Thermal Analysis of Biodiesel from Soybean and Sunflower Oils. II.

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Biodiesel is an attractive energy resource because it comes from renewable resources. It is biodegradable and nontoxic, obviously decreasing emissions of greenhouse gases. Soybean and sun-flower oils are alkali-catalyzed transesterified with methanol (the molar ratio oil: alcohol is 1:6) in different conditions of reaction in order to obtained biodiesel (Fatty Acid Methyl Esters). As a catalyst, potassium hydroxide is used. In this paper is presented the thermal analyses of soybean and sun-flower FAME (Fatty Acid Methyl Esters). TG and DSC thermograms of biodiesel allow an assessment on his behavior at different temperatures which helps us to establish optimal condition of storage and handling.

Keywords: thermograms, TG, DSC, FAME

Biodiesel appears to be an attractive energy resource for several reasons. First, biodiesel has a renewable raw material for energy that could be sustainably supplied. It is believed that the petroleum reserves will be depleted in less than 50 years, if the present rate of consumption is maintained. Second, biodiesel appears to have several favorable environmental properties resulting in no net increased release of carbon dioxide and very low sulfur content. The release of sulfur content and carbon monoxide would be cut down by 30% and 10%, respectively. Using biodiesel as energy source, the gas generated during combustion could be reduced, and the decrease in carbon monoxide is owing to the relatively high oxygen content in biodiesel. Moreover, biodiesel contains no aromatic compounds and other chemical substances which are harmful to the environment. Recent investigation has indicated that the use of biodiesel can decrease 90% of air toxicity and 95% of cancers compared to common diesel source. Third, biodiesel appears to have significant economic potential because as a non-renewable fuel the fossil fuel price will increase inescapably further in the future. Finally, biodiesel is better than diesel fuel in terms of flash point and biodegradability [1-9].

Biodiesel is obtained by the alkali-catalyzed trans-esterification of the vegetable oils or natural fats with an alcohol, in three consecutive steps. The transesterification reaction requires a catalyst in order to obtain reasonable conversion and rates. Base catalysis such as sodium or potassium hydroxide is preferred, due to the lower prices. The alcohol usually employed in the transesterification is methanol, but ethanol can be also used [9-14].

In the last few years, thermal analyses (TG - thermo-gravimetry, DSC - differential scanning calorimetry) have become very important supply of useful data e.g., the evaluation of thermal stability. Such techniques are now used for biodiesel characterization [15-20].

This paper presents the synthesis and the thermal analysis of biodiesel from soybean and sun-flower oils. 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, which give to the fluid a cloudy appearance).

Experimental part

Materials

Commercial soybean oil *Pietro Coricelli* and comercial sun-flower oil *Floriol*, absolute methanol (Merck), potassium hydroxide (Merck), calcium chloride (Merck), methyl linoleate (Merck), methyl oleate (Merck), methyl palmitate (Merck), methyl stearate (Merck) were used.

Syntheses

Soybean oil or sun-flower 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) is removed. The ester is

Sample	S1	S2	S3	S4	S5	S6	S7	CS1	CS2	CS3	CS3	TF1	TF2	TF3	TF4
t [min]	30	45	60	75	90	105	120	45	45	45	45	45	45	45	45
T (°C)	50	50	50	50	50	50	50	55	55	55	55	45	50	55	60
Ac (%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.5	0.75	1.0	0.5	0.5	0.5	0.5
RM	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6	1:6

Where: t = reaction time; T = reaction temperature; Ac = amount of catalyst (weight of KOH/weight of oil); MR = molar ratio oil: alcohol; S1-S2 and CS1-CS4 are samples of biodiesel from soybean oil; TF1-TF4 are samples of biodiesel from sun-flower oil.

Table 1
THE NOTATIONS AND THE REACTION CONDITIONS FOR EACH SAMPLE OF BIODIESEL

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washed several times with water (to remove traces of glycerin). Calcium chloride is added as drying agent and after 24 h at room temperature the ester is filtered. Table 1 lists the notation 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 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 soybean oil is a mixture of methyl linoleate (56.2%), methyl oleate (23.2%), methyl palmitate (13.9%), methyl stearate (2.1%) and others (4.6%). Biodiesel from sun-flower oil is a mixture of methyl linoleic (72.9%), methyl oleate (17.7%), methyl palmitate (6.4%), methyl stearate (2.9%) and others (0.1%) [21].

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 [22 ,23]. 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, soybean oil biodiesel presents four transition temperatures corresponding to each peak (fig. 2). In table 2 are presented the transition temperatures for biodiesel synthesized at different reaction times. The first transition temperature is around -88°C and it is associated with methyl linoleate. The second and the third transition temperatures corresponds to methyl oleate and it is around -70°C for the exothermic peak and around -50°C for the endothermic peak. The fourth transition temperature is around -4°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 considered 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 from the mixture is around -4°C in comparison with the transition temperature of the standard, which is around 32°C. The lower transition temperatures of the mixture are an advantage for biodiesel. The fact that the last transition temperature of the mixture is around -4°C allows us to conclude that the cloud point of biodiesel must be almost the same. Cloud point of biodiesel should be as small as not to create problems in the engine in cold weather. High cloud point leads to clogged nozzles.

It is noted that S2 has the lowest cloud point (-4.7°C). This sample presented the best yield in methyl esters. S1 has a different behavior from the others because this sample presents less emphasized peaks. This is predictable because this sample has been obtained at a reaction time of 30 min. This reaction time leads to a low conversion on methyl esters. We can notice that the cloudy point presents a slight increase if the reaction time is higher or less than 45 min.

DSC diagrams of biodiesel from soybean oil using various amounts of catalyst are similar to those from figure 2. Table 3 presents the transition temperatures obtained from DSC diagrams. As the biodiesel from soybean oil produced at different reaction times the biodiesel from soybean oil obtained with different amounts of catalyst also presents four significant peaks. First peak temperature is around -88°C and is associated with methyl linoleate which is the major compound of soybean oil biodiesel. The second and third peaks correspond to methyl oleate. Methyl palmitate is represented by the fourth peak. For an amount of catalyst

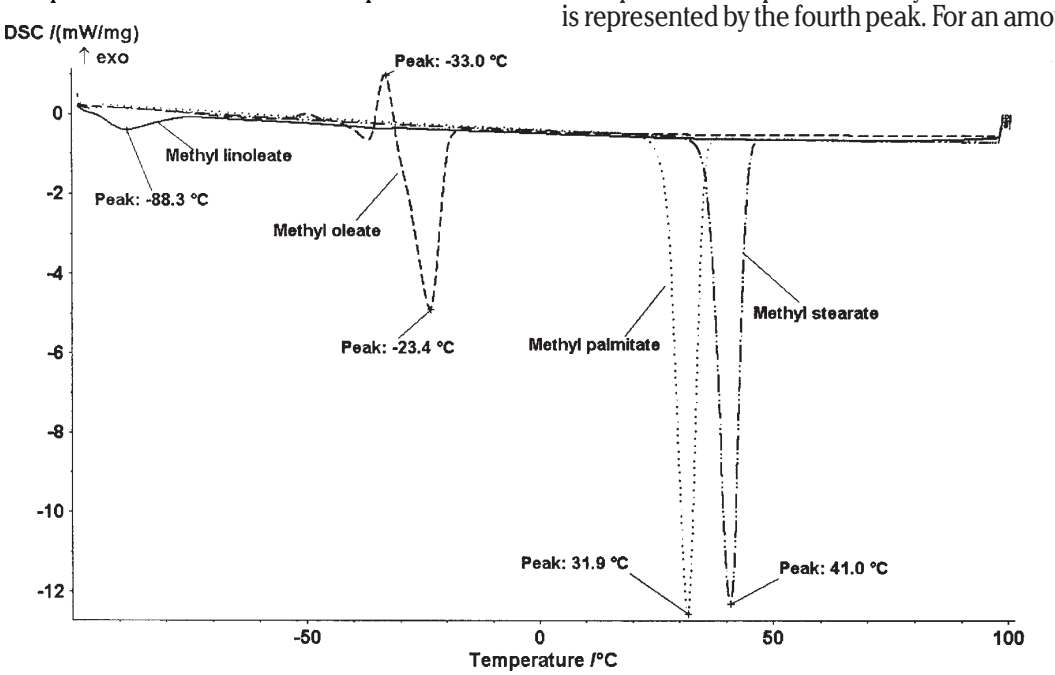

Fig. 1. DSC diagrams for methyl linoleate, methyl oleate, methyl palmitate, methyl stearate standards

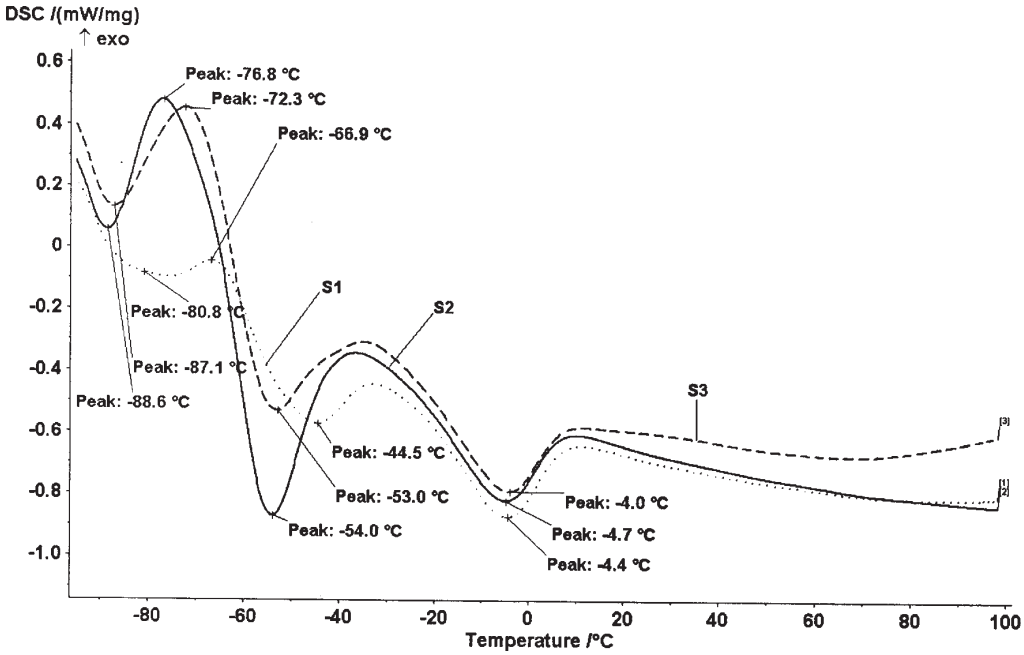

Fig. 2. DSC diagrams for S1-S3 samples

Table 2

DSC DATA FOR THE SAMPLES S1 - S7

Sample	$Peak_1$ (°C)	$Peak_2$ (°C)	$Peak_3$ (°C)	$Peak_4$ (°C)
S1	-80.8	-66.9	-44.5	-4.4
S2	-88.6	-76.8	-54.0	-4.7
S3	-87.1	-72.3	-53.0	-4.0
S4	-84.4	-68.6	-42.2	-3.7
S5	-89.5	-78.7	-54.9	-3.8
S6	-81.5	-66.6	-42.2	-3.5
S7	-79.7	-70.2	-42.4	-3.6

larger or less than 0.5%, the transition temperature of each methyl ester increases. Thus we concluded that the cloud point of biodiesel increases with the increases of the catalyst amount. This can be explained by the fact that increasing of the catalyst amount leads to the formation of fatty acids potassium salts (soap). This soap causes a foaming effect during the separation process and for this reason the methyl ester yield decrease. The higher cloud point is for the biodiesel obtained with a catalyst amount of 0.25%, because in this case the reaction is incomplete. Comparing biodiesel produced at different reaction time (reaction temperature 50°C) and biodiesel obtained using different amounts of catalyst (reaction temperature 55°C); we can note that the transition temperature is lower in the second case because the conversion in methyl esters is slightly lower at lower reaction temperatures.

Table 3

DSC DATA FOR THE SAMPLES CS1 – CS4

Sample	$Peak_1$ (°C)	$Peak_2$ (°C)	$Peak_3$ (°C)	$Peak_4$ (°C)
CS1	-87.0	-64.8	-44.7	-3.1
CS2	-88.3	-77.3	-57.8	-8.6
CS3	-86.6	-69.4	-53.7	-5.9
CS4	-86.2	-66.6	-50.1	-5.2

DSC diagrams of biodiesel from sun-flower oil are almost similar to those of biodiesel from soybean oil (fig. 2). This is well thought-out to be the result of their composition, which is almost similar. In table 4 are shown the data obtained from DSC diagrams of biodiesel from sunflower oil obtained at different reaction temperatures. The four peaks are characteristics for the three major methyl esters. Cloud point of sunflower oil biodiesel is slightly lower than that for the biodiesel from soybean oil. This is reasonable because sunflower oil contains a higher quantity of methyl linoleate and a smaller quantity of methyl palmitate than soybean oil. Also, we can note that the cloud point of biodiesel decreases slightly with the increasing of the reaction temperature.

Table 4

DSC DATA FOR THE SAMPLES TF1 – TF4

Sample	$Peak_1$ (°C)	$Peak_2$ (°C)	$Peak_3$ (°C)	$Peak_4$ (°C)
TF1	-86.3	-57.9	-46.4	-7.0
TF2	-87.4	-62.0	-49.8	-7.4
TF3	-87.6	78.3	-52.9	-9.0
TF4	-86.9	79.8	-49.0	-9.4

TG analyses

The weight losses on temperatures ranging from 20 to 500°C and the temperatures of the inflection points of soybean oil biodiesel obtained from various reactions times are presented in table 5. All TG curves of biodiesel obtained have a single inflection point, so the weight loss occurs in a single step. It is noted that the most samples present a weight loss of approximately 100% until 400°C, except S1. The weight loss at 400°C for S1 is 95% and the total weight loss occurs around 450°C. Is expected because this sample of biodiesel has been obtained at a reaction time of 30 min and this reaction time is not enough for a complete transesterification reaction. The temperature of the inflection point of this sample is slightly higher than for the others.

Sample	Weight loss (%) from 20°C to						Temperature (°C)
	100°C	200°C	300°C	400°C	450°C	500°C	Inflection
S1	0.04	14.90	90.05	95.22	99.09	99.72	255.0
S2	0.01	12.04	92.28	99.54	100.00	100.00	243.5
S3	0.07	11.87	92.92	99.33	100.00	100.00	241.9
S4	0.03	12.42	90.45	99.27	99.99	100.00	243.8
S5	0.22	15.73	95.38	99.39	100.00	100.00	240.8
S6	0.15	9.44	90.05	99.25	99.97	100.00	242.0
S7	0.24	18.41	93.01	99.52	100.00	100.00	239.8

Table 5
DATA FROM TG
TERMOGRAMS FOR S1 –S7

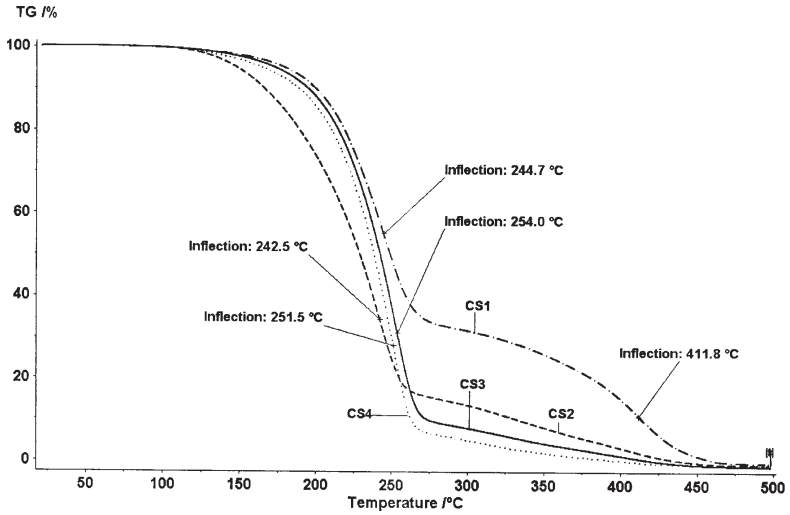

Fig. 3. TG termograms for CS1-CS4

Sample	Weight loss (%) from 20°C to						Temperature (°C)	
	100°C	200°C	300°C	400°C	450°C	500°C	Inflection 1	Inflection 2
CS1	0.22	10.02	68.36	84.95	98.79	100.00	244.8	411.7
CS2	0.26	26.00	86.63	98.75	100.00	100.00	242.5	-
CS3	0.19	11.86	92.24	98.85	100.00	100.00	254.1	-
CS4	0.25	14.19	95.10	99.98	100.00	100.00	251.5	-

Table 6
DATA FROM TG TERMOGRAMS
FOR CS1 – CS4

Sample	Weight loss (%) from 20°C to						Temperature (°C)
	100°C	200°C	300°C	400°C	450°C	500°C	Inflection 1
TF1	0.10	12.95	83.10	94.08	99.39	99.97	246.9
TF2	0.29	24.6	84.89	94.19	99.89	99.96	241.0
TF3	0.18	11.63	84.70	95.43	100.00	100.00	249.4
TF4	0.25	13.63	85.93	96.89	100.00	100.00	244.5

Table 7
DATA FROM TG TERMOGRAMS
FOR TF1 – TF4

It is evident that CS2, CS3 and CS4 present a single inflection point, so the weight loss occurs in a single step around 400°C (fig. 3). In table 6 are presented the weight losses on temperatures ranging from 20 to 500°C and the temperatures of the inflections points for soybean oil biodiesel obtained with different amounts of catalyst. The weight loss for CS1 occurs in two steps. The first inflection point is around 244.8°C and the second inflection point at 411.7°C. For this sample at 400°C the weight loss is only 85%, the total weight loss occurs at 500°C. This is predictable because in this case we used a smaller amount of catalyst and the conversion is lower. Therefore the total

weight loss for CS1 occurs in two steps and at a higher temperature than others.

TG termograms for the sun-flower oil biodiesel are similar with those for the soybean oil biodiesel (fig. 3). This fact is explainable because the two tips of biodiesel are of similar composition. In table 7 are presented the weight losses on temperatures ranging from 20 to 500°C and the temperatures of inflection points of sunflower oil biodiesel obtained at different reaction temperatures. It may be noted that all samples have a single inflection point, so the weight loss occurs in a single step. The fact that the total weight loss for TF1 and TF2 requires higher temperatures than the weight loss for TF3 and TF4 is explainable because the lowers temperatures of reaction give a lower conversion. We conclude that an increased reaction temperature decreases the temperature required for the total weight loss, too.

Conclusions

Soybean oil and sun-flower oil biodisel was synthesized under different reaction conditions.

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. Also we should note the cloud point of soybean oil biodiesel (3.5 and -8.6°C) and the cloud point sunflower oil biodiesel (-7.0 and -9.4°C) is estimated to be the last transition temperature. DSC diagrams give us information about the phase and physical transformation of biodiesel, thereby allowing an assessment on his behaviour at low temperatures.

From TG thermograms we found that most mixtures of soybean oil and sun-flower oil methyl esters presents a single step weight loss around 400°C. An exception is soybean oil biodiesel synthesized at a reaction time of 30 minutes and the soybean oil biodiesel for which has been used a catalyst amount of 0.25%. Analyzing the TG thermograms of sunflower oil and soybean oil biodiesel can be concluded that the temperature required for the total weight loss for the sun-flower oil biodiesel is higher than that for the soybean oil biodiesel.

TG termograms data are important because they allow a regarding on the thermal stability of biodiesel, which helps us to establish optimal condition of storage and handling.

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