesel from Palm Oil, I.

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Biodiesel has many merits as renewable energy resource; thereby biodiesel relieving reliance on petroleum fuel, and it is biodegradable and non-toxic. This paper presents the thermal analysis (TG and DSC thermograms) of biodiesel (fatty acid methyl esters - FAME) from palm oil. FAMEs are obtained in various reaction conditions. The biodiesel is synthesized by alkali-catalyzed transesterification of palm oil with methanol (molar ratio oil: alcohol is 1:6). Potassium hydroxide was used as a catalyst. TG and DSC thermograms provide information on thermal stability and phase and physical transformations of biodiesel.

Keywords: biodiesel, FAME, alkali-catalyzed transesterification, thermograms

The production of biodiesel has recently received much attention worldwide. Follow the world energy crisis; many countries have started programs to resolve this problem. Finding alternative energy resources is a pressing mission for many countries, especially for those lacking conventional resources. In the 1930’s and 1940’s, vegetable oils have been used as diesel fuels in the emergency situations. With the rapid development of the modern industry, the demand for energy has been greatly increased in recent years, and therefore alternative energy sources are being explored. Thus, the term “biodiesel” has appeared frequently in several reports [1-4].

Biodiesel is obtained by the alkali-catalyzed transesterification of the vegetable oils or natural fats with an alcohol. Three consecutive reactions are required to complete the transesterification of a triglyceride molecule (scheme 1). The transesterification reaction requires a catalyst to achieve reasonable conversion rates. A base catalyst, such as sodium or potassium hydroxide is preferred. Usually methanol is used as alcohol in the transesterification, but ethanol is also suitable for this purpose [5-8].

Biodiesel belongs to ecological fuels for the reason of its composition: carbon 77%, hydrogen 12%, oxygen 11%, only traces of nitrogen and sulfur being present [12-13].

In the last few years, thermal analyses (TG - thermogravimetry, DSC - differential scanning calorimetry) have become very important as sources of useful data; for example founding their thermal stability. Such techniques have also been employed for biodiesel characterization [14]. Only few reports describe the use of this technique for liquid fuels; these papers report results on sunflower oil, palm oil, cotton oil biodiesel and corn oil biodiesel [15-19].

This paper presents the synthesis and the thermal analysis of biodiesel from palm oil. The TG and DSC data provides information on the thermal stability and phase and physical transformations. Also, DSC diagrams provide information on the cloud point of biodiesel (the temperature, at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance).

Experimental part

Materials

Commercial palm oil “Olina”, absolute methanol (Merck), potassium hydroxide as powder (Merck), calcium chloride (Merck), methyl linoleate (Merck), methyl oleate (Merck), methyl palmitate (Merck), methyl stearate (Merck) were used.

Syntheses

Palm oil is put into a flask (fitted with magnetic stirring and thermometer) and is heated at a required temperature. Potassium hydroxide powder is dissolved separately into methanol and then added to the oil. The mixture is stirred at the reaction temperature a determined time. Then the reaction is stopped and the flask content is placed into a separation funnel. The inferior darker layer (containing glycerin and impurities) is removed. The ester is washed several times with water (to remove traces of glycerin). Calcium chloride is added as drying agent and after 24h at room temperature the ester is filtered. Table 1 lists the acronyms and the reaction conditions for each sample of biodiesel.
Characterization of biodiesel

The thermal analyses of biodiesel were performed using Netzsch TG 209, in nitrogen atmosphere at temperatures ranging from 20 to 500°C with a heating rate of 5 K/min) and Netzsch DSC 204, in nitrogen atmosphere at temperatures ranging from -100°C to 100°C with a heating rate of 5 K/min. The data were collected and processed using Proteus – Thermal Analysis data system, from Netzsch.

Results and discussions

Biodiesel from palm oil is a mixture with the mean composition: methyl linoleate (10.1%), methyl oleate (40.5%), methyl palmitate (42.6%), methyl stearate (4.4%) and others (2.4%) [20].

DSC analysis

DSC diagrams for methyl linoleate, oleate, palmitate and stearate standards are shown in figure 1. Each standard shows a single transition temperature, which is characteristic for each compound [21]. The transition temperature of methyl linoleate is around -88°C. Methyl oleate is different because it shows two transition temperatures revealed by two peaks, an exothermic one (-33.0°C) and an endothermic one (-23.4°C). The exothermic peak is associated with a molecules rearrangement and the endothermic peak is associated with a physical transformation. Methyl linoleate and methyl oleate have transition temperatures below 0°C, while methyl palmitate and methyl stearate present peaks in the area of positive temperatures. The transition temperature of methyl palmitate is at 31.9°C and that of methyl stearate is at 41.0°C.

As can be seen, palm oil biodiesel presents four transition temperatures corresponding to each peak (fig. 2). The transition temperatures for the different biodiesels synthesized are presented in table 2. The first transition temperature is around -50°C and it is associated with methyl oleate. The second and the third transition temperatures correspond to methyl oleate and it is around -50°C for the exothermic peak and around -30°C for the endothermic peak. The fourth transition temperature is around 10°C and it is associated with methyl palmitate. Transition temperatures corresponding to the three methyl esters of fatty acids from biodiesel are lower compared to those of the standards. This is well thought-out to be the result of interaction between the components of the mixture of these methyl esters. Thereby, methyl linoleate is the first component of the mixture which suffers a transition and it becomes a solvent for the next (methyl oleate) and the two together become the solvent for the third one (methyl palmitate). The transition temperature of the methyl palmitate in the mixture is around 10°C in comparison with the standard transition temperature, which is around 32°C. The lower transition temperatures of the mixture are an advantage for biodiesel. The last transition temperature of the mixture being around 10°C, let us to conclude that the cloud point of biodiesel must be almost the same. Palm oil biodiesel has the cloud point quite high because his major compound (methyl palmitate) is solid. Cloud point of biodiesel should be as small so that not to create problems to the engine in cold season. High cloudy point leads to clogged injectors.

As we have seen beforehand in the case of biodiesel synthesized at different reaction time, for the palm oil biodiesel obtained with different amounts of catalyst we

<table>
<thead>
<tr>
<th>Sample</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>CP1</th>
<th>CP2</th>
<th>CP3</th>
<th>CP4</th>
<th>TP1</th>
<th>TP2</th>
<th>TP3</th>
<th>TP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>t [min]</td>
<td>30</td>
<td>45</td>
<td>60</td>
<td>75</td>
<td>90</td>
<td>105</td>
<td>120</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>T (°C)</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>45</td>
<td>50</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>Ac (%)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25</td>
<td>0.75</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Where: t = reaction time; T = reaction temperature; Ac = amount of catalyst (weight of KOH/weight of oil); MR = molar ratio oil: alcohol

Table 1

THE ACRONYMS AND THE REACTION CONDITIONS FOR EACH SAMPLE OF BIODIESEL

Fig. 1. DSC diagrams for methyl linoleate, methyl oleate, methyl palmitate, methyl stearate standards
can distinguish four peaks associated with the three methyl esters (fig. 3). The sample CP4 behaves differently from the others because of the absence of the peak from -90°C corresponding to the methyl linoleate and also the peaks are less emphasized. This is explainable because the sample CP4 had a lower conversion in methyl esters due to the large amount of catalyst used in reaction. A large amount of catalyst causes the formation of fatty acid

![Fig. 2. DSC diagrams for the samples P1, P2, P5](image)

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak₁ (°C)</th>
<th>Peak₂ (°C)</th>
<th>Peak₃ (°C)</th>
<th>Peak₄ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>-92.0</td>
<td>-54.0</td>
<td>-31.7</td>
<td>9.7</td>
</tr>
<tr>
<td>P2</td>
<td>-92.5</td>
<td>-51.4</td>
<td>-35.4</td>
<td>8.1</td>
</tr>
<tr>
<td>P3</td>
<td>-91.8</td>
<td>-52.2</td>
<td>-36.9</td>
<td>10.7</td>
</tr>
<tr>
<td>P4</td>
<td>-91.9</td>
<td>-52.0</td>
<td>-35.4</td>
<td>10.6</td>
</tr>
<tr>
<td>P5</td>
<td>-92.3</td>
<td>-52.1</td>
<td>-35.3</td>
<td>10.6</td>
</tr>
<tr>
<td>P6</td>
<td>-91.9</td>
<td>-53.8</td>
<td>-30.8</td>
<td>12.9</td>
</tr>
<tr>
<td>P7</td>
<td>-91.7</td>
<td>-53.9</td>
<td>-34.3</td>
<td>14.7</td>
</tr>
</tbody>
</table>

![Fig. 3. DSC diagrams for the samples CP2, CP3 and CP4](image)
potassium salts (soap) and that is why during the phase separation a foaming effect occurred.

DSC diagrams for palm oil biodiesel at different reaction temperatures are presented in figure 4. TP3 and TP4 show obviously peaks associated with the three methyl esters, while the peaks for TP1 and TP2 are less emphasized and the first peak corresponding to the methyl linoleate are missing. This can be explained by the fact that at lower reaction temperatures (40-50°C), the reaction is not

Table 3
DATA FROM TG TERMOGRAMS FOR P1 – P7

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss (%) from 20°C to</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
<td>200°C</td>
</tr>
<tr>
<td>P1</td>
<td>0.04</td>
<td>7.36</td>
</tr>
<tr>
<td>P2</td>
<td>0.20</td>
<td>16.13</td>
</tr>
<tr>
<td>P3</td>
<td>0.20</td>
<td>15.93</td>
</tr>
<tr>
<td>P4</td>
<td>0.40</td>
<td>16.41</td>
</tr>
<tr>
<td>P5</td>
<td>0.14</td>
<td>14.25</td>
</tr>
<tr>
<td>P6</td>
<td>0.14</td>
<td>16.42</td>
</tr>
<tr>
<td>P7</td>
<td>0.07</td>
<td>15.91</td>
</tr>
</tbody>
</table>

Fig. 4. DSC diagrams for the samples TP1 - TP4

Fig. 5. TG termograms for CP2, CP3, CP4
complete and the conversion is lower than at higher temperature (55-60°C).

**TG analyses**

All TG curves of biodiesel from palm oil obtained at different reaction times have a single inflection point, so weight loss occurred in a single step. Table 3 presents the weight losses on temperatures ranging from 20 to 500°C and the temperatures of the inflections points for biodiesel. We can note that for most samples weight loss is approximately 100% until 400°C, except for P1. Weight loss at 400°C for P1 is only 93%, its total weight loss occurs around 450°C. This is expected because a reaction time of 30 min is not sufficiently for a complete transesterification reaction. Therefore, the temperature corresponding to the inflection point is significantly higher than for the others.

As results from table 4, the weight losses on temperatures ranging from 20 to 500°C and the temperatures corresponding to the inflection points for palm oil biodiesel obtained at different reaction temperature are presented in table 5. The fact that weight loss for TP1 and TP2 occurs in two steps is explainable because at lower reaction temperatures, the transesterification reaction has a low conversion. In comparison with TP2, the total weight loss for TP1 required a higher temperature. In comparison with the others samples of biodiesel for which the weight loss around 400°C is 99%; at this temperature TP1 lost only 93% of its total weight. We can conclude that with the decreases of the reaction temperature, the temperature required for a total weight loss increases.

**Conclusions**

Palm oil biodiesel was synthesized under different reaction condition.

From TG thermograms we found that almost all the mixtures of methyl esters present a weight loss of approximately 100% until 400°C. This weight loss occurs in a single step and the temperature of the inflection point is around 240°C. Exceptions are biodiesels synthesized at shorter reaction time, lower temperature and those synthesized using an excessive amount of catalyst. These biodiesels present two inflection points, so a two steps weight loss.

TG termogravimetric data are important because they allow an estimation of the thermal stability of biodiesel, which helps us to find optimal condition of storage and handling.

Comparing the DSC diagrams of different biodiesels with those of standards, we found displacement of the peaks, which are caused by a solvent effect of the melted components in the mixture. We should note also that the cloud point of the biodiesel is estimated to be last transition temperature (7 to 15°C).
DSC diagrams give us information about the phase and physical transformation of biodiesel, allowing an assessment on his behavior at low temperatures.

References
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