DETERMINATION OF ACTIVATION ENERGY FOR ANIMAL FAT AND CRUDE GLYCEROL USING THERMOGRAVIMETRIC ANALYSIS

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Abstract. *The present study deals with the determination of the activation energy of animal fat and crude glycerol from a biodiesel production plant. The activation energies were investigated by thermogravimetric analysis in the temperature range of ΔT = 25–600 °C. The transient experiments were run for every sample (10 mg) at five different heating rates (2.5, 5.0, 10.0, 20.0 and 30.0 °C/min) in atmosphere of synthetic air. It is possible to establish a direct relation between the activation energy and the ignition delay, which characterizes the combustion quality of a fuel. The activation energy could be determined as a function of the conversion degree and the temperature by the isoconversional model free kinetics. Four distinct phases were found for each sample and one of these phases was identified as low-temperature oxidation (LTO). As this region is responsible for the first vaporization of the fuel, the activation energies were determined for this special region along the whole conversion range (0 – 100 %). The following mean values could be determined: animal fat = 108.87 ± 52.28 kJ/mol, and crude glycerol = 65.37± 13.17 kJ/mol. From these data, it was possible to conclude that animal fat is the most complex sample between the ones studied in this work.*

Keywords*: biofuels, activation energy, crude glycerol, animal fat*

1. INTRODUCTION

Crude oil reserves are limited and only concentrated in certain regions of the world. As the oil production costs increase, the development of renewable fuels becomes more attractive (Demirbas, 2009). In contrast to crude oil abundant biomass resources are available in most regions of the world (Hamelinck and Faaij, 2006) which is an alternative in the production of cleaner and almost non-toxic fuels.

Different fats and oils from plant or animal resources can be considered sources for renewable fuels.

These fats and oils have almost the same potential of petroleum- based diesel fuels, but they require plenty of research concentration. Kerihuel et al.(2005) analyzed the lower heating values of animal fat based fuels. The results obtained from the calorimeter test were 38.3 kJ/kg with animal fat and 42.5 kJ/kg with standard diesel.

According to the definition of the National Biodiesel Board of the USA (in http://www.biodiesel.org/ resources/definitions), biodiesel is a monoalkyl ester of long-chain fatty acids derived from renewable feedstock, such as vegetable oils and animal fats, for use in compression ignition engines. At present biodiesel is produced mainly from soybean, rapeseed and palm oils (Demirbas, 2009). Besides these resources, animal fat can be used to produce alternative diesel fuels to reduce the cost of raw materials. The costs of animal fat are estimated to be half of the price of virgin vegetable oil (Adebanjo et at, 2005). The production of meat leads simultaneously to the generation of animal fat in a large amount (Adebanjo et at, 2005). On the one hand, the use of these non-utilized potentials can reduce the waste problem, but on the other hand it can support the energy balance of meat production.

The quality of a combustion process in a compression ignition engine can be characterized by the ignition delay, which indicates the time between the injection and the ignition of the fuel in direct injection diesel engines. This characteristic is of great importance, as it is directly linked to the intensity of heat release and indirectly associated with the engine noise and pollutant formation (Assanis et al, 2003). The period of ignition delay is composed of two parts: a physical delay, which encloses the atomization, vaporization and mixing, and a chemical delay, which is a result of precombustion reactions in the air-fuel mixture. In 1938, Wolfer proposed a relationship between the activation energy and the ignition delay (Equation 1), which was based on the Arrhenius relation (Alligrot et al, 1994):

$$\tau = A p^{-n} e^{\left(E_a / RT\right)} \tag{1}$$

where p and T are the pressure and temperature respectively, R is the universal gas constant, Ea is the activation energy, and A, n are adjustable constants that depend on the fuel.

Based on the above-mentioned equation, it is possible to observe that the better the ignition process, the lower the activation energy, as a good ignition process is labeled by the shortest ignition delay.

Glycerol is generated as a byproduct of the biodiesel production. With the increasing production of biodiesel, an excess of glycerol is expected, which becomes a waste problem (Akhikari S. et al,2007). As crude glycerol is a very poor fuel and contains many impurities, it can not be used directly in either diesel or petrol engines, therefore, it is important to find alternatives for its use. One of the possibilities could be its simple thermal utilization as a combustible. Another method could be the steam reforming, an endothermic process that uses a catalyst to promote a reaction between glycerol and water to create hydrogen (Slinn et al., 2008). However, for the design of a steam reforming process it is important to understand the behavior of crude glycerol pyrolysis.

The activation energy of a fuel can effectively be obtained by an experimental setup, particularly by a thermal analysis. These techniques have gained wide acceptance in the study of the combustion and pyrolysis behavior of a potential fuel, as they require small samples, have low price and proceed fast.

Dou et al. (2009) performed thermogravimetric analysis (TG/DTG) to determine the kinetic parameters of crude glycerol. They observed four phases of mass loss in the pyrolysis process. The authors could obtain the second phase of the process as the percentage of the main loss of mass depends on the heating rate.

Animal fats, as a resource for alternative fuels, have not been studied to the same extent as vegetable oils (Ma and Hanna, 1999). Thus, studies that concentrate on the determination of kinetic parameters of animal fat are hardly founding the literature.

Several authors have analyzed the thermogravimetric behaviors of animal-derived products (and all of them could detect a main region of mass loss. The appearance of further regions of mass loss depends on the material used. In the analysis of animal bones, Jankovic et al. (2009) found one further region at a higher temperature. Bojanowski et al. (2007) studied the weight loss of animal meat-and-bone meal and animal fat. For the meat-and-bone, they detected two regions of mass loss: the dehydration region and the main mass loss region. For the animal fat sample they detected only one reaction that occurred in a temperature range between 400 °C and 500 °C. Skodras et al. (2007) also studied the thermal conversion of meat-and-bone meal and detected a total of four regions.

This paper aims to present the determination of the activation energy through thermogravimetric analysis for the main region of the thermal decomposition for both glycerol and animal fat applying model-free kinetic. Starting from the direct relation between the ignition delay and the activation energy, one can qualify different possible fuels by their activation energy.

2. EXPERIMENTAL

Kinetics parameters of crude glycerol and animal fat were analyzed in the experiments. The glycerol used in this work was obtained from an industry of biodiesel located in Piracicaba, São Paulo State, Brazil. The animal fat was obtained directly from a slaughterhouse beef. For the experiments both samples were used “in natura”, i.e., they did not suffer any treatment before using.

The experiments were realized in a Shimadzu TGA-51 thermogravimetric analyzer. In each case the temperature increased from room temperature up to 600 °C at five heating rates: 2.5, 5.0, 10.0, 20.0 and 30.0 °C/min. All experiments were run once for each sample to calculate the activation energy. The samples were placed inside an aluminum crucible and a mass of 10.0 mg with an allowance of ± 0.5 mg was used. The experiments were performed in aluminum crucibles. The reacting atmosphere was synthetic air which streamed with a constant volume flow rate of 100 ml/min over the samples.

2.1. Kinetic Study

The reaction rate of a chemical reaction depends on conversion (α), Temperature (T) and time (t). The reaction rate as a function of the conversion is different for each process and must be detected experimentally. For simple reactions the function f (α) can be determined, but for complex reactions it is generally unknown.

The model-free kinetics method allows evaluating the Arrhenius parameters without choosing a reaction model. This method uses Vyazovkin´s theory (Vyazovkin and Wight, 1999), which is based on isoconversional techniques and calculates the activation energy Ea as a function of the conversion level of a chemical reaction, Ea = f (α). The theory is based on the assumption that

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \tag{2}$$

where T is the temperature, t is the time, $f(\alpha)$ is the reaction model and $k(T)$ is the Arrhenius rate constant. Substituting this equation in Eq. (2), one obtains:

$$\frac{d\alpha}{dt} = A\, e^{-E_a/RT}\, f(\alpha) \tag{3}$$

where R is the universal gas constant, A is the pre-exponential factor and Ea is the activation energy. The Arrhenius Parameters (A and Ea), together with the reaction model are sometimes called kinetic triplet. There is an existing temporal dependence on non-isothermal conditions, which can be eliminated dividing f(α) by the heating rate β = dT/dt. After rearranging Eq. (3) one obtains:

$$\frac{1}{f(\alpha)}d(\alpha) = \frac{A}{\beta}e^{-E_a/RT}\,dT \tag{4}$$

Integrating Eq. (4) up to the conversion α at the local temperature T, one has:

$$\int_0^{\alpha}\frac{1}{f(\alpha)}d(\alpha) = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} e^{-E_a/RT}dT \tag{5}$$

Provided that the term $E/2RT >> 1$, the temperature integral on the right hand side can be approximated by

$$\int_{T_0}^{T} e^{-E_a/RT}dT \approx \frac{R}{E_a}T^2 e^{-E_a/RT} \tag{6}$$

After inserting Eq. (6) in Eq. (5), rearranging Eq. (5) and taking the logarithm of the generated expression one has:

$$\ln\left(\frac{\beta}{T_a^{\,2}}\right) = \ln\left(\frac{R\,A}{E_a\,g(\alpha)}\right) - \frac{E_a}{R}\frac{1}{T_\alpha} \tag{7}$$

Equation 7 is linearized by taking the logarithm. A great advantage of this method is that the function g (α) is isolated in the linear coefficient and must not be accounted for determining the activation energy. A complex reaction possesses a highly complex conversion function. From this principle, the model-free kinetics method is capable of determining the activation energy for the complex processes, such as combustion reactions. The activation energy can be obtained graphically by plotting $\ln(\beta/T^2)$ versus 1/T.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the TG and DTG mass loss curves of crude glycerol and animal fat with a heating rate of 30 °C/min. For the glycerol sample it is possible to obtain different regions of thermal decomposition, which are presented in Fig. 1.

The decomposition of animal fat proceeds within four reaction regions, shown in Fig. 2. The initial, maximum and final mass loss temperatures for each phase of crude glycerol decomposition are shown in Tab. 1 for all heating rates. Tab. 2 lists the same parameters for the decomposition of animal fat.

Three pronounced regions can be detected in DTG-curves, for the crude glycerol the mass loss in the first phase (PH1) was about 10 -15 % in a temperature range from (25-75) °C to (33-114) °C, depending on the heating rate.

The removal of water and some low-temperature volatiles, such as ethanol, the co-reactant in the transesterification of vegetable oil, were responsible for the mass loss for this low-temperature step.

The main loss of mass occurred in the second phase (PH2) from (108-225) °C to (139-324) °C, depending on the heating rate. The percentage of mass loss in the second phase was about 55-60 %. The third region of the glycerol sample extended between (439-471) °C and (476-561) °C. According to Dou et al. [10], the degradation of impurities, such as fatty acid methyl esters and residues from former degradation during PH2, is responsible for the third phase of degradation (PH3). Furthermore the authors detected another degradation region in a temperature range of 550-850 °C, depending on the heating rate. The final temperature in this work was limited to 600 °C, thus, the above-mentioned temperature range could not be reached and a further region of decomposition could not be detected.

Figure 2 shows the TG and DTG curves of animal fat recorded in synthetic air atmosphere at a heating rate of 30 °C/min. The four degradation regions can clearly be seen as they are defined by the pronounced peaks in the DTG curve. The first region, which corresponds to the dehydration, has less than 1 % of mass loss. The second region, called low-temperature oxidation, is considered the main step in this study. Its mass loss, between 80 % and 85%, spanned from (153-359) °C up to (225-413) °C, depending on the heating rate. Two further regions of fuel decomposition could be detected. PH3, with mass loss of 7%, extended from (384-430) °C to (421-496) °C depending on the heating rate. In addition, a final phase with mass loss between 8% and 13%, spanned from (445-517) °C to (515-597) °C.

Table 1. TGA results of crude glycerol.

Phase	Heating Rate (°C/min)	2.5	5.0	10.0	20.0	30.0
Phase 1	Initial mass loss temperature (°C)	25	32	27	31	33
	Maximum mass loss temperature (°C)	45	54	65	77	80
	Final mass loss temperature (°C)	75	102	105	117	114
Phase 2	Initial mass loss temperature (°C)	108	120	123	136	139
	Maximum mass loss temperature (°C)	182	198	217	231	246
	Final mass loss temperature (°C)	225	256	302	353	324
Phase 3	Initial mass loss temperature (°C)	439	449	453	464	476
	Maximum mass loss temperature (°C)	450	483	502	526	527
	Final mass loss temperature (°C)	471	506	536	574	561

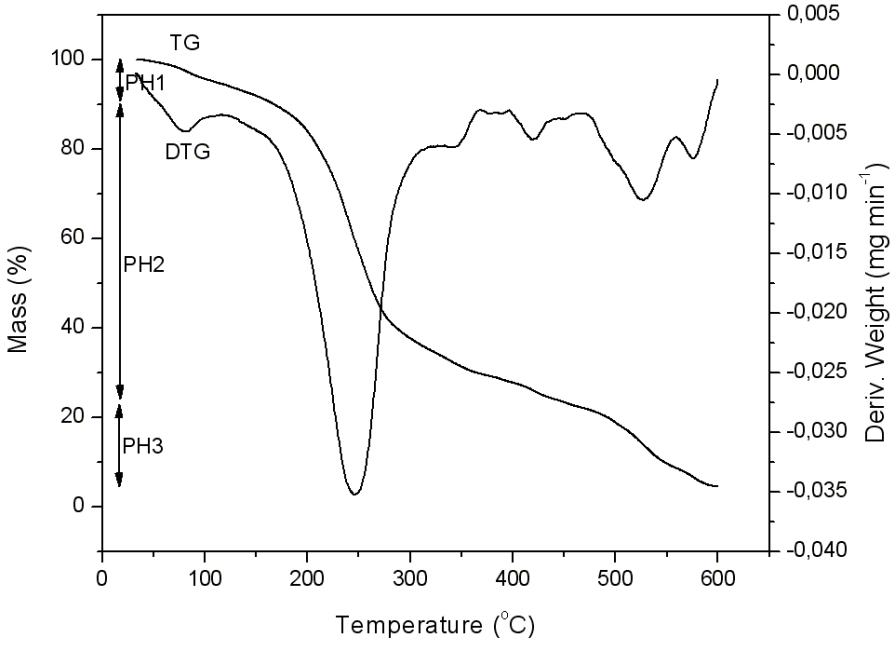

Figure 1. TG and DTG curves of crude glycerol with a heating rate of 30 °C/min.

Table 2. TGA results of animal fat.

Phase	Heating Rate (°C/min)	2.5	5.0	10.0	20.0	30.0
Phase 1	Initial mass loss temperature	30	30	27	26	27
	Maximum mass loss temperature	52	53	56	60	67
	Final mass loss temperature	103	105	100	115	113
Phase 2	Initial mass loss temperature (°C)	153	164	187	233	225
	Maximum mass loss temperature (°C)	272	287	332	353	356
	Final mass loss temperature (°C)	359	388	393	491	413
Phase 3	Initial mass loss temperature (°C)	384	395	400	423	421
	Maximum mass loss temperature (°C)	396	412	426	442	449
	Final mass loss temperature (°C)	430	455	468	482	496
Phase 4	Initial mass loss temperature (°C)	445	463	481	506	515
	Maximum mass loss temperature (°C)	488	511	528	551	565
	Final mass loss temperature (°C)	517	544	572	595	597

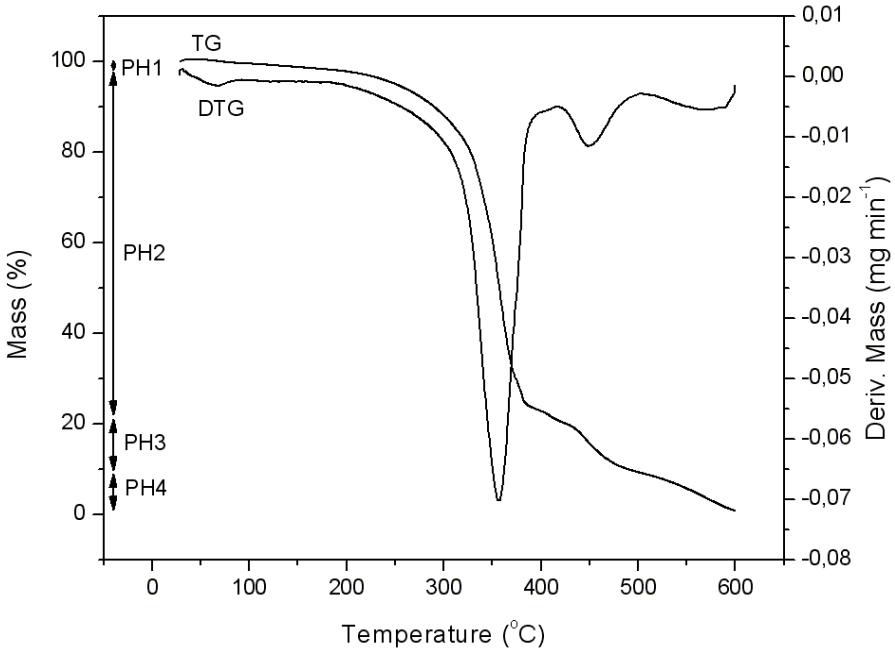

Figure 2. TG and DTG curves of animal fat with a heating rate of 30 °C/min.

The process that takes place in the region of the main mass loss can generally be called low-temperature oxidation. This low-temperature region indicates the first vaporization of the moisture and volatile hydrocarbons and then the oxidation of low molecular weight compounds by the exothermic reaction (Ali et al, 1998). According to Law and Binark, (1979)\, the combustion rate is frequently controlled by the rate of vaporization of droplets within the spray. This region was the major object of this study, as most released matters in this step are combustible. Thus, the activation energy of the low-temperature oxidation region can be associated with the quality of the fuel. Since the evaluation of this region in the present work is made through TGA, it is important to realize that the location and characteristics of this event depending on the heating rate. As showed in Figs. 3 and 4, with an increasing heating rate the maximum rate of weight loss is located at higher temperatures with more salient peaks.

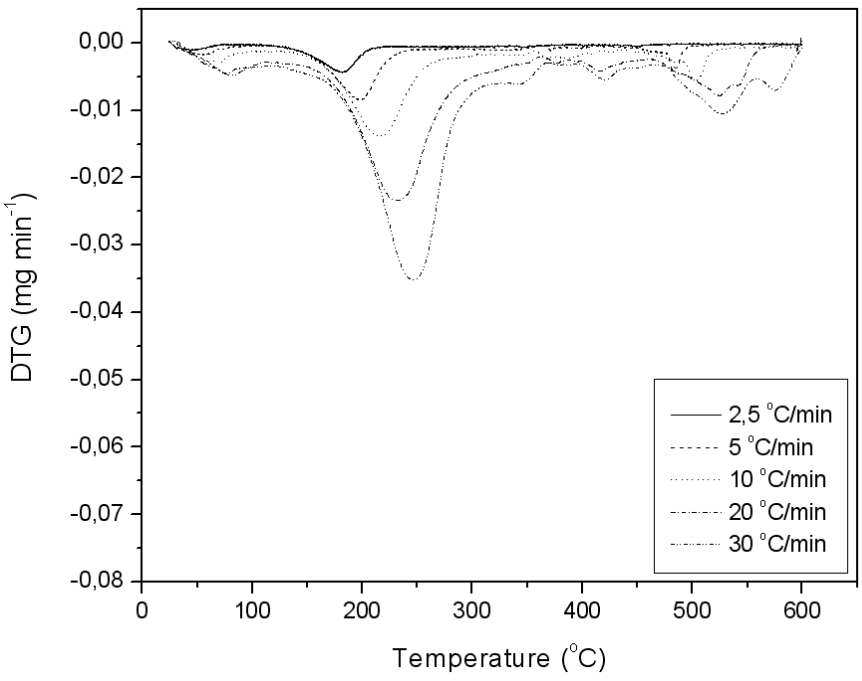

Figure 3. DTG curves of the glycerol sample at different heating rates.

As seen in Fig. 3 and 4, the highest rate of fuel decomposition in both cases is reached at a heating rate of 30 °C/min and the lowest rate of fuel decomposition occurred at a rate of 5 °C/min. The maximum mass loss rate of the animal fat sample (-0.070 mg/min) is twice the number of the maximum rate of the glycerol sample (-0.035 mg/min) and is reached at a higher temperature, corresponding a heating rate of 30 °C/min. For the animal fat this region is located at around 350 °C and for the glycerol sample it is located at 250 °C.

The maximum mass loss temperature is also called peak temperature and the final mass loss temperature is also called burn-out temperature. Both temperatures are listed for each sample and heating rate in Tab. 1 and 2.

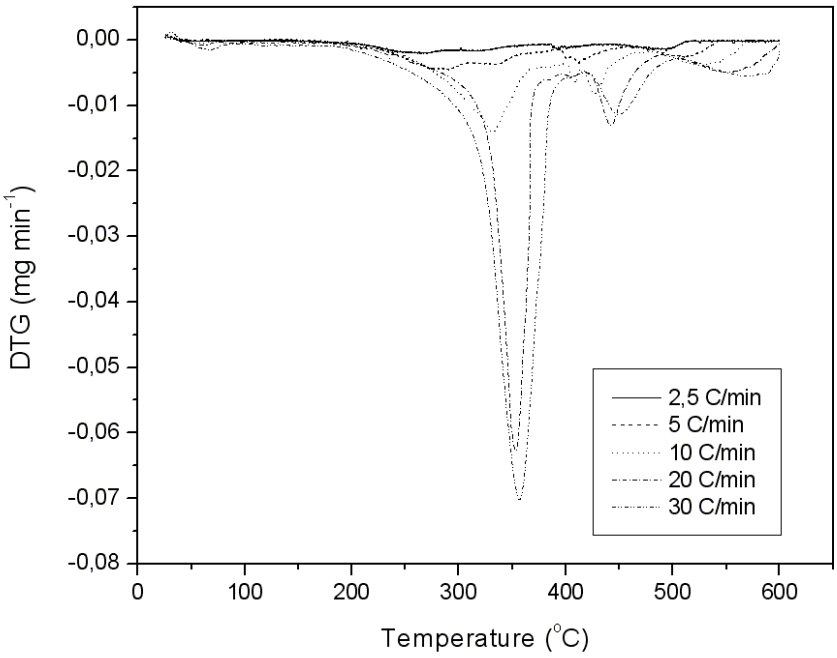

Figure 4. DTG curves of the animal fat sample at different heating rates.

As previously mentioned, the activation energy E_a is a function of the conversion degree α. Thus, it is necessary to evaluate the conversion degree of the low-temperature oxidation region using the model-free kinetics method. The conversion degree is determined as shown in Eq. (8):

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{8}$$

where m is the local sample mass that varies with the time, m_0 is the initial sample mass and m_∞ is the final sample mass.

Figure 5 shows the conversion degree plotted against the temperature for all different heating rates for the glycerol sample in the region of main mass loss (LTO). It is possible to observe that the run of the conversion curve is shifted to a higher temperature with an increasing heating rate. The quality of the run of animal fat is the same as the run of glycerol but it occurs at higher temperatures. The graph of animal fat is shown in Fig. (6). The burn-out temperature is reached at the end of the event (α=1) and the peak temperature is located at the inflection point of each curve.

Figures 5 and 6 show some levels of the fuel decomposition (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.8), and it is possible to observe that every conversion level is associated with a different temperature at different heating rates. By plotting $ln(\beta/T_\alpha^2)$ against $1/T_\alpha$, one obtains a curve with a slope of $-E_\alpha/R$, and for each level of conversion a different curve with independent slopes is obtained . Based on this principle the activation energy can be plotted as a function of the conversion, as shown in Fig. 6.

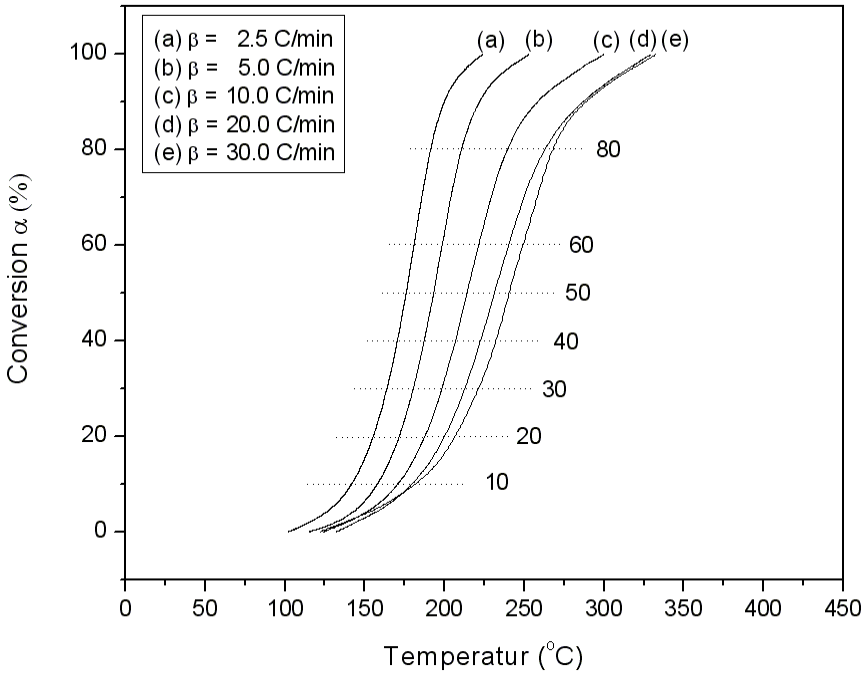

Figure 5. Conversion plotted against temperature for the LTO region of the glycerol sample.

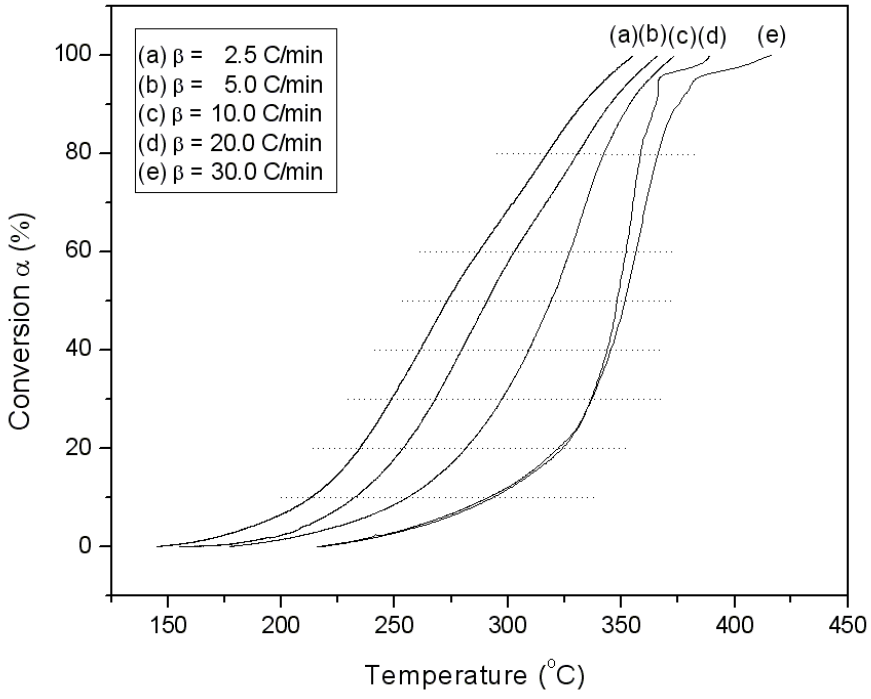

Figure 6. Conversion plotted against temperature for the LTO region of the glycerol sample.

Table 3. Activation energies of the glycerol and animal fat sample at exclusive conversion levels.

Conversion (%)	Activation Energy E_a (kJ/mol)	
	Animal Fat	Glycerol
10	60.25	82.78
20	59.28	75.80
30	63,65	71.75
40	71.41	69.38
50	82.18	67.38
60	100.85	64.45
80	175.16	58.70

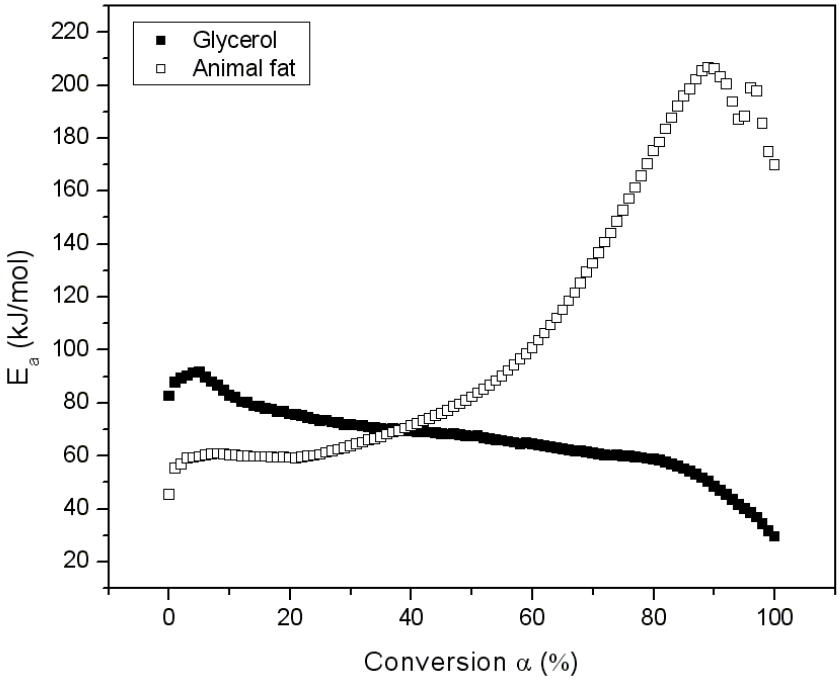

Figure 7. Activation energy against conversion along the LTO region.

Figures 7 shows activation energy variation with the conversion in both cases. The qualitative runs of both samples are very different. The glycerol sample reaches the maximum activation energy (92.25 kJ/mol) at a conversion of 0.05 with an insignificant decreasing run afterwards, reaching a conversion of 0.8. After that point the negative slope rises and the curve falls down to the lowest value of activation energy (29.64 kJ/mol).

The run of the animal fat sample starts at the lowest point of the curve (54.69 kJ/mol), increases slightly and proceeds constantly until a conversion of 0.2. At this point, the curve increases up to a complex peak with two distinctive maxima. At the highest point, the activation energy reaches a value of 206.91 kJ/mol. After the highest peak, the run decreases to a value of 169.8 kJ/mol at a conversion of $\alpha = 1$.

In order to compare both samples, the average activation energies of the samples were considered for the whole LTO-region. For the animal fat sample this value was 108.87 kJ/mol with a standard deviation of 52.28 kJ/mol. The mean value of the crude glycerol sample was determined as 65.37 kJ/mol with a standard deviation of 13.17 kJ/mol. From these both values of standard deviation and the higher activation energy for animal fat we can understand that animal fat is the more complex material than glycerol.

Table 3 shows the activation energy values corresponding to the seven conversion degrees. These points are marked in the conversion run of glycerol and animal fat in Fig. 5 and 6 respectively.

4. CONCLUSIONS

Thermogravimetric analysis of the crude glycerol and the animal fat were studied in this paper. It could be demonstrated that both materials have different groups of reactions occurring in different temperature zones and exhibiting a different region of main mass loss (LTO). With an increasing heating rate, the TG curves and the DTG peaks were shifted to higher temperatures and the main reaction interval of each sample became longer.

For the animal fat sample the second region was identified as the low-temperature oxidation and was followed by two further regions.

The main weight loss of the glycerol sample occurred during the second step after a first step of dehydration and removal of other low-temperature volatiles.

Activation energy for crude glycerol obtained in this work was 65.37± 13.17 kJ/mol and from literature (Dow *et al* 2009) was 40-50 kJ/mol). These results should considered very close considering that crude glycerol is a co-product from biodiesel production and they were collected from different processes and industries. For animal fat results obtained in this work (108.87 ± 52.28 kJ/mol) were also close than others presented in literature (Skudras *et al*, 2007) , which value obtained was 117.38±14.32 kJ/mol.

As the activation energy E_a is an important characteristic to qualify a fuel, this kinetic parameter was determined for both samples at low-temperature oxidation region. LTO region was selected for this study because most released matters in this step are combustible and it is associated with the quality of the fuel.

The activation energy can be thought as a potential barrier that must be overcome in order for a chemical reaction to occur. Reactions with high activation energy need a higher temperature or a longer reaction time. As animal fat is a more complex substance than glycerol, its activation energy approximately 1.7 times higher than the activation energy of glycerol. The peak value of animal fat is even almost twice higher than the peak value of glycerol.

Using fuels with low activation energy, combustion chamber can be operated with lower pressure and lower temperatures than when fuels with high activation energy are used. The lower the activation energy of a reaction, the lower the ignition temperature will be and less energy during the starting of spark is needed.

5. ACKNOWLEDGEMENTS

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