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Chapter 12

Thermoanalytical Methods in Verifying the Quality of Biodiesel

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/59479

1. Introduction

Fossil fuels (petrol, coal and natural gas) are nowadays the main used energy source to move most part of overland, aquatic and air means of transportation, likewise several industries and even public lighting [1]. Petrol is the most used raw material among these energetic resources, as it is a limited energetic source there is a great concern toward substituting it, petrol shows unstable price and its unbalanced distribution has even caused wars. The global petrol reserves had reached 1,668.9 billion gallons in the end of 2012, enough to guarantee 53 years of the worldwide energy production. The dada is in the annual statistic report, 2013 edition, by BP (multinational enterprise headquartered in United Kingdom, which operates in the energetic sector, mainly petrol and natural gas) thus a reference document to the sector. According to the study, throughout the last decade, global petrol reserves have increased 26%. Other Opep countries are still top ranking, controlling worldwide petrol reserves [2].

There also is the environmental concern to restraining the current climatic changing process caused mainly by CO_2, methane and nitrogen oxides. The current scientific and technological development context aims to emerge new technologies and the global goal of transiting to a sustainable economy [3].

However, Brazil, as well as other countries, is facing a severe energetic crisis due to the fuel consumption increase, either for production and for fuel consumption as for petrochemical industry. Likewise the climatic changes have caused long drought periods in months that supposedly had great quantity of rain. Each of these factors contribute to focusing efforts to establish alternative sources effectively applicable in energy production.

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One way is the use of resources produced by agribusiness [3]. This transition to sustainability was mainly determining the need or strategic interest to replace oil with other materials. Vegetable oils as alternative fuels have begun being studied in the late nineteenth by Rudolph Diesel, inventor of the internal combustion engine century, and these were used in natura. But the direct use in engines came up with many problems, for example, oily material accumulation in the injection nozzles, the incomplete oil burnt, coal deposit formation in the combustion chamber, low power efficiency and, as a result of firing, the release of acrolein (propenal) which is toxic. Studies of alternatives have been considered for best performance of vegetable oils in diesel engines, for example, dilution, micro-emulsion with methanol and ethanol, catalytic cracking and trans-esterification reaction with short alcohols chains. Among these alternatives, the trans esterification reaction has been the most used, since the process is relatively simple and the product (biodiesel) has properties similar to those of petro diesel, such as viscosity and density [4].

Biodiesel can be produced from a variety of materials. These raw materials include most vegetable oils (soybean oil, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut oil) and animal fats (tallow) and discard oil (frying oils). The raw material choice for biodiesel production depends largely on geographical factors. Depending on the origin and quality of the raw material, changes in the production process may be required [5].

One of the great advantages of using biodiesel as fuel is linked to the environmental benefits; it has some features that represent advantages over petroleum-based fuels, such as absence of aromatics and sulfur; high cetane amount; average oxygen content; higher flash point; lower pollutants emission and good lubricity. Another advantage of biodiesel is the substitution of those in diesel engines without the need for any modifications to the engine [6].

The petroleum oils are stable at distillation temperature, even in the presence of excess oxygen. Unlike vegetable oils containing unsaturated compounds, the oxidation reaction can be observed up to room temperature and the temperature close to 250 °C because of the additional thermal decomposition reactions, leading to the formation of polymeric compounds by condensation reaction [7].

Toward such facts, the current context of scientific and technological development aimed at the emergence of new technologies and feasibility of application throughout the shortest time, as well as innovations that allow the search for global goal of transition to a sustainable economy. For this purpose, a possible alternative would be to replace the fossil diesel for biodiesel production or diesel/biodiesel mixture, which allows increasing the volumes of the mixtures reservations, what is highly interesting toward biodiesel production from a variety of renewable raw materials. Regarding to such purpose the use of analysis tools physico-chemical behavior of biodiesel or biodiesel blends containing, enabling the acquisition of information and the establishment of values that ensure the optimal operation of engines, are desirable. Therefore, the use of thermal analysis techniques, such as Thermogravimetry/ Derivative Thermogravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC) has produced excellent results, contributing to a historical development of scientific applications. Thermal analysis is an important tool for the determination of thermodynamic properties, heat capacity, phase transition temperatures, among other perfectly applicable for determining the

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thermal characteristics of biodiesel, as decomposition temperature/combustion degree of oxidation, temperature crystallization, a polymerization potential and others.

Along the chapter, it will be discussed data about of methyl biodiesel obtainment from soybean oil at laboratory scale and its physicochemical characterization compared to two samples produced on an industrial scale: one obtained from recycled soybean oil and other from new soybean oil and diesel/biodiesel blends in varying proportions. The physical chemical parameters established by ANP were used as reference density, kinematic viscosity, acid number and iodine, flashpoint, accelerated oxidation test (RANCIMAT), cold filter plugging point, carbon residue and water content (Karl Fischer). In order to obtaining data from thermal behavior profile of the samples of biodiesel and diesel/biodiesel blends, such as thermal stability, thermal decomposition process, crystallization temperature and residue content were applied thermoanalytical TG/DTG and DSC techniques.

2. Traditional methods used in biodiesel characterization

The quality biodiesel must be produced following strict industry specifications, according to ASTM D6751 international level. In Brazil, the National Agency of Petroleum, Natural Gas and Biofuels (ANP) by ANP Resolution Nº 45, dated 08.25.2014 specifies the characteristics of the product. According to the resolution Physicochemical characteristics of biodiesel must be made through the use of the guidelines of the Brazilian Association of Technical Standards (ABNT) standards "American Society for Testing and Materials" (ASTM), "International Organization for Standardization" (ISO) and the "Comité Européen de Normalisation" (CEN). Some of the characteristics of the specification of biodiesel can be seen in Table 1.

In Brazil, through an aggressive government policy, thousands of Biodiesel production industries have been installed in all regions of the country, and this material is already mixed with diesel consumed at the pump stations. This fact makes the ANP hold a national monitoring program of the fuel sold in the country, with the association of accredited laboratories for this purpose. Testing methodologies validated by ASTM protocols are employed routinely evaluating samples collected in various parts of the country supply.

Biodiesel, when subjected to low temperatures is likely to present problems in the performance of fuel systems of cars. In winter, the crystallization of the methyl esters of saturated fatty acids can cause clogging of filters and pipes [8]. The cold flow properties of diesel are usually characterized by three temperature measurements following: Point cloud point (CP) connecting the cold (CFPP) filter and pour point (PP). Initially, the cooling temperatures causes the formation of seed crystals of wax which are solid at submicron invisible to the human eye level. Further decreases in temperature cause the nuclei to grow crystal [9]. Temperature at which crystals become visible is defined as the cloud point (CP), since the crystals form a generally hazy and cloudy suspension. The temperature at which the agglomeration of the crystal is large enough to prevent leakage of fluid free is defined as the pour point (PP). The filter plugging point at low temperature (CFPP) is then defined as the lowest temperature at which

40 mL of oil passes through the filter securely within 60 s. Crystallization of these compounds may lead to filters and pipes connected.

Previous studies concerning the cold flow properties of biodiesel have determined that the lengths of the hydrocarbon chains and the presence of unsaturated structures significantly affect its low-temperature properties [10-12].

In addition to these cold temperature tests, DSC should also be used to monitor the crystallization of multicomponent mixtures like biodiesel because CP results represent only the beginning of the crystallization process, and PP and CFPP cover the beginning of the operative problems; but none of these tests monitor the full range of crystallization. DSC is a well-established method for determining latent heat changes in a material upon either cooling (exothermic crystallization peaks) or heating (endothermic melting peaks). This method has been applied to monitor biodiesel crystallization and is generally considered to be more repeatable and more accurate than classical methods, such as PP or CP measurements, commonly used in industrial settings [13].

3. Biodiesel

Biodiesel is defined as alkyl esters (methyl, ethyl, propyl), commonly obtained from a chemical reaction of a vegetable oil or animal fat [14-17] with an alcohol (usually methanol) in the presence of a catalyst (usually sodium hydroxide or potassium hydroxide) in a call type for the trans-esterification [18-19] (Figure 1). This reaction produces glycerin as a byproduct, which ought to be widely applied in the chemical industry [5].This glycerin vegetable oil removed leaving the less viscous oil [20]. With its break, glycerin joins caustic soda (sodium hydroxide or potassium hydroxide) [21]. The remainder of the molecule (fatty acid) binds to the alcohol, forming biodiesel. Besides the glycerin, the biodiesel production chain generates a number of other co-products (pie, bran etc.) that can add value and constitute other important sources of income for farmers. Biodiesel is formed by different types of fatty acid esters, particularly the acids: oleic, linoleic and palmitic acids [22-25]; that can also be obtained by esterification and cracking process [26].

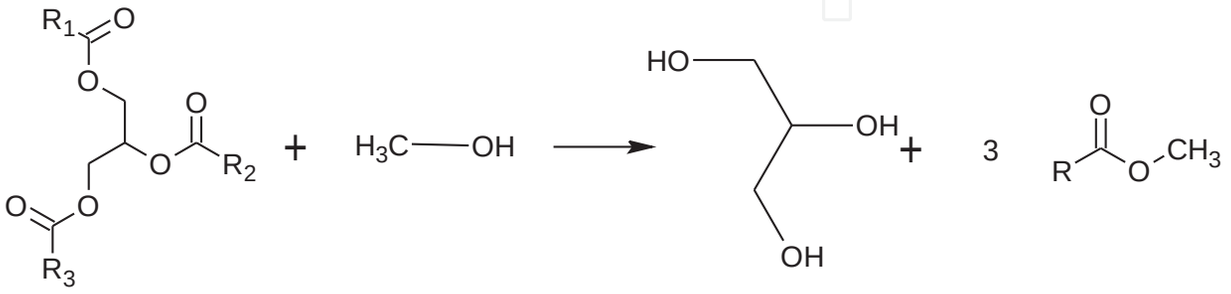


Figure 1. Transesterification Reaction

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3.1. Biodiesel production

The transesterification reaction ought to be carried out in a reactor glass, jacketed for temperature control by circulating water, and mechanical agitation. The system temperature maintained around 50 °C. By adding 230 mL of anhydrous methanol and about 8.2 g of catalyst (NaOH), then completed dissolution of the catalyst by adding to 900 mL of soybean oil, establishing this moment as time zero of the reaction. The reaction time lasted about 45 min, in the first minutes were observed the conversion of esters by the sudden darkening of the mixture. Once the reaction is complete, the reactional mean is transferred a separator funnel and the formation of an upper layer corresponding to the methyl esters, a bottom phase containing glycerol formed from the reaction and add to excess methanol hydroxide sodium which does not react. Gathered to the reaction were formed soaps, and some traces of methyl esters and partial glycerides. Then the separated the two phases by decantation.

After the phases' separation, the obtained esters must be purified by washing them with a solution containing distilled water at 90 °C and 0,5 % concentrated HCl in order to neutralize the remaining catalyst of the reaction. The total neutralization is confirmed by adding phenolphthalein indicator 1 % (w/v), to the washing water. The aqueous phase, separated by decantation, followed ester and traces of moisture removed by subsequent filtration over anhydrous sodium sulfate. For the recovery of the excess methanol added in, there shall be the glycerin residue distillation at 80 °C under moderate vacuum [6].

3.2. Biodiesel physical-chemical characterization

Physicochemical parameters of biodiesel samples (methyl route) obtained by following the rules set by the Technical Regulation of ANP contained in Resolution Nº45/2014 of the National Agency of Petroleum, Natural Gas and Biofuels-ANP. Three samples of soybean biodiesel were analyzed, one that was produced in the laboratory (BL) and two industrial, one trans esterified with used oil (BI-01) and another with new oil (BI-02). All traits and methods used are in table 1.

Biodiesel developed in the laboratory (BL) has filed all within the parameters established by the Resolution of the ANP, except oxidation stability. Biodiesel oxidation occurs because the oils used as its raw materials containing unsaturated compounds, which are subject to oxidation reactions that take place at ambient temperature. Oxidation products cause corrosion in engine parts and deposit formation causing obstruction in the filters and injection system [5]. Therefore, the less subject to oxidation, the better the quality of biodiesel during its useful cycle. However, the value obtained for the oxidation stability out of specification is significant not to cause corrosion in the short term, long term only [5]. This parameter out of specification can be explained by the fact that after the transesterification process has not any added antioxidant (slow oxidative process biodiesel) unlike the industrial biodiesels.

The industrial biodiesel 01 (BI-01) showed three parameters that are out of specification the ester content, carbon residue, and total glycerol. The raw material used by the industry in producing biodiesel is the soybean oil used according to [5], oils used contain water, typically

CHARACTERISTICS	UNIty	LIMIT	MÉTHOD	BL	BI-01	BI-02
Aspect	-	*CIA		*CIA	*CIA	*CIA
Density at 20 ºC	kg/m^3	850-900	ASTM D 4052	881,6	880,3	881,7
CKinematic Viscosity at 40°C	mm^2/s	3,0-6,0	ASTM D 445	4,275	4,708	4,19
Water Teor, max.	mg/kg	500	ASTM D 6304	347	405	276
Flash Point, min.	°C	100	ASTM D 93	187,5	175,5	177,5
Esther Teor, min.	% mass	96,5	EN 14103	96,6	91,0**	97,4
Carbon Residue	% mass	0,05	ASTM 4530	0,0004	0,057**	0,01
Cold Filter Plugging Point, max.	°C	19	ASTM D 6371	-3,5	2,0	-4,0
Acid Value, max.	mg KOH/g	0,5	ASTM D 664	0,0081	0,2580	0,7391**
Free Glycerol, max.	% mass	0,02	ASTM D 6584	0	0,01	0,01
Total Glycerol, max	% mass	0,25	ASTM D 6584	0,175	0,27**	0,19
Mono, Di, Triacylglycerol	% mass	take note	ASTM D 6584	Mono - 0,3855; Di - 0,3266; Tri - 0,2814	Mono – 0,75; Di – 0,46; Tri – 0,08	Mono – 0,68; Di – 0,06; Tri – 0,00
Methanol, max.	% mass	0,2	EN 14110	<0,01	0,01	0,01
Iodine Index	g/100g	take note	EN 14111	119,02	88,997	122,97
Oxidation Stability at 110 ° C, min.	Hours	6	EN 14112	5,52**	6,9	11,34

*CIA – clear and impurities absent

**Out range parameters

Table 1. Biodiesel Samples Physical-chemistry Characteristics

from 2 to 7% FFA, Free Fat Acid, when an alkali catalyst (e.g. KOH) is added to these raw materials FFA react with the catalyst to form soap and water. The soaps formed during the reaction are removed with the glycerol in the aqueous washing step. When the concentration of FFA is too large soaps inhibit the phase separation between methyl ester and glycerol and contribute to emulsion formation during the aqueous rinse. With all this explains why the ester content, carbon residue and total glycerol present parameters out of specification. It is likely that the raw material should not have had a proper treatment for the transesterification reaction having a high content of FFA, with that, there was a decrease in the yield of the reaction, which may have been the reason for the ester content display a value specified below and the content of total glycerol be above specified. This above total content of glycerol may explain the residue carbon, as these fuels with high amounts of free glycerol present problems with deposition in

storage tanks glycerol creating a viscous mixture that can clog fuel filters and in the case being responsible for above the value specified for the carbon residue. To be able to prove it would be necessary to make analysis with the raw material.

The industrial biodiesel 02 (BI-02) showed only the acid out of the specified. In this case biodiesel, one possible explanation microbial growth in the fuel owing to the presence of water in its shell. The presence of microbes cause increased acidity and formation of sludge that can clog fuel filters. Another cause of high acidity could be related to the process of preparation of biodiesel, because if it is not washed with acid and the withdrawal is made correctly, the product may present acidity nonstandard.

4. Thermoanalytical methods

The International Confederation of Thermal Analysis and Calorimetry (ICTAC) defines thermal analysis as a group of techniques in which a physical property of a substance and / or its reaction products is measured as a function of temperature while the substance is subjected to a controlled program Temperature [27].

Thermal analysis provides information regarding: variation of density, thermal stability; and free water; bound water; purity, melting point, boiling point, heats of transition, specific heats, phase diagrams, reaction kinetics studies of catalysts, glass transitions, etc.

The advantages are many thermal analysis (requires little sample for tests, variety of results on a single graph), and its applicability occurs in several areas: food, catalysis, ceramics, civil engineering, pharmaceuticals, inorganic, organic, petrochemical, polymers, glass, among others. But there are some disadvantages in the use of thermal analysis such as the relatively high cost of equipment [28].

4.1. Thermogravimetry and Derivate Thermogravimetry (TG/DTG)

Thermogravimetry or thermo gravimetric analysis is based on studying the variation in weight of a sample, resulting in a physical change (sublimation, evaporation, condensation) or chemical (degradation, decomposition, oxidation) versus time or temperature. It is a technique with wide application area in determining the thermal behavior of materials. The principle is based on obtaining the thermogravimetric curve (TG), by plotting mass (mg) or percentage of weight loss (y-axis) versus temperature or time (X axis). The sample container is wrapped and placed on an analytical balance in a controlled environment, where it performs the continuous and programmed heating. Upon degradation, the sample loses mass, in the form of volatiles and the sensor registers the corresponding mass loss [29-30]. The method allows to obtain the first derivative of the TG curve, called DTG curve, which allows you to view the start and end of each event of mass loss, indicating the temperature range where a particular decomposition reaction occurs.

Typically TGA curve and its derivative DTG curve are presented as in Figure 2:

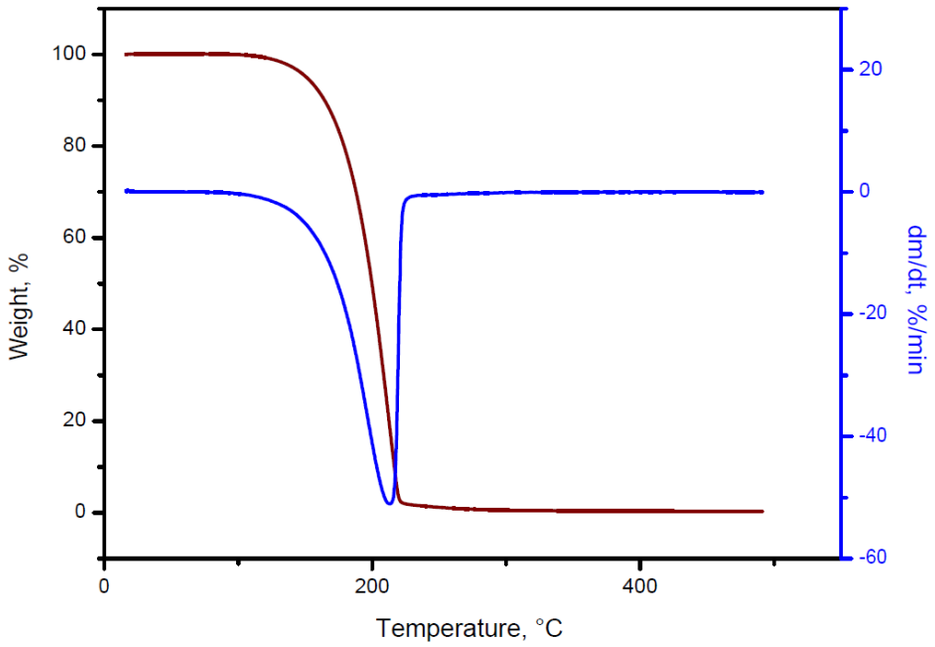


Figure 2. TGA curve (dark-red) and its derivative, DTG (blue)

4.2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is defined as a technique which measures the temperatures and energy change associated with transitions in materials as a function of temperature or time.

DSC measures the difference in energy required for the substance and a reference material, thermally inert, while both are subjected to a controlled temperature variation so that the sample and reference are maintained under isothermal conditions, in relation the other, regardless the thermal event that is occurring in the sample.

The DSC curve provides qualitative and quantitative information about physical and chemical changes that involve endothermic processes (heat absorption), exothermic (releasing heat) or change in heat capacity [28].

There are two types of equipment that perform the Differential Scanning Calorimetry, the former is called a power compensation DSC and second DSC heat flow.

In power compensation DSC for the sample and the reference are placed in separate compartments of individual heat sources where the temperature and energy are monitored and generated by filaments of the same platinum, acting as resistive heaters and thermometers. This technique keeps constant the supplied heat. However, instead of measuring the difference in temperature between sample and reference during the reaction, a control system immediately increases the power supplied to the sample when the process is endothermic and increases the energy supplied to the process when reference is exothermic, thus preserving the sample and reference at the same temperature.

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The second type of instrument is called by DSC "heat flow". In the oven the crucibles are arranged on a base of a highly conductive metal, usually platinum. The sample and the reference are then heated by the same power supply system. Each time the sample reacts energy flow is established between the crucibles through the base of platinum. The data in the form of electric potential (microvolts) corresponding to the temperature increase of both crucibles inside the oven should increase linearly and symmetrically. Thus, a uV versus time curve can be computed.

The flow is then measured by means of temperature sensors placed in each crucible, thereby obtaining a proportional to the thermal capacity difference between the sample and the reference signal.

Typically DSC curve with glass transition, crystallization and fusion events, respectively, are presented as in Figure 3:

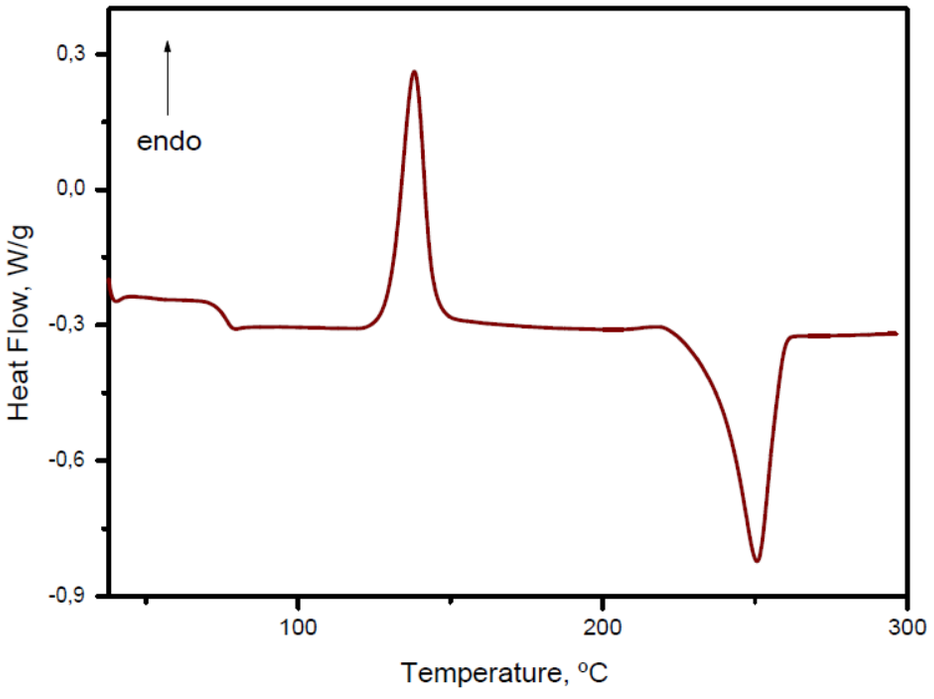


Figure 3. DSC curve with endothermic and exothermic events

5. TG profile of biodiesel samples

The TG curves were obtained in TGA equipment-Q50 from TA Instruments in an atmosphere of nitrogen at a flow rate of 100 mL min^{-1}, heating rate 20 °C min^{-1} in crucibles of platinum (Pt) as a support, in temperature range 30-650 °C.

In the TG curves of the methyl esters was only one event, which consumed more than 99 % of the sample mass. This step of weight loss is associated to vaporization of the methyl esters and

the TG curve show the process end around 300 °C. Figure 4 and 5, show the comparison of the profile of the TG and DTG curves of the three samples, where it ought to be observed the similarity between them.

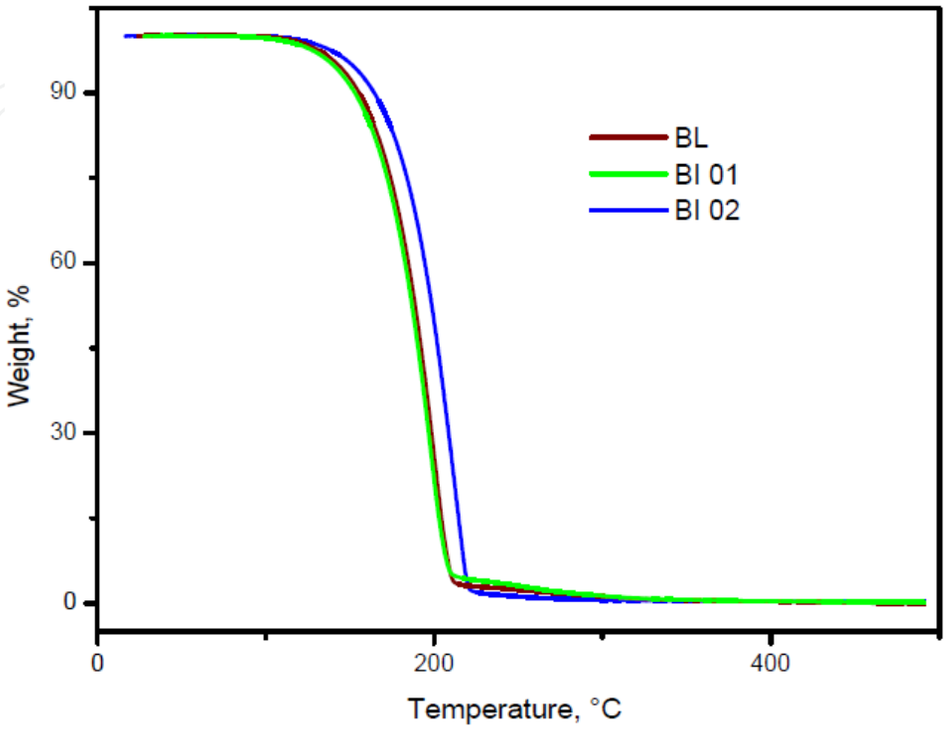


Figure 4. TG Profile of Biodiesel Samples

These curves showed very similar profile among them, the BI 02 showed a slightly higher thermal stability than the BI and BL-01, this fact can be related to oxidative stability, BI-02 showed higher oxidative stability than the other samples. The profile of the TG curves of the samples of biodiesel was similar to the soybean oil and fossil diesel, with only one step weight loss. The difference is in the temperature range in which vaporization of the methyl ester, soybean oil and fossil diesel occurs, begin around 155 °C, 357 °C and 30 °C respectively, as shown in Figure 6.

The large difference in thermal stability between the soybean oil and biodiesel is due to the fact that the oil molecules are larger than the samples of biodiesel oil is composed primarily of triacylglycerols while the biodiesel is composed of the methyl esters of fatty. Despite Soybean Oil satisfactory performance as a fuel or as a fuel source its spread is compromised, because its cost is high when compared to petroleum. Apart from being highly viscous, causing poor fuel atomization in the combustion chamber of the engine, causing serious operational problems such as the occurrence of deposits in their inner parts [5].

The biodiesel commercialization is made by mixtures with fossil diesel, the energy matrix was introduced in 2005 with the addition of 2 % of this fuel and currently the law determines to be

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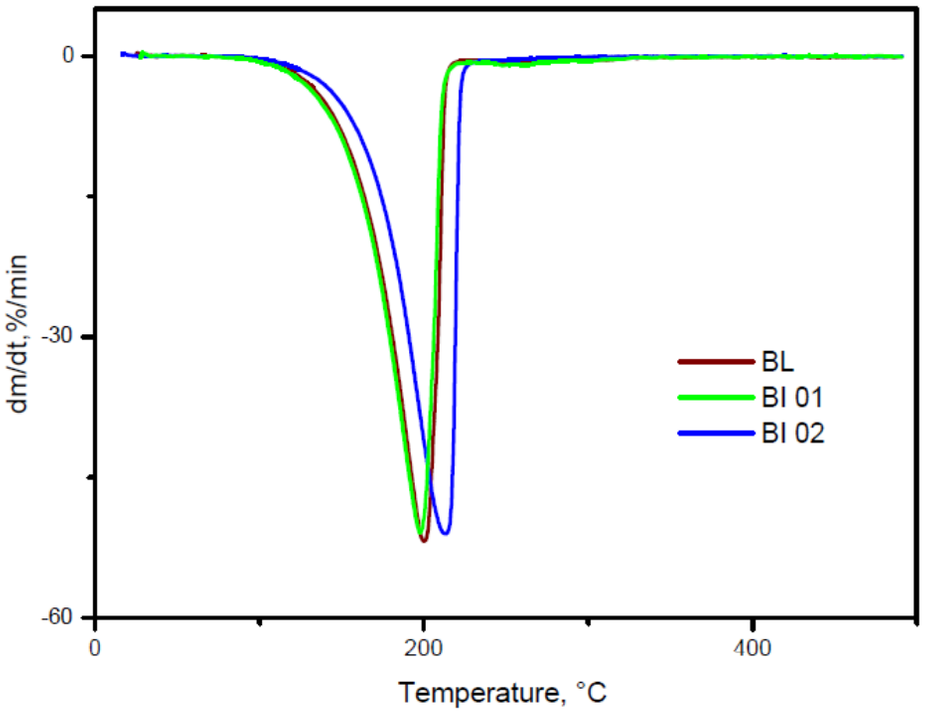


Figure 5. DTG Profile of Biodiesel samples

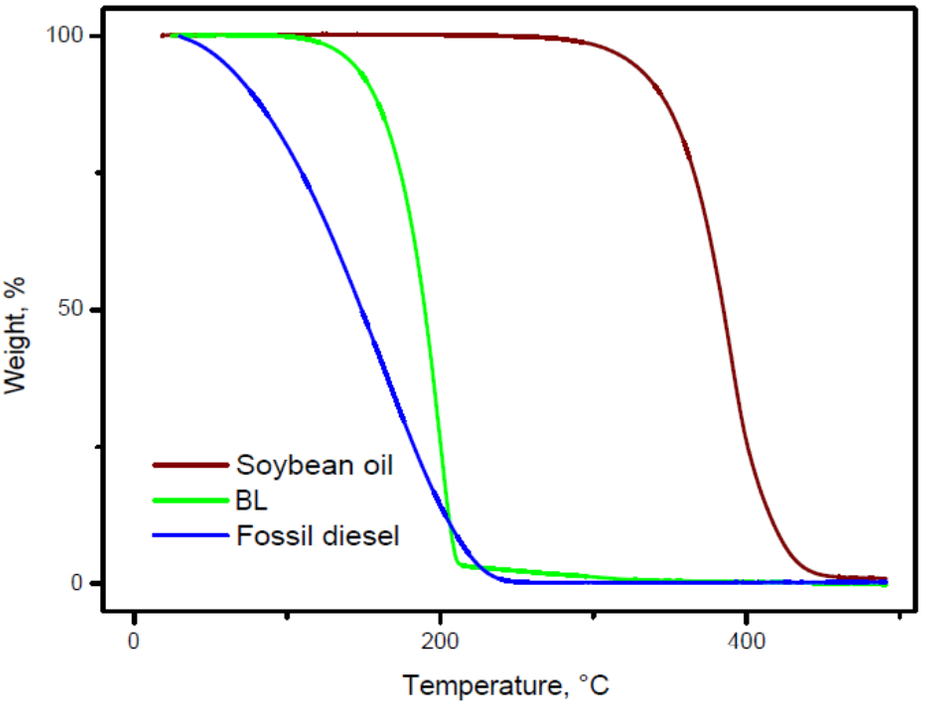


Figure 6. Soybean Oil, Biodiesel and Diesel Fossil TG Profile

plus 5 % biodiesel to fossil diesel. We observed the TG/DTG profile of the mixtures as shown in figure 7 and 8.

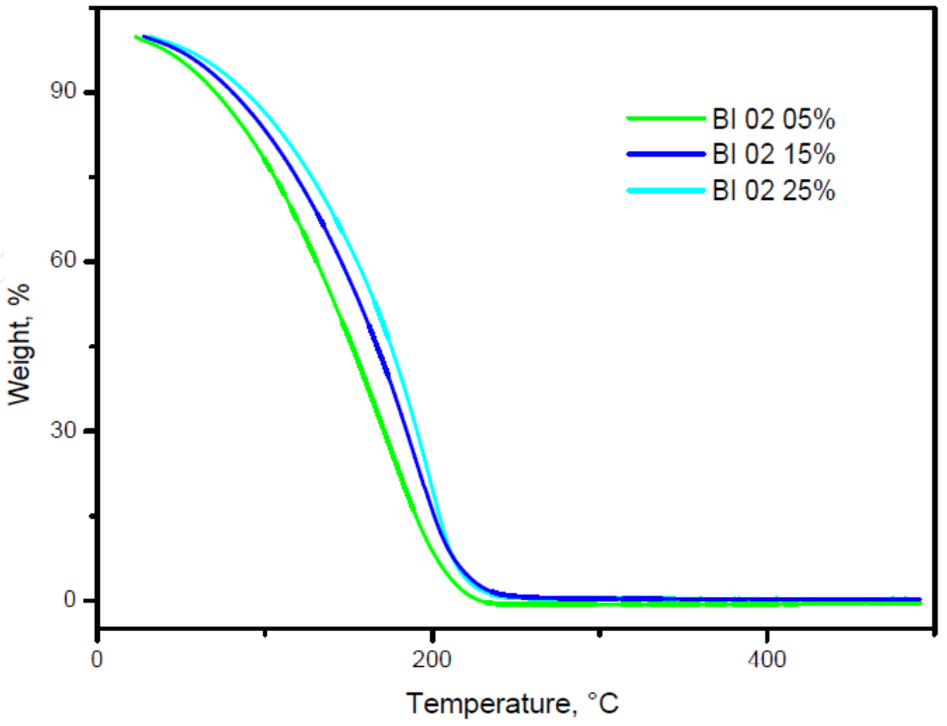


Figure 7. Profile of TG Fossil Diesel and biodiesel (BI 02) blends

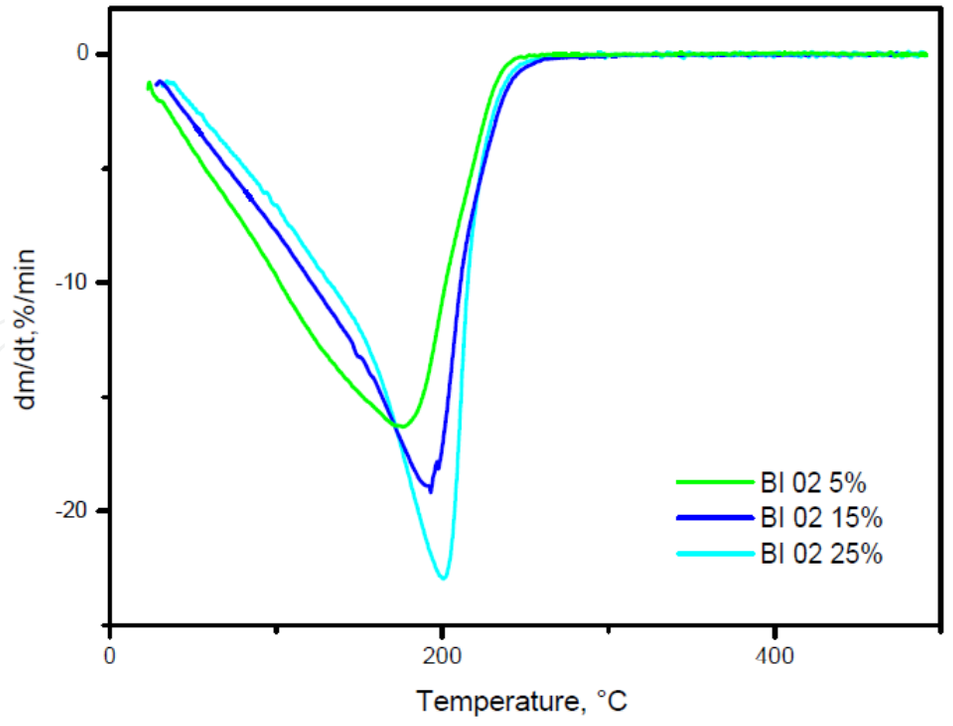


Figure 8. Profile of DTG Fossil Diesel and Biodiesel (BI 02) blend

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The TG curves of mixtures of samples added to Biodiesel Diesel Fossil showed similar profiles with only one stage of mass loss (for mixtures with BL and BI 01 curves were similar to BI 02 profile, so only presented a figure 7. The curves profile of mixtures in all ratios, was similar to that of vaporization of fossil diesel profile, it was found that an increase of the concentration of biodiesel there was a displacement of the curve to higher temperatures, indicating a higher relative stability of the mixture to pure fossil diesel.

6. DSC biodiesel samples

The DSC curves were obtained in the device DSC-Q20 with cooling system RCS-90 from TA Instruments, using as a sample holder, aluminum crucibles with cover and stuck to both the crystallization and to volatilization. As a reference, a similar empty crucible was used. Nitrogen atmospheres with flow rate of 50 mL min^{-1} and heating rate of 20 °C min^{-1} (vaporization) and 5 °C min^{-1} (crystallization and melting) at temperatures from -80 to 550 °C.

6.1. DSC profile

For the three biodiesels, there was only one endothermic event with a temperature around 250 °C. Thus it can confirm that the event was indeed observed in the TG vaporization of biodiesel. The differential scanning calorimetry was used to check the physical and chemical transitions occurring in the vaporization of soybean biodiesel process. According to the DSC curve, there is an endothermic transition for each biodiesel: BL showed a ΔH=329.1 J g^{-1}, BI 01 showed a ΔH=252.5 J g^{-1} and BI 02 showed a ΔH=272.7 J g^{-1}. These transitions can be attributed to the processes of vaporization of methyl esters [31]. Such events can be seen in Figure 9:

6.2. Biodiesel crystallization

Comparing the curves of biodiesels (BL, BI-01 and BI-02) can be seen that all curves have two state transitions, the first liquid-liquid crystal formation, which is the solidification of a fraction rich in unsaturated compounds and the second, which is a freeze, which corresponds to the fraction rich in unsaturated compounds [32]. Crystallization of saturated compounds is represented by an exothermic peak at around-5 °C. In this range crystallization BL has the lowest crystallization temperature, -4 °C, followed by BI-02 and BI-01 which crystallize to -2.8 °C and 1.9 °C respectively. The crystallization points of unsaturated compounds are below -50 °C, as observed for the BL, BI-02 and BI-01 have the second crystallization temperature of -61.2 °C, -59.8 °C and -57.6 °C, respectively, as observed in the curves of cooling to -80 °C in Figure 10.

Because the greatest amount of unsaturated compounds in soybean biodiesel be unsaturated compounds that peak is observable below – 50 °C is larger in area, requiring more energy to crystallize than the saturated compounds. The peak around-50 °C needed for the phase transition of 68 and 58 J g^{-1} to BL and BI-02 respectively compounds. The peak at around-5 °C needed 16 and 15 J g^{-1} to BL and BI 02 respectively compounds. BI-01 for the peak around -50

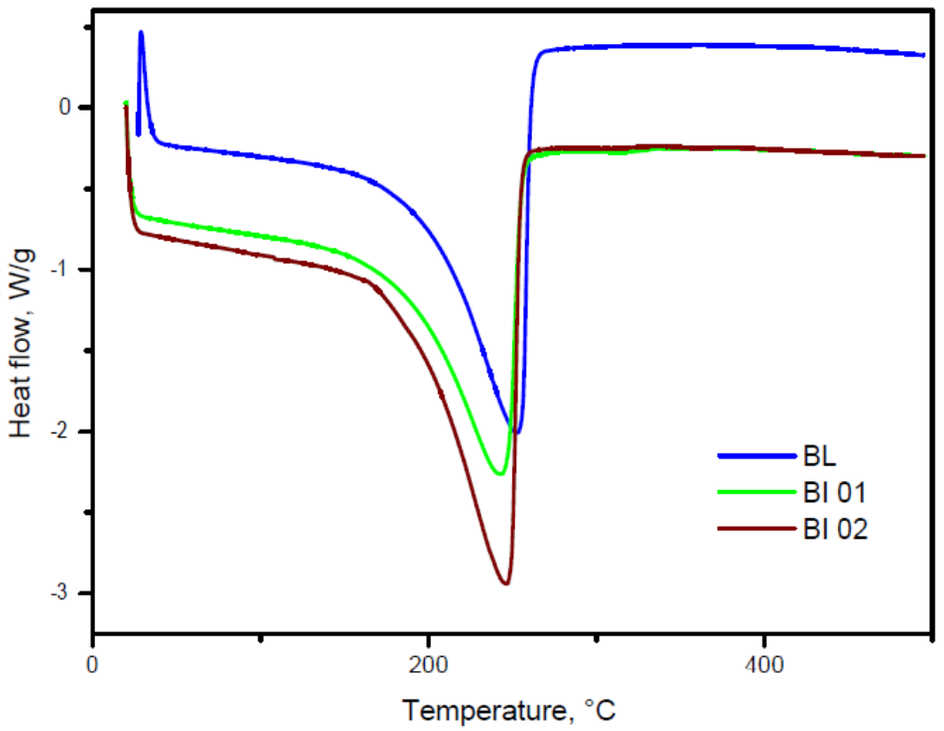


Figure 9. biodiesel sample DSC profile

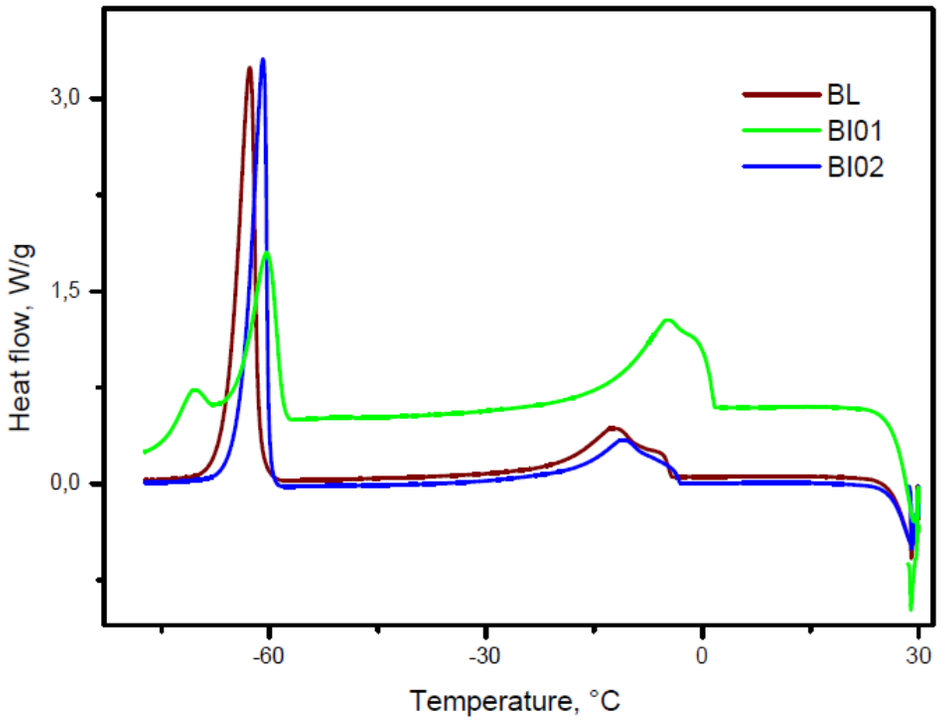


Figure 10. Crystallization of samples of biodiesel – Cooling curve

°C took 32 J g^{-1} for the largest peak and 7 J g^{-1} for the smaller peak. For the peak at around 0 °C took 30 J g^{-1} for the phase transition.

In the heating curves from – 80 °C to 30 °C may be seen two peaks of the curves BL and BI-02, referring to melting of the unsaturated (-46 °C) saturated (0 °C) compounds. To BI-01 may be seen three peaks related to the two unsaturated compounds (-53 to -40 °C) and references to unsaturated compounds (5 °C). BI-01 showed different behavior in crystallization of unsaturated compounds, there were two peaks of the onset of crystallization while BL and BI-02, showed only a peak of crystallization.

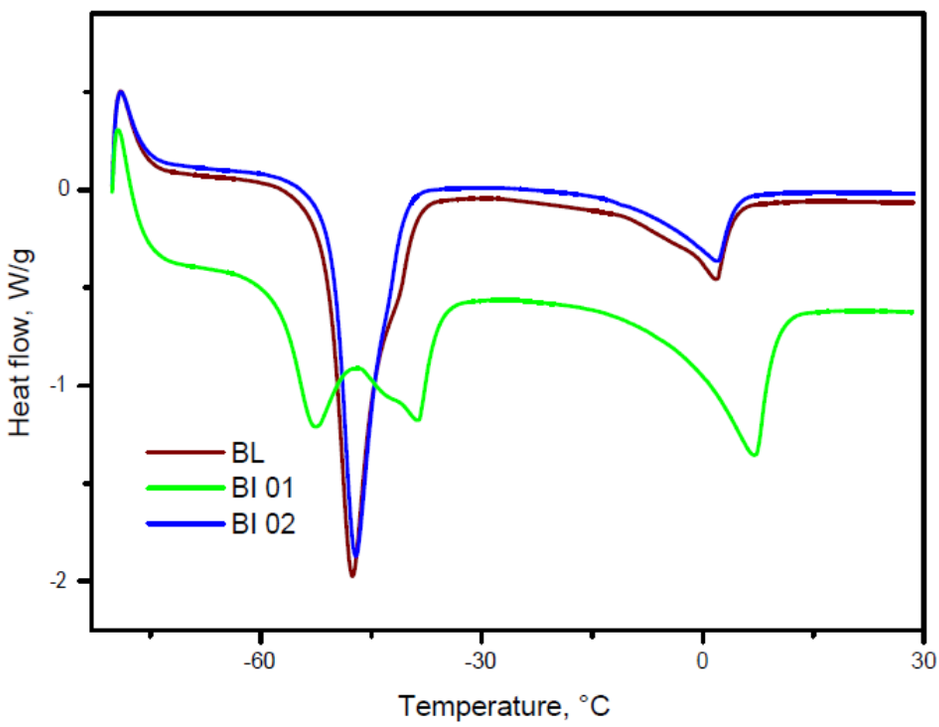


Figure 11. Crystallization of samples of biodiesel – heating curve

This fact may be related to the type of oil used in biodiesel production. As is reused oil underwent oxidation and hydrolysis of their triglycerides, causing increase in conjugated *dienes* and *trienes* unsaturated bonds [5], causing another peak appears in the unsaturated region.

7. Future development areas

Various types of vegetable oils have been tested in the preparation of biodiesel (canola, soybean, corn, sunflower, castor beans, cotton, etc.). The type of oil to be used in the production of biodiesel depends on geographical factors, as each region produces a certain kind of oil, according to their fitness. In some European countries, for example rapeseed oil, Brazil is

already in use, depending on the region, can be produced from soy, castor oil or babassu [6] oil. Another highlight is the use of oils used in frying whose nobler purpose was hitherto the production of soap or disposed of in a sanitary [33] landfill. The high price of vegetable oils has become non-competitive biodiesel economically forward to petroleum diesel, programs and government incentives are needed. The search for new raw materials for the production of biodiesel and are more environmentally friendly and economically viable.

Biodiesel is a cleaner-burning alternative fuel, produced from renewable resources, does not contain oil, but it can be added to form a mixture. Can be used in compression-ignition engines (diesel) without modification. Non-toxic, essentially free of sulfur and aromatics [34] compounds. Its main disadvantages include low pour point (on cold) and maintain fuel quality during long-term storage [35]. A good source for development would address this disadvantage that has biodiesel.

8. Conclusions

Biodiesel production in the laboratory of alkaline transesterification reaction and the treatment of methyl esters were successful. All parameters except the oxidative stability were within the established in ANP Nº 45/2014, indicating a good quality biodiesel. The oxidative stability below specification may have been due to lack of the addition of antioxidant.

Industrial biodiesels showed some parameters out of specification. BI-01 showed three parameters out of specification (ester content, carbon residue content of glycerol), which is probably associated with the raw material. The BI-02 showed only one parameter out of spec (Acid Value) which can be associated to microbial growth in storage tanks or the fact that after neutralization of excess acid base with the same has not been washed properly.

By TG curves, soybean oil showed higher thermal stability than Biodiesel and Fossil Diesel. In oil, the onset of decomposition was 358 °C, while biodiesels began to vaporization around 160 °C. For fossil diesel mass loss started around 30 °C, whereas the increase in the binary mixtures Biodiesel slightly increased thermal stability.

The biodiesels were tested at a heating rate of 5, 10, 15 and 20 °C and all were obtained in the same profile.

The DSC curves of biodiesels calorimetric showed a similar profile. The analysis of biodiesels had only one endothermic peak on the vaporization of the esters. Comparing ΔH of biodiesels BL> BI-02> BI-01 with the respective ΔH 329.1> 272.7> 252.5 J g^{-1}.

The TG curves of the binary mixtures have very similar profile to that of fossil diesel, biodiesel from the addition made to increase the thermal stability of the mixture. When compared with fossil diesel, it begins to loss mass around 30 °C and the Biodiesel that begins to vaporization at 160 °C there has been a small increase in the temperature at which it begins to lose mass, and that the More mixture containing biodiesel B25, takes a longer time to fully decompose when compared with the mixture of 5 %, indicating greater thermal stability.

In the curves of crystallization of biodiesels (BL, BI-01, BI-02) shows that all the curves have two transitions of liquid-solid state, one that represents the solidification of a fraction rich in saturated compounds and the other corresponding to rich fraction unsaturated compounds. Crystallization of saturated compounds is represented by an endothermic peak at around 0 °C, and the unsaturated compounds endothermic peak around – 60 °C.

Acknowledgements

The authors thank the Brazilian funding agencies FUNDECT, CAPES and CNPq for financial support and UFMS by assigned space.

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References

[1] Goldemberg J. Biomassa e Energia. Química Nova. 2009, 32,582

[2] Exame. As 20 maiores reservas de petróleo do mundo. http:/exame.abril.com.br (accessed 21 September 2013)

[3] Galembeck F, Barbosa CAS, Sousa RA. Aproveitamento Sustentável de Biomassa e de Recursos Naturais na Inovação Química. Quím. Nova. 2009, 32, 571.

[4] Lima JRO, Da Silva BR, Da Silva CCM, Dos Santos LSS, Santos JR, Ribeiro J, Moura EM, Moura VCR. Biodiesel de babaçu (ORBIGNYA SP) obtido por via Etanólica. Química Nova, v. 30, n. 3 p. 600-603, 2007.

[5] Knothe, G.; Gerpen, J. V.; Krahl, J.; Ramos, L. P. Manual de Biodiesel, 1ª ed. São Paulo: Editora Blucher, 2006

[6] Ferrari RA, Oliveira VS, Scabio A. Biodiesel de Soja – Taxa de conversão em ésteres etílicos, caracterização Físico-Química e consumo em gerador de energia. Química Nova, 2005, 28 (n.1), 19.

[7] Galvão LPFC. Avaliação termoanalitica da estabilidade oxidativa do biodiesel de Mamona. Dissertação de Mestrado. Universidade Federal do Rio Grande do Norte; 2006.

[8] Kerschbaum S, Rinke G, Schubert K. Winterization of biodiesel by micro process engineering. Fuel 87, 2590–2597, 2008

[9] Kaya C, Hamamci C, Baysal A, Akba O, Erdogan A, Saydut A. Methyl ester of peanut (Arachis hypogea L.) seed oil as a potential feedstock for biodiesel production. Renewable Energy 34, 1257–1260, 2009.

[10] Soriano NU, Migo VP, Matsumura M. Ozonized vegetable oil as pour point depressant for neat biodiesel. Fuel 85, 25–31, 2006.

[11] Ramos MJ, Fernández CM, Casas A, Rodríguez L, Pérez A. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresource Technology 100, 261–368, 2009.

[12] Papadopoulos CE, Dazaridou A, Koutsoumba A, Kokkinos N, Christoforidis A, Nikolaou N. Optimization of cotton seed biodiesel quality (critical properties) through modification of its FAME composition by highly selective homogeneous hydrogenation. Bioresource Technology 101, 1812–1819, 2010.

[13] Knothe G, Dunn RO. A comprehensive evaluation of the melting points of fatty acids and esters determined by differential scanning calorimetry. Journal of the American Oil Chemists' Society 86, 843–856, 2009.

[14] Soares, C.M., Itavo, L.C.V., Dias, A.M., Arruda, E.J., Delben, A.A.S.T., Oliveira, S.L., de Oliveira, L.C.S. Forage turnip, sunflower, and soybean biodiesel obtained by ethanol synthesis: Production protocols and thermal behavior. Fuel, 89, 12, 3725-3729, 2010

[15] Canakci M, Van Gerpen J. Biodiesel Production From Oils and Fats with High Free Fatty Acids. Trans. ASAE, 2001, 44, 1429

[16] Monyem A, Van Gerpen JH. The effect of biodiesel oxidation on engine performance and emissions. Biomass & Bioenergy, 2001, 20, 317-325.

[17] Monyem A, Van Gerpen JH, Canakci M. The Effect of Timing and Oxidation on Emissions from Biodiesel-Fueled Engines. Transactions of the ASABE. Vol. 44(1), 35-42.

[18] Encinar JM, González JF, Rodríguez JJ, Tejedor A. Biodiesel Fuels from Vegetable Oils: Transesterification of Cynaracardunculus L. Oils with Ethanol. Energy Fuels, 2002, 16, 443.

[19] Noureddini H, Harkey D, Medikonduru VA. A continuous process for the conversion of vegetable oils into methyl esters of fatty acids. Journal American Oil Chemical Society, 1998, 75, 1775.

[20] Freddman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil 1. Journal of the American Oil Chemists Society 1986, 63, 1375-1380.

[21] Kusdiana D, Saka S. Methyl Esterification of Free Fatty Acids of Rapeseed Oil as Treated in Supercritical Methanol. Journal of Chemical Engineering of Japan 2001, 34, 383.

[22] Shuchrdt, U.; Sercheli, R.; Vargas, M. Transesterification of Vegetable Oils: a Review. Jounal of the Brazilian Chemical. Society, 1998, 9, 190.

[23] Noureddini H, Medikonduru V. Glycerolysis of fats and methyl esters. J. Am. Oil Chem. Soc., 1997, 74, 419.

[24] Dorado MP, Arnal JM, Gómez J, Gil A, Lopez FJ. The effect of a waste vegetable oil blend with diesel fuel on engine performance. Trans. ASAE, 2002, 45, 519.

[25] Lago RCA, Szpiz RR, Hartman L. Transformação de óleos vegetais de alta acidez em ésteres etílicos na presença de catalisadores ácidos para fins combustíveis. Química Industrial, 1988, 666, 8-11.

[26] SEBRAE. Biodiesel. http://www.sebrae.com.br/sites/PortalSebrae/bis/Conhe%C3%A7a-a-cartilha-do-biodiesel (acessed July 2012).

[27] Ionashiro M, Giolito I. Fundamentos da termogravimetria, Análise térmica diferencial, Calorimetria exploratória diferencial. São Paulo. 2004

[28] Mothé CG, Azevedo AD. Análise térmica de materiais. São Paulo: iEditora, 2002.

[29] Lucas, E. F.; Soares, B. G.; Monteiro, E. Caracterização de Polímeros.Determinação de Peso Molecular e Análise Térmica. Rio de Janeiro, LTC, 2001.

[30] Haines, P. J. Thermal Methods of Analysis, Blackie Academic & Professional, 1995.

[31] Gondim AD. Avaliação da estabilidade térmica e oxidativa do biodiesel de algodão e do efeito da adição de antioxidantes (α – tocoferol e BHT). Tese de doutorado. Universidade Federal do Rio Grande do Norte; 2009.

[32] Pérez, A. et. al. Winterization of peanut biodiesel to improve to cold flow properties. Bioresource Technology, 101, 2010, 7375-7381.

[33] Zaher F. Utilization of used frying oil as diesel engine fuel. Energy Sources 2003, 25, 819-826.

[34] Parente EJS. Biodiesel: uma aventura tecnológica num país engraçado. Fortaleza: Tecbio, 2003.

[35] Dunn RO. Effect of Antioxidants on The Oxidative Stability of Methyl Soyate (Biodiesel). Fuel Processing Technology. 2005, 86, 1071-1085.

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