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2012

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BIOMASS & BIOENERGY, OXFORD, v. 44, n. 4, supl. 1, Part 3, pp. 8-16, SEP, 2012

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# Determination of the activation energies of beef tallow and crude glycerin combustion using thermogravimetry

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## ARTICLE INFO

### Article history:

Received 25 July 2011

Received in revised form

25 March 2012

Accepted 10 April 2012

Available online 14 May 2012

### Keywords:

Biofuels

Crude glycerin

Beef tallow

Kinetics

Thermal analysis

Ignition delay

## ABSTRACT

The present study deals with the determination of the activation energy for the thermal decomposition of two renewable fuels – crude glycerin and beef tallow. The activation energies were investigated by using a thermogravimetric analyzer (TGA) in the temperature range of 25–600 °C in atmosphere of synthetic air. The TG curves of the thermal decomposition process of both samples were divided into several phases and the second, called PH2, was chosen for the kinetic study because it is associated with the combustion ignition. Differential Thermal Analysis (DTA) showed an endothermic event at the PH2 region for the crude glycerin corresponding to devolatilization, while for beef tallow, this step presented an exothermic event, called LTO (low-temperature oxidation), which is correlated with devolatilization followed by combustion. For the entire PH2, activation energy values for crude glycerin were between 90 kJ mol<sup>-1</sup> and 42 kJ mol<sup>-1</sup>, while for the beef tallow they ranged from 50 kJ mol<sup>-1</sup> to 113 kJ mol<sup>-1</sup>. The activation energy values obtained at the pre-ignition stage - conversion between 0 and 0.45 - showed that the crude glycerin with higher values requires an additional energetic support at the start of combustion processes and the beef tallow ignites more easily, presenting lower values. According to the Wolfer's equation, a direct relation between the activation energy and the ignition delay is established and the results of this study provides useful data for the development and design of new combustion chambers and engines when non-traditional fuels are used as feedstock.

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## 1. Introduction

Crude oil reserves are limited and concentrated only in certain regions of the world. As the oil production costs increase, the development of renewable fuels becomes more attractive [1]. In contrast to crude oil, abundant biomass resources are available in most regions of the world [2], and have become an alternative in the production of cleaner and almost non-toxic fuels.

Due to the increasing interest in replacing fossil fuels, renewable energy sources, such as alternative and non-traditional fuels, are subjects of great interest around the world, although their use is still a challenge in both practical and modeling combustion systems. Renewable energy sources include materials that supply energy without depleting their existence and are considered environmentally friendly when used in thermochemical conversion technologies.

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doi:10.1016/j.biombioe.2012.04.013

Beef tallow and crude glycerin can be considered sources for renewable fuels. Fats and oils have almost the same potential of petroleum-based diesel fuels, but they require plenty of research concentration, since the chemical composition of the fuels plays an important role in the combustion characteristics and emissions [3]. Kerihuel et al. [4] analyzed the lower heating values of animal fat-based fuels and the results obtained of the calorimeter test were  $38.3 \text{ kJ kg}^{-1}$  for animal fat and  $42.5 \text{ kJ kg}^{-1}$  for standard diesel. Besides biodiesel production, beef tallow can be used to produce alternative diesel fuels in an attempt to reduce the cost of raw materials [5] and [6].

Crude glycerin (or crude glycerol) is generated as a byproduct of the biodiesel production and alternative uses for this material are currently being investigated [7].

With the increasing production of biodiesel, an excess of crude glycerin is expected, which becomes a waste problem. As crude glycerin is a very poor fuel and contains many impurities, it cannot be used directly in diesel and petrol engines. However, it is important to find alternatives for its use. Several proposals, such as pyrolysis and gasification [8] and [9] and steam reforming [10] and [11] can be found in the literature, but there is still a lack of studies related to thermal behavior including kinetic data.

The combustion mechanism, fuel characteristics and ignition behavior play an important role in the development of new combustion chambers and engines. As stated by Shen et al. [12], the understanding of the thermochemical conversion of the biomass is important for the development of efficient technological processes.

The early stage of combustion includes two steps: pre-ignition and ignition. The quality of combustion is also related to its ignition, which controls the startability of the process [13]. The time between the start of fuel injection and the start of detectable combustion phenomena is the ignition delay [14], [15], and [16].

Although the ignition delay of a fuel is commonly related to diesel engines, it can also be applied to other combustion processes since they are affected by air temperature, pressure, and oxygen concentration [13].

The period of ignition delay is composed of a physical delay and a chemical delay. Both are responsible for the fuel pre-ignition and it is difficult to distinguish between them due to their overlapping [13] and [16]. However, physical processes are the early stage of the pre-ignition, which is followed by chemical changes. Such changes are considered the last stage of pre-ignition and yield in intermediate species.

The critical concentration of such species is important to trigger the combustion process and can be, therefore, correlated with ignition delay, which is also related to this activation energy as presented in Equation (1) - proposed by Wolfer in 1938 [13],[14], and [16],

$$\tau = Ap^{-n}e^{\left(\frac{E_a}{RT}\right)} \quad (1)$$

where  $\tau$  is the ignition delay,  $p$  is the pressure,  $n$  is an exponent and  $A$  is the pre-exponential factor dependent on the combustion chamber and interactions of the fuel and oxidizer.

In the original Wolfer's work,  $A$ ,  $n$  and  $E_a$  are constants, but in the present work we have assumed that they are

dependent on the characteristics of fuel and experimental conditions.

Based on Equation (1), it is possible to observe that the better the ignition process, the lower the activation energy, since a good ignition process is labeled by the shortest ignition delay. From this statement, in this work, activation energy is used to qualify the fuel related to the ease of igniting in the combustion process.

The activation energy of a fuel can effectively be obtained by an experimental setup, particularly by thermal analyses. These techniques have gained wide acceptance in the study of the combustion and pyrolysis behavior of potential fuels [17], as they require small samples, are very useful from a fundamental viewpoint and comparison between samples, proceed fast, are high-precision techniques and can provide information about the partial process and reaction kinetics [18], [19] and [20].

Thermogravimetric analysis (TG/DTG) has been used to study animal-derived products [21],[22], and [23]. These studies could detect several regions of mass loss with one of them been the main region. However, studies that concentrate on the determination of kinetic parameters of thermal behavior of beef tallow are hardly found in the literature. TG experiments have also been used for the determination of kinetic parameter of the pyrolysis for crude glycerol [24] and the second phase was chosen as the main region of the thermal decomposition.

Considering that very little is known about the combustion process of alternative fuels sources mainly regarding the pre-ignition chemical reactions, this paper presents the determination of the activation energy of the combustion for two renewable fuels. Thermogravimetric analyses were carried out and the model-free kinetic method was applied to both crude glycerin and beef tallow in the second region of the thermal decomposition, which is responsible for the pre-ignition and ignition in a combustion process. Starting from the direct relation between the ignition delay and the activation energy, one can qualify different possible fuels by their activation energies.

## 2. Materials and methods

Samples were obtained from a biodiesel industry located in Piracicaba, São Paulo State, Brazil. Beef tallow is the raw material for biodiesel production and crude glycerin is the byproduct from the same process. For the experiments, samples were used "in natura", i.e., they did not suffer any treatment before use.

Here we used the denomination crude glycerin instead of glycerol because crude glycerin is a blend of many impurities from the biodiesel process. However, it is important to realize that glycerol is the major compound present in the crude glycerin composition.

The main physical-chemical characteristics of both samples are given in Table 1. Proximate Analysis was performed according to the methodology described in Karatepe and Kuçukbayrak [25], and ultimate analysis was determined on the CE Instruments analyzer, model EA1110- CHNS-O.

From elemental composition, the crude glycerin molar formula is  $\text{C}_3\text{H}_7\text{O}_{1.7}\text{N}_{0.1}$ , i.e., higher C/H and C/O ratios than

**Table 1 – Proximate, ultimate analysis and high heating value of crude glycerin and beef tallow.**

Analysis as received	Samples	
	Crude glycerin	Beef tallow
<i>Proximate analysis</i>		
Moisture (%)	16.5	0.5
Volatile matter (%)	79.7	98.6
Fixed carbon (%)	–	0.9
Ash	3.7	–
<i>Ultimate analysis</i>		
Carbon (%)	50.2	76.7
Hydrogen (%)	9.7	11.6
Oxygen (%)	37.5	11.3
Nitrogen (%)	2.6	0.33
High heating value (MJ kg <sup>-1</sup> )	25.5	38.2

glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>), this difference may have been contributed by presence of the triglycerides and fatty acid methyl esters produced in the transesterification process.

### 2.1. Experimental procedures

Thermal analysis experiments were performed in a Shimadzu TGA-51H thermogravimetric analyzer and in a DTA- 50 differential thermal analyzer. The TG technique determines changes in the sample mass as a function of temperature and DTG is the derivative of the TG curve, representing the change rate in the sample mass. DTA measures the temperature difference between a sample and an inert reference material, and allows to determining enthalpic transitions when both sample and reference are subjected to the same heat treatment [26]. In this study, an empty crucible was used as reference since it is part of the calibration of the equipment.

In all experiments the temperature raised from room temperature up to 600 °C at five heating rates: 2.0, 5.0, 10.0, 20.0 and 30.0 °C min<sup>-1</sup>. All experiments were run three times for each sample and a set of average curves was used 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 applied. The reacting atmosphere was synthetic air, which streamed at a constant volume flow rate of 100 mL min<sup>-1</sup> over the samples.

### 2.2. Kinetic study

Kinetic parameters of crude glycerin and beef tallow were obtained using non-isothermal thermogravimetric (TG) experiments and model-free kinetics.

The reaction rate of a chemical reaction depends on conversion, temperature and time. Conversion is defined as  $\alpha = (m_0 - m)/(m_0 - m_\infty)$ , where  $m$  is the local sample mass that varies with time,  $m_0$  is the initial sample mass and  $m_\infty$  is the final sample mass. The reaction rate as a function of conversion is different for each process and may be detected experimentally. For simple reactions, the function of conversion,  $f(\alpha)$ , 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 is based on isoconversional techniques and calculates the activation energy as a function of the conversion level of a chemical reaction,  $E_a = f(\alpha)$  [27],[28], and [29]. The method is based on the assumption that

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (2)$$

where  $T$  is the temperature,  $t$  is the time,  $f(\alpha)$  is the reaction model and  $k(T)$  is the constant of reaction rate,  $R$  is the universal gas constant,  $A$  is the pre-exponential factor and  $E_a$  is the activation energy.

There is an existing temporal dependence on non-isothermal conditions, which can be eliminated dividing  $f(\alpha)$  by the heating rate  $\beta = dT/dt$ . After rearranging Equation (2) one obtains:

$$\frac{1}{f(\alpha)} d(\alpha) = \frac{A}{\beta} e^{-E_a/RT} dT \quad (3)$$

Integrating Equation (3) up to the conversion at the local temperature, one has:

$$\int_0^\alpha \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad (4)$$

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

$$\int_{T_0}^T e^{-E_a/RT} dT \approx \frac{R}{E_a} T^2 e^{-E_a/RT} \quad (5)$$

After inserting Equation (5) in Equation (4), rearranging Equation (4) and taking the logarithm of the generated expression one has:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{RA}{E_a g(\alpha)}\right] - \frac{E_a}{R} \frac{1}{T} \quad (6)$$

where subscript  $\alpha$  represents the values related to a given conversion.

A great advantage of this method is that the function  $g(\alpha)$  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 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

### 3.1. TG/DTG and DTA experiments

Figs. 1 and 2 show the TG (thermogravimetric) and DTG (Derivative thermogravimetric) curves with a heating rate of 30 °C min<sup>-1</sup> of the crude glycerin and the beef tallow, respectively. These figures show the curves for only one

heating rate in order to present the different phases of thermal decomposition in a form that is more visually accessible. However, for various heating rates (2.0, 5.0, 10.0 and 20 °C min<sup>-1</sup>) similar profiles were obtained.

Both materials have different thermal behaviors presenting groups of reactions with different temperature zones. In these non-isothermal experiments, for the crude glycerin sample three different regions of thermal decomposition can be observed and distinguished in the DTG curve. The thermal decomposition of beef tallow proceeded within four reaction regions. Different regions in the TG curves for both samples were distinguished through DTG curves, in which a series of peaks are obtained.

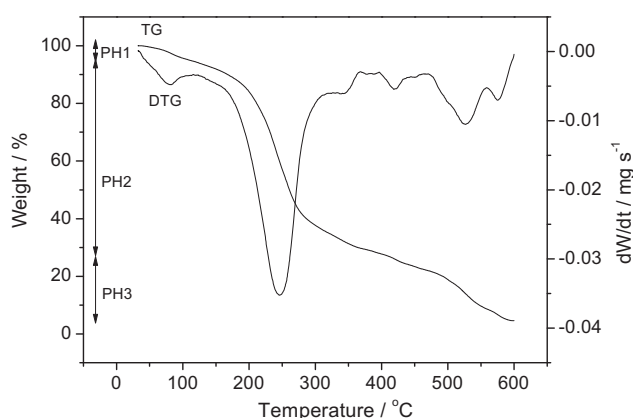
The initial, maximum and final mass loss temperatures for each phase of the crude glycerin decomposition are shown in Table 2 for all heating rates. The maximum mass loss temperature is also called peak temperature and the final mass loss temperature is also called burn-out temperature.

The mass loss in the first phase (PH1) was approximately 10–15% in a temperature range from (25–75) °C to (33–114) °C, depending on the heating rate, i.e., as the heating rate is increased, the maximum mass-change of the event shifts to higher temperatures. Such a behavior is attributed to the variations of heat transfer in function of the change in the heating rate.

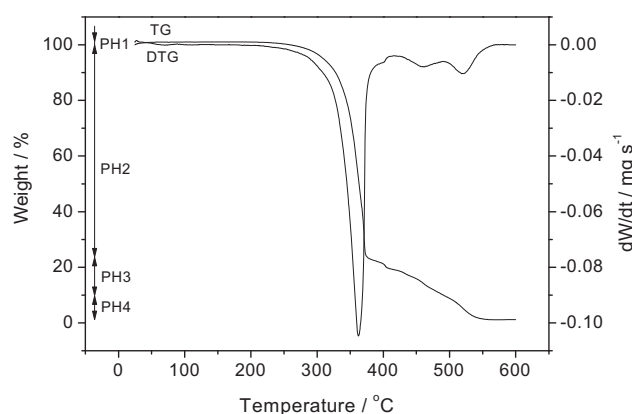
The removal of water and some low-temperature volatiles, such as methanol, the co-reactant in the transesterification reaction, are considered to be the responsible for the mass loss for this first step [24].

The second decomposition region, also called second phase (PH2) occurred from (108–139) °C to (225–324) °C, depending on the heating rate. The PH2 was considered the main region, and chosen for the kinetics study, because it was characterized by the major weight loss corresponding to the main released components. The percentage of mass loss in the second phase was approximately 55–60%.

The third region of the crude glycerin sample extended between (439–469) °C and (471–551) °C. According to Dou et al. [24], the degradation of impurities, such as fatty acid methyl



**Fig. 1** – TG and DTG curves of the crude glycerin sample at heating rate of 30 °C min<sup>-1</sup>. The three phases (PH1, PH2, and PH3) for the thermal decomposition of the crude glycerin are indicated. Sample mass = 9.87 mg, air atmosphere (100 mL min<sup>-1</sup>).



**Fig. 2** – TG and DTG curves of the beef tallow sample at heating rate of 30 °C min<sup>-1</sup>. The four phases (PH1, PH2, PH3 and PH4) for the thermal decomposition of the beef tallow are indicated. Sample mass = 10.00 mg, air atmosphere (100 mL min<sup>-1</sup>).

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.

The final temperature in the present study was limited to 600 °C because PH2 for both samples was the main region of thermal degradation, and major object of this study. The main mass loss takes place in this region and most released matter in this step, responsible for the pre-ignition and ignition in a combustion process, is combustible.

Fig. 2 shows the TG and DTG curves of beef tallow recorded at the heating rate of 30 °C min<sup>-1</sup>. The four degradation regions can clearly be seen as they are defined by the pronounced peaks in the DTG curve. The initial, maximum and final mass loss temperatures for each phase of the beef tallow decomposition are shown in Table 3 for all heating rates.

The first region, which corresponds to dehydration, has less than 1% mass loss. The second region is also considered

**Table 2** – TGA results of the crude glycerin for five heating rates.

Phase	Region of mass loss	Heating rate (°C min <sup>-1</sup> )				
		2.0	5.0	10.0	20.0	30.0
Temperature (°C)						
PH1	Initial	25	32	27	31	33
	peak	45	54	65	77	80
	burn-out	75	102	105	117	114
PH2	Initial	108	120	123	136	139
	peak	182	198	217	231	246
	burn-out	225	256	302	353	324
PH3	Initial	439	449	453	464	476
	peak	450	483	502	526	527
	burn-out	471	506	536	574	561



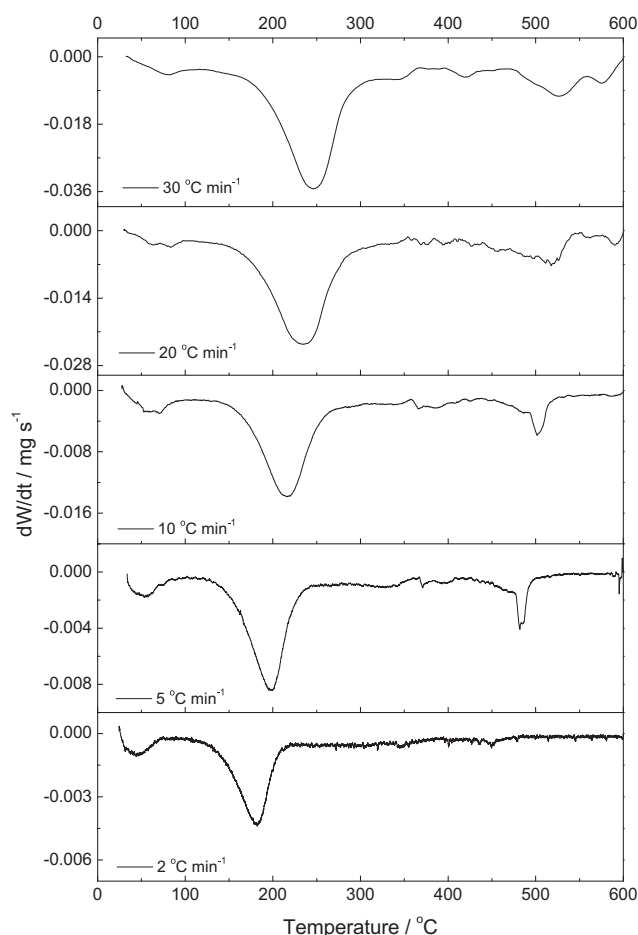
the main step for this sample because its mass loss corresponds to 80% and 85% of the total mass loss. This region spanned from (139–244) °C up to (360–400) °C, and it is important to notice that the location and characteristics of this event is also dependent on the heating rate. In addition, two further regions of fuel decomposition could be detected. PH3, with mass loss of 7%, extended from (365–423) °C to (440–494) °C and a final phase with mass loss between 8% and 13%, spanned from (445–500) °C to (512–595) °C.

As presented in the Figs 3 and 4, DTG curves showed that with an increasing of heating rate, the maximum rate of weight loss is located at higher temperatures with more salient peaks and the reaction interval of each sample became longer.

The highest rate of fuel decomposition, in both cases, was reached at a heating rate of 30.0 °C min<sup>-1</sup> and the lowest rate of fuel decomposition occurred at a rate of 2.0 °C min<sup>-1</sup>. The maximum mass loss rate of the beef tallow sample (0.10 mg min<sup>-1</sup>) located at 362 °C is more than twice the value of the maximum rate of the crude glycerin sample (0.035 mg min<sup>-1</sup>), located at 246 °C. Thus, for beef tallow the compounds would be released faster than crude glycerin. The size and sharpness of the peak significantly differ between both samples. The beef tallow DTG curves exhibited pronounced and narrow peaks while crude glycerin exhibited a much wider temperature range.

From DTA curves, which show endothermic and exothermic enthalpic transitions, it can be observed that the region around 240 °C for crude glycerin corresponds to an endothermic event (Fig. 5) and for beef tallow, the region at around 380 °C corresponds to a pronounced exothermic event, as presented in Fig. 6. It seems that the exothermic peak in the temperature range of 225 °C and 467 °C in the DTA curve of the beef tallow is a reflection of the combustion of the released volatiles, and for crude glycerin, the endothermic peak at 184–332 °C is a reflection of the decomposition or dissociation reaction.

This difference in the enthalpic transitions for the second decomposition stage shows that the thermal degradation process differs for each sample. In the case of the crude



**Fig. 3 – DTG curves of the crude glycerin sample at five heating rates. Sample mass = 10.00 ± 0.50 mg, air atmosphere (100 mL min<sup>-1</sup>).**

**Table 3 – TGA results of the beef tallow for five heating rates.**

Phase	Region of mass loss	Heating rate (°C min <sup>-1</sup> )				
		2.0	5.0	10.0	20.0	30.0
		Temperature(°C)				
PH 1	Initial	30	30	27	26	27
	peak	52	53	56	60	67
	burn-out	103	105	100	115	113
PH 2	Initial	153	164	187	233	225
	peak	292	304	334	347	364
	burn-out	359	388	393	491	413
PH 3	Initial	384	395	400	423	421
	peak	396	412	426	442	449
	burn-out	430	455	468	482	496
PH 4	Initial	445	463	481	506	515
	peak	488	511	528	551	565
	burn-out	517	544	572	595	597

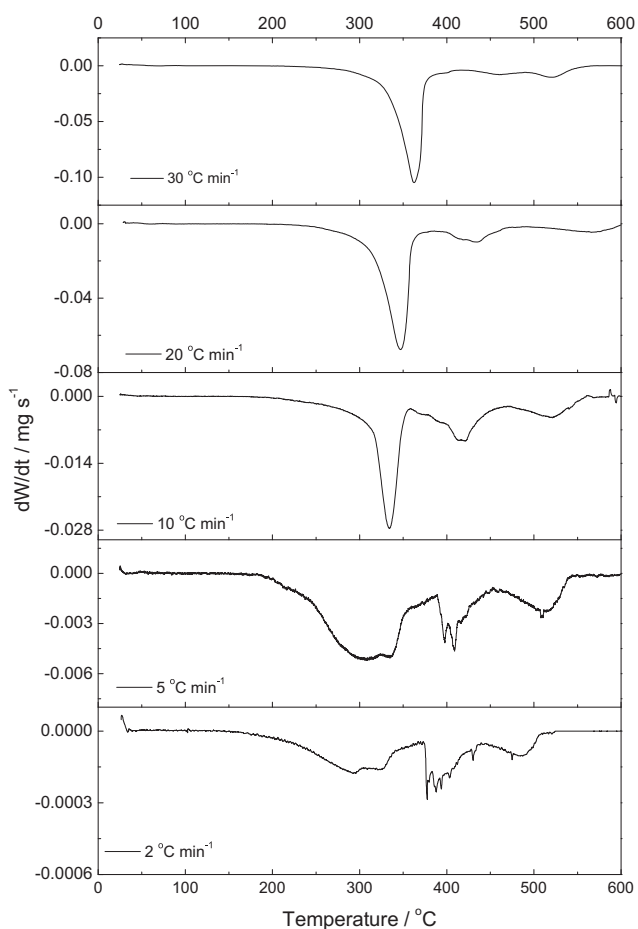
glycerin, PH2 can be called devolatilization process and in the beef tallow case, this region can be called LTO (low-temperature oxidation).

LTO is the process in which there occurs firstly the vaporization of volatile hydrocarbons and their decomposition into lighter molecular weight compounds followed by combustion [30] and [31]. This LTO region is responsible for the intermediate species formation, which in a critical concentration are responsible for the propagation of exothermic chemical reactions [32].

Thus, the activation energy of the PH2 can be associated with the quality of the fuel in the ignition step of a combustion process.

### 3.2. Activation energy determination

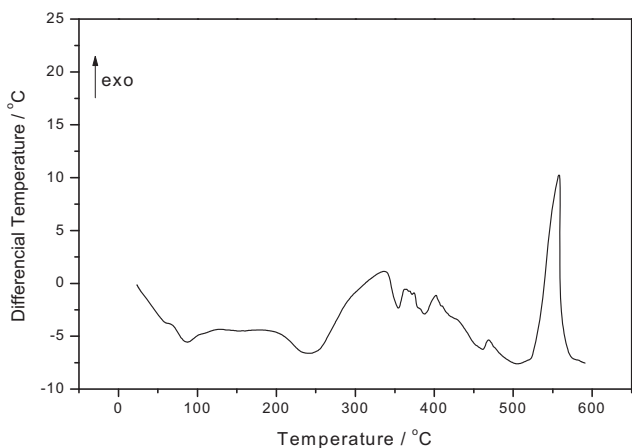
Fig. 7 shows the conversion degree plotted against temperature for all different heating rates for the crude glycerin sample in the PH2. It is possible to observe that the run of the conversion curve is shifted to a higher temperature with an increasing heating rate. The quality of the run of the beef tallow is the same as the run of crude glycerin but it occurs at



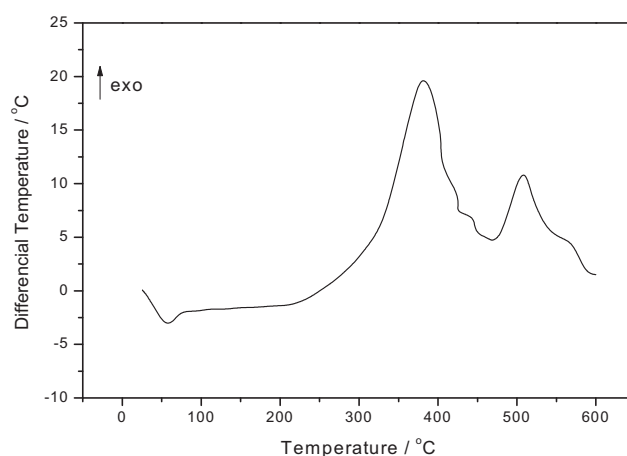
**Fig. 4 – DTG curves of the beef tallow sample at five heating rates. Sample mass = 10.00 ± 0.50 mg, air atmosphere (100 mL min<sup>-1</sup>).**

higher temperatures. The graph of conversion against temperature for the PH2 of the beef tallow is shown in Fig. 8.

Figs 7 and 8 also 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



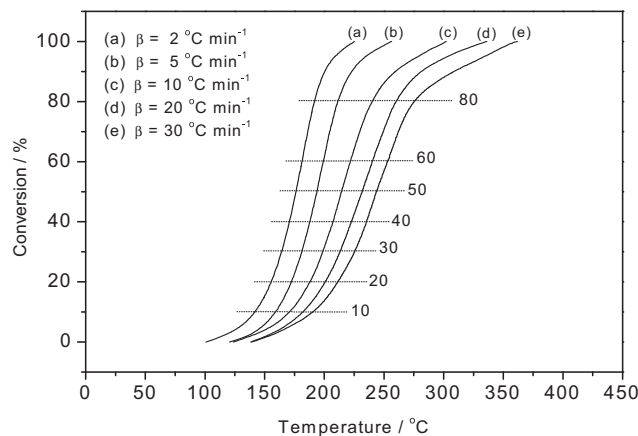
**Fig. 5 – DTA curve of the crude glycerin at heating rate of 30 °C min<sup>-1</sup>. Sample mass = 10.40 mg, air atmosphere (100 mL min<sup>-1</sup>).**



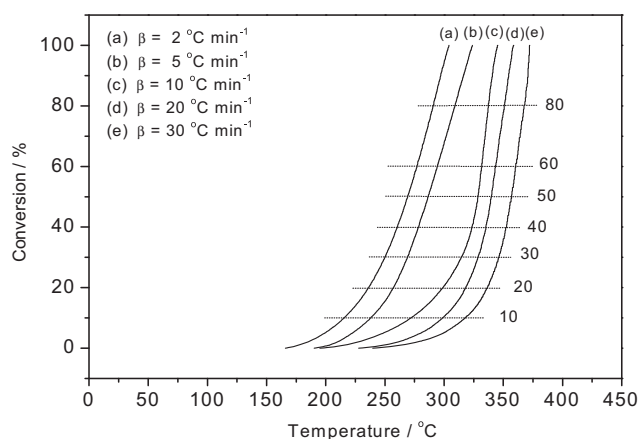
**Fig. 6 – DTA curve of the beef tallow at heating rate of 30 °C min<sup>-1</sup>. Sample mass = 10.50 mg, air atmosphere (100 mL min<sup>-1</sup>).**

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 slope is obtained. Table 4 shows the activation energy values corresponding to these seven conversion degrees. Based on this principle the activation energy can be plotted as a function of the conversion in both cases, as shown in Fig. 9.

Fig. 9 shows that the qualitative runs of both samples are very different. Crude glycerin reaches the maximum activation energy (90 kJ mol<sup>-1</sup>) at a conversion of 0.05 with a slight decreasing run afterward, reaching a conversion of 0.8 with activation energy of 58.7 kJ mol<sup>-1</sup>. After that point the negative slope rises and the curve falls down to the lowest value of activation energy (42 kJ mol<sup>-1</sup>). On the other hand, the run of the beef tallow sample starts at 59 kJ mol<sup>-1</sup>, decreases slightly reaching the lowest point of the curve (50 kJ mol<sup>-1</sup>), increases and proceeds constantly until the highest point, in which the activation energy is 113 kJ mol<sup>-1</sup> at the conversion of  $\alpha = 1$ .



**Fig. 7 – Conversion plotted against temperature for the PH2 of the crude glycerin sample. Conversion range normalized for 0–100%.**

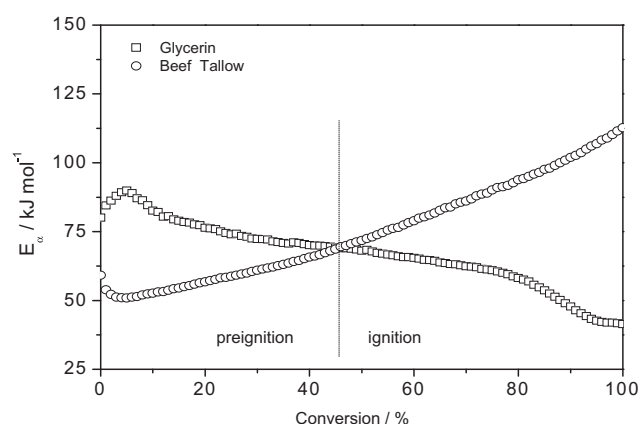


**Fig. 8** – Conversion plotted against temperature for the PH2 of the beef tallow sample. Conversion range normalized for 0–100%.

Considering the lowest and the highest values of the activation energy obtained by model-free kinetics, for the crude glycerin sample the range was between  $90 \text{ kJ mol}^{-1}$  and  $42 \text{ kJ mol}^{-1}$  and in the literature, values ranged from 40 to  $50 \text{ kJ mol}^{-1}$  [24]. These results should be considered close since crude glycerin is a co-product of biodiesel production and they were collected from different industrial processes. For beef tallow, the activation energy values ranged from  $50 \text{ kJ mol}^{-1}$  to  $113 \text{ kJ mol}^{-1}$ , which is also within the range ( $117.38 \pm 14.32 \text{ kJ mol}^{-1}$ ) presented in Skodras et al. [23].

For comparison with diesel, Aligrot et al. [33] determined activation energy for six different diesel fuels and values ranged from  $65 \text{ kJ mol}^{-1}$  and  $85 \text{ kJ mol}^{-1}$ . In average, values of activation energies for both crude glycerin and beef tallow are close to the range for diesel. However Model Free kinetics assumes that this parameter does not remain constant during the reaction. In addition the range determined for both crude glycerin and beef tallow is an indicative that the activation energy should be considered as several values instead of an average value, and this information is expected to play an important role mainly when new fuels have been used in combustion processes.

Fig. 9 also shows that from the beginning up to the conversion of 0.45, the activation energy of crude glycerin is



**Fig. 9** – Activation energy against conversion along the PH2 for both samples: crude glycerin and beef tallow.

higher than those of the beef tallow. From this point there is an inversion of behavior, i.e., the activation energy values of the beef tallow became considerably higher than those of the crude glycerin. Such an inversion may have occurred because the chemical structure of the glycerol (the main compound in crude glycerin) is simpler than that of triglycerides, which are the main compounds in the beef tallow.

The aforementioned activation energy is related to ignition delay (Equation (2)), hence combustion quality. The differences in the activation energies for both samples are related to their ignition combustion behavior. These results suggest that at the pre-ignition stage ( $0 < \alpha < 0.45$ ) of crude glycerin, an additional energetic support must be supplied to trigger the formation of intermediate species; for beef tallow, the lower activation energy is an indication that this material ignites more easily.

As expected, due to the higher heating value ( $38.2 \text{ MJ kg}^{-1}$ ) of the beef tallow this material is easier to burn than crude glycerin, which has moderate heating value ( $25.5 \text{ MJ kg}^{-1}$ ). However, fundamental knowledge related to kinetics and thermal behavior is essential in modeling studies, flame stabilization systems, improvements in burners and combustion chamber designs, in which the early stages of the ignition processes are dominated by chemical changes [13].

The step of mass loss for both samples studied in this work is important for the ignition process. While for crude glycerin it corresponds to volatile release, for beef tallow it corresponds to volatile release followed by combustion, which turns the complexity of the activation energy behavior understandable.

**Table 4** – Activation energies of crude glycerin and beef tallow sample at exclusive conversion levels.

Conversion (%)	Activation energy ( $\text{kJ mol}^{-1}$ )	
	Crude glycerin	Beef tallow
10	82.6	52.6
20	76.4	56.8
30	72.4	60.9
40	70.1	65.7
50	68.1	71.8
60	65.4	78.9
80	58.2	93.8

#### 4. Conclusions

Activation energies for the combustion process of crude glycerin and beef tallow have been determined using both non-isothermal thermogravimetric experiments and Model Free Kinetics. Results have showed that both materials have different thermal behaviors and groups of reactions (phases) with different temperature zones.



The second phase (PH2) of thermal decomposition was chosen for the kinetic study because it corresponds to the main mass loss in the thermogravimetric curves. PH2 is also associated with the formation of intermediate compounds responsible for the pre-ignition stage of the combustion, and it is the rate-controlling stage of the process as a whole.

Differential thermal analysis (DTA) was also used to assess the burning characteristics, whose curves showed that, for crude glycerin, PH2 corresponds to the devolatilization process and in the beef tallow case, this region can be called LTO (low-temperature oxidation).

For the entire PH2 process, on average, the activation energy for beef tallow is higher than that for crude glycerin and for both samples the results are similar to those presented in the literature, i.e. for crude glycerin, values were between 90 and 42 kJ mol<sup>-1</sup> and for beef tallow, between 50 and 113 kJ mol<sup>-1</sup>. However, it is important to realize that the activation energy does not remain constant during reaction, which is fundamental information to predict the behavior of these fuels in combustion processes.

In addition, activation energy is an important parameter to qualify a fuel. Since this parameter is also related to the behavior of pre-ignition and ignition delay, the values obtained at the pre-ignition stage ( $0 < \alpha < 0.45$ ) indicate that the crude glycerin requires an additional energetic support at the start of combustion processes due to its higher activation energy. On the other hand, at this stage, the beef tallow has a lower activation energy value, indicating that this material ignites more readily.

This information is important since fundamental knowledge related to kinetics and thermal behaviors is essential in the design of combustion chambers and burners. Using fuels with low activation energy, combustion chambers can be operated with lower pressure and temperature than those required when fuels with high activation energy are used.

## Acknowledgments

The authors are grateful to CAPES (processes PNPd 0034088 and BEX 1149/10-5) and FAPESP (processes 2011/00183-2 and 2011/11321-7) for the financial support provided to this research. They are also indebted to Dr. Fernando Cesar Almada and Prof. Angela Giampetro for their assistances.

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