



THERMOGRAVIMETRIC STUDY AND KINETIC ANALYSIS OF SUGARCANE STRAW

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Abstract. *The aim of this work was analyze the sugarcane straw as a solid fuel in a thermal conversion process. The thermal decomposition of sugarcane straw in inert atmosphere (nitrogen) has been studied by thermogravimetric (TG) and differential thermogravimetric (DTG) analysis, in order to determine the one of the most important kinetic parameter of the pyrolysis reaction, the apparent activation energy. The apparent activation energy was determined using two different integral methods reported in literature, Coats and Redfern modified and Ozawa-Flynn-Wall. Different heating rates, 1.25, 2.5, 5, 10, 20°C/min were used from 25 to 900°C, in order to compare the thermal behavior of samples (+420-600 µm). The TG results showed that, the higher heating rate, the higher is the temperature of beginning of the decomposition reaction. The DTG curve showed one shoulder and one peak, concerning to the hemicellulose and cellulose decompositions. Also, the apparent activation energies between 160 kJ/mol-220 kJ/mol were obtained. The knowledge of this kinetic parameter allows a better understanding of the thermal decomposition behavior of sugarcane straw.*

Keywords: biomass, thermal decomposition, kinetic methods, pyrolysis.

1. INTRODUCTION

There are many different ways in which the abundance of energy in the world can be stored, converted and amplified for different utilities. The energy sources can be divided into three categories: fossil fuels, renewable sources (hydroelectric, wind, solar, agricultural biomass, geothermal) and nuclear sources. The limited amount of fossil fuels is a major issue, in addition, the damage caused to the environment by the pollution generated in the burning process. We need to find a way to reduce the damage made by fossil fuels and need to develop an alternative energy source. The use of biomass to produce energy is only one form of renewable energy that can be utilized to reduce the impact of energy production and use on the global environment (Cai *et al.*, 2013). The use of ethanol and biodiesel as transport fuels reduces the emission of CO₂ per unit of energy production. It also reduces the dependence on fossil fuels. Thus, biomass-based energy not only is renewable, but is also clean from a greenhouse gas (GHG) emission standpoint, and can be the center stage on the global energy scene (Basu, 2010).

Biomass is formed by combination of carbon dioxide received from atmosphere and water, in the photosynthesis process. Therefore, if biomass is burned efficiently, there will be production of carbon dioxide and water, providing a cyclic process, thus, the biomass is a renewable resource (Georges, 2011).

Due to the high generation of this agricultural residue in the bioethanol production industry, it is necessary find an energetic application for the sugarcane straw. Pyrolysis is one of the most important ways for processing and transforming the biomass in to value added products (biochar, bio-oil, fuels, synthesis gas, chemicals, etc.) with several industrial applications. The sugarcane straw is composed by fresh leaves and partially dry leaves of the sugarcane plant. Considering wet basis, for each 100 ton of sugarcane in plantation, 80 ton are utilized in bioethanol production and about 20 ton are considered as sugarcane straw (Hassuani *et al.*, 2005).

Thermogravimetric analysis (TG) is the most commonly used thermo analytical technique for solid-phase thermal degradation studies. The basic principle of TG is online measurement of mass changes as a function of temperature or time in a controlled atmosphere (Cai *et al.*, 2013). Yao *et al.* (2008) analyzed 10 types of natural fibers, including bamboo, wood, agricultural residues and bast fibers, using dynamic TG analysis under nitrogen atmosphere. The authors determine the apparent activation energy (160-170 kJ/mol) by using the kinetic methods of Kissinger (1957), Friedman (1965), Ozawa-Flynn-Wall (1965, 1966) and Coats-Redfern (1965) modified by Burnham and Braun (1999).

Cardoso *et al.* (2011) used the same experimental technique for the biomasses, sorghum bagasse and tobacco waste, for the estimation of apparent activation energy. Considering Ozawa (1965) and Starink (1996) kinetic methods, the activation energy values were: 103.94 kJ/mol and 135.95 kJ/mol for tobacco waste and 120.01 kJ/mol and 148.91 kJ/mol for sorghum bagasse, respectively.

Jiang *et al.* (2012) determined the apparent activation energy (E_a) of moso bamboo (*Phyllostachys Pubescens*) using the Ozawa-Flynn-Wall (1965, 1966) and Coats-Redfern (1965) modified by Burnham and Braun (1999) methods obtaining 153.37–198.55 kJ/mol and 152.14–197.87 kJ/mol, respectively. The increase in the conversion rate from 10 to 70 led to increased of E_a .

Nascimento (2012) studied the physical, chemical and thermal characteristics of three Amazonian biomasses (Brazil nut, *sapucaia* nut and *tucumã* fruit endocarp) to evaluate the feasibility of these biomasses as solid fuels. The thermal decomposition under nitrogen atmosphere of these biomasses was investigated through dynamic TG analysis at different heating rates (5 °C/min, 10 °C/min, 20 °C/min and 40 °C/min). The kinetics of these biomasses were estimated by using the Ozawa (1965) and Kissinger (1957) methods, obtaining apparent activation energies of 131.29–138.89 kJ/mol, 135.14–142.91 kJ/mol, 128.52–142.71 kJ/mol by O-F-W method and 138.86 kJ/mol, 146.74 kJ/mol and 137.16 kJ/mol by Kissinger method for Brazil nut, *sapucaia* nut and *tucumã* fruit endocarp, respectively.

The aims of this work were to analyze the thermal decomposition of sugarcane straw by dynamic TG and to estimate the apparent activation energy using the kinetic methods of Ozawa-Flynn-Wall (1965, 1966) and Coats-Redfern (1965) modified by Burnham and Braun (1999).

2. THEORETICAL APPROACH

Thermogravimetric analysis has been used to determine the kinetic parameters, activation energy, pre-exponential factor and reaction order, considering the Coats and Redfern (1965), Ozawa (1965) and Flynn and Wall (1966) methods. These methods were developed to analyze the thermal degradation of polymers, and assume the conversion rate, $d\alpha/dt$, as shown in Eq. (1):

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where k is the reaction rate constant and $f(\alpha)$ is referred to the reaction mechanism of biomass decomposition.

The biomass conversion was calculated by Eq. (2):

$$\alpha = (w_0 - w_t)/(w_0 - w_f) \quad (2)$$

where w_0 , w_t and w_f are initial, in a certain time and final weights (mg) of the biomass decomposition, respectively. According to Arrhenius, the reaction rate constant, k , is given by Eq. (3).

$$k = Aexp(-E/RT) \quad (3)$$

where A is the pre-exponential factor (min^{-1}), E is the activation energy (J/mol), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).

By combining Eq. (1) and (3) gives:

$$d\alpha/dt = Af(\alpha)exp(-E/RT) \quad (4)$$

If the variation of sample temperature is controlled by a constant heating rate, $\beta=dT/dt$, the variation on the degree of conversion can be evaluated as a function of temperature, which is dependent of heating time. Therefore, the non-isothermal reaction rate can be written as:

$$d\alpha/dT = (A/\beta)f(\alpha)exp(-E/RT) \quad (5)$$

The integration of Eq. (5) from initial temperature, T_o , corresponding to a conversion α_o , up to a final process temperature, T_f , corresponding to a conversion α_f , give the Eq. (6).

$$\int_{\alpha_o}^{\alpha_f} d\alpha/f(\alpha) = (A/\beta) \int_{T_o}^{T_f} exp(-E/RT)dT \quad (6)$$

Assuming that no reaction occurs at low temperatures, between 0 e T_o , then the conversion α_o is zero.

$$g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha) = (A/\beta) \int_0^{T_f} \exp(-E/RT) dT \quad (7)$$

where $g(\alpha)$ is an integral function of the conversion, dependent of the reaction and of the sample.

2.1 Integral kinetic models

The integral methods involve an approximate solution of the Eq. (7), assuming a function $p(x)$ as shown below:

$$A/\beta \int_0^{T_f} \exp(-E/RT) dT = \Phi = AE/\beta R \{-\exp(x)/x + \int_{-}^x (\exp(x)/x) dx\} = AE/\beta R p(x) \quad (8)$$

where $x = -E/RT$.

Coats-Redfern method (1965) modified by Burnham and Braun (1999)

The Coats and Redfern (1965) method is based in an asymptotic expansion [Eq. (9)] to obtain an approximate solution of function $p(x)$ in Eq. (8). The authors observed that analyzing up to second term in the expansion, yields acceptable results.

$$p(x) = \exp(x)/x^2 (1 + 2!/x + 3!/x^2 + 4!/x^3 + \dots) \quad (9)$$

with $x = -E/RT$:

$$p(-E/RT) = (R^2 T^2 / E^2) (1 - 2RT/E) \exp(-E/RT) \quad (10)$$

Combining Eq. (10) and Eq. (8) and rearranging:

$$g(\alpha) = (AE/\beta R) p(x) = (AE/\beta R) (R^2 T^2 / E^2) (1 - 2RT/E) \exp(-E/RT) \quad (11)$$

$$g(\alpha)/T^2 = (AR)/(\beta E) [(1 - 2RT/E) \exp(-E/RT)] \quad (12)$$

Burnham and Braun (1999) proposed a modification [Eq. (13)] of this method. Some authors (Yao *et al.*, 2008 and Jiang *et al.*, 2012) used this modified method to compare the results obtained with the Ozawa-Flynn-Wall (1965, 1966) method.

$$\beta/[T^2(1 - 2RT/E)] = (AR)/(g(\alpha)E) [\exp(-E/RT)] \quad (13)$$

Applying natural logarithm and rearranging the Eq. (13), we obtain the Eq. (14) representing the Coats-Redfern modified method.

$$\ln\{\beta/[T^2(1 - 2RT/E)]\} = \ln[(AR)/(g(\alpha)E)] - E/RT \quad (14)$$

Equation (14) is linear and the apparent activation energy is determined by plotting $\ln(\beta/T^2)$ versus $1/T$, where the angular coefficient, a , is related with the activation energy by the Eq. (15).

$$E = a * R \quad (15)$$

Ozawa-Flynn-Wall method (1965, 1966)

This model was developed independently by Ozawa (1965) and Flynn e Wall (1966). This method is based in the approximate solution of function $p(x)$ proposed by Doyle (1961), given by Eq. (16), with $x \geq 20$ as the restriction ($x = E/RT$). Flynn e Wall (1966) demonstrated that this approximate solution can be used in the range of $20 \leq E/RT \leq 60$, with a maximum variation of $\pm 3\%$ of the constant 0.4567 in Eq. (16).

$$\log[p(x)] = -2.315 - 0.4567E/RT \quad (16)$$

Applying logarithm in Eq. (8), we have the Eq. (17).

$$\log[g(\alpha)] = \log(AE/\beta R) + \log[p(x)] \quad (17)$$

Replacing the value $\log[p(x)]$ of Eq. (16) in Eq. (17) and rearranging, we obtain the Eq. (18):

$$\log \beta = [\log(AE/R) - \log[g(\alpha)] - 2.315] - 0.4567E/RT \quad (18)$$

The apparent activation energy is determined by plotting $\log(\beta)$ versus $(1/T)$ for each conversion evaluated, forming a straight line, in which the angular coefficient, a , is related with the activation energy according to Eq. (19).

$$E = aR/0.4567 \quad (19)$$

3. EXPERIMENTAL

3.1 Material

Sugarcane straw was the biomass selected for this work. It provided by the Brazilian Bioethanol Science and Technology Laboratory (CTBE). The raw material was washed with water and naturally dried. The size of particles was 50-100 mm length and 10 mm width. The biomass was milled by batches of 10 g during 20 s in an electric hammer mill (Tigre S.A., CV2, Brazil) and then sieved (Produtest, model T, Brazil). The samples were separated with particle size between 420 μm and 600 μm , providing a mean diameter of 510 μm . Finally, was utilized a rotary sample divider (Fritsch, model laborette 27, Germany), to obtain the sample used in the thermogravimetric analysis.

3.2 Test procedures

Thermogravimetric analyzer (Shimadzu Corp., TGA-50, Japan) was used to performed the thermal decomposition experiments (TGA/DTG). This apparatus measures the sample weight with a resolution of 0.0001 mg. The samples were installed in an open sample pan (6 mm internal diameter and 2.5 mm depth) with an initial amount of 3.0 ± 0.2 mg. The temperature change was controlled from room temperature ($25 \pm 3^\circ\text{C}$) up to 900°C at five different heating rates, 1.25, 2.5, 5, 10, $20^\circ\text{C}/\text{min}$. The acquisition rate was programmed to measure the sample weight every 5 s, corresponding to 12 samples/min. High purity (99.996%) nitrogen flow of 50 mL/min was used. The equipment was purged with nitrogen for 10 min before starting the run in order to eliminate any trace of air, avoiding the sample oxidation (combustion).

3.3 Data processing

The TG and DTG curves obtained from TGA runs were carefully smoothed by using least squares method, and analyzed by using TA-50WS software from Shimadzu Corporation. Apparent activation energies were calculated with MS Excel, which takes specific TG and derivative thermogravimetric (DTG) data from the TA-50WS software.

4. RESULTS AND DISCUSSION

4.1 Thermal decomposition process

Figure 1 presents the thermogravimetric decomposition process of sugarcane straw at several heating rates (1.25 $^\circ\text{C}/\text{min}$, 2.5 $^\circ\text{C}/\text{min}$, 5 $^\circ\text{C}/\text{min}$, 10 $^\circ\text{C}/\text{min}$, 20 $^\circ\text{C}/\text{min}$). Main decomposition occurs in the range of temperatures of 150°C - 450°C .

By using lower heating rates to achieve some temperature between 150°C and 450°C , it is necessary more time, which allows the break of polymeric linkages of biomass compounds. This break generates more volatiles and therefore, greater biomass decomposition. This analysis is valid for slow pyrolysis, which is the process that fits to the employed heating rates.

Figure 2 presents the DTG curves and it can be observed one shoulder and one peak, related to hemicellulose and cellulose decomposition reactions in the biomass. The thermal decomposition of lignin occurs between 200°C to 900°C , therefore, a part of lignin was reacting in the same time with the other biomass components. However, the main reaction is related for each component previously reported. It was verified that, the increase the heating rate, increases the biomass decomposition in the maximum temperature (peak temperature).

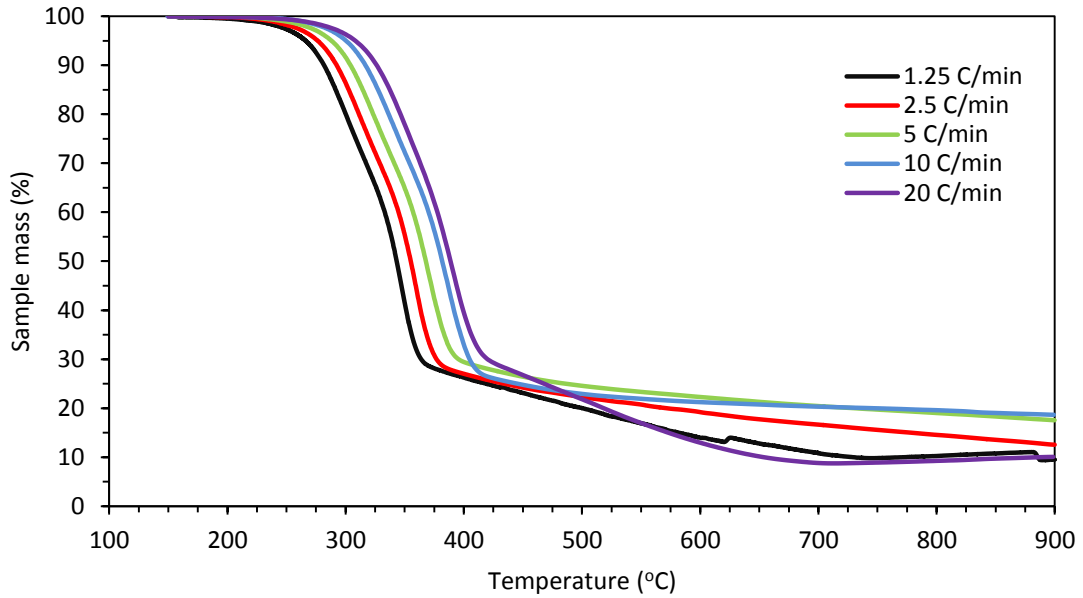


Figure 1. Thermogravimetric curve of decomposition of sugarcane straw at several heating rates

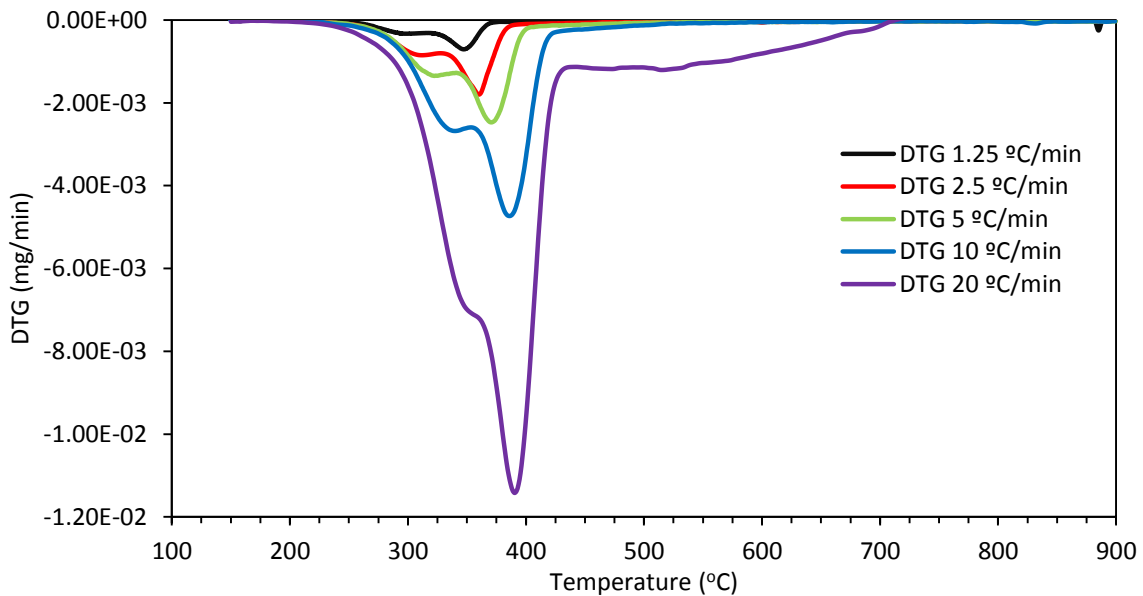


Figure 2. Differential thermogravimetry of decomposition process of sugarcane straw at several heating rates

Figure 3 shows the conversion (α) and non-isothermal reaction rate, $d\alpha/dT$, as a function of temperature. It was observed that for any heating rate between the conversion range of 0 and 0.45, the main decomposition corresponds to hemicellulose. In this conversion range, the effect of heating rate on the non-isothermal reaction rate is low, i.e., the variation in the reaction velocity is low.

Yesid Rueda Ordóñez, Edgardo Olivares Gómez and Katia Tannous
Thermogravimetric Study and Kinetic Analysis of Sugarcane Straw

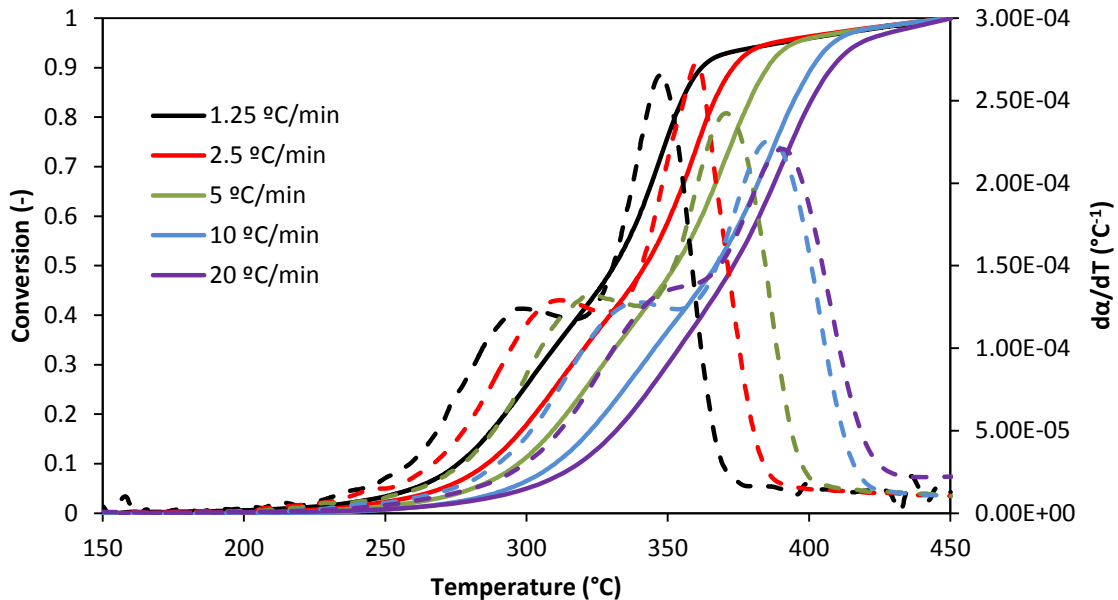


Figure 3. Conversion and non-isothermal reaction rate as a function of temperature

The main decomposition corresponds to cellulose for any heating rate between the conversion of 0.45 and 1.00. At this conversion range, the non-isothermal reaction rate decreases with the increasing of heating rate, i.e., the reaction velocity decreases with the increasing of heating rate. This behavior is only observed in a slow pyrolysis.

4.2 Determination of apparent activation energy

The curves obtained with Ozawa-Flynn-Wall (1965, 1966) and Coats-Redfern (1965) modified by Burnham and Braun, (1999) methods, are presented in Fig. 4 and Fig. 5, respectively. It was observed that the curves obtained by both methods, at each conversion, show slight differences in slope, behavior that is more remarked at low conversions (less than 0.45), affecting the values of kinetic parameters.

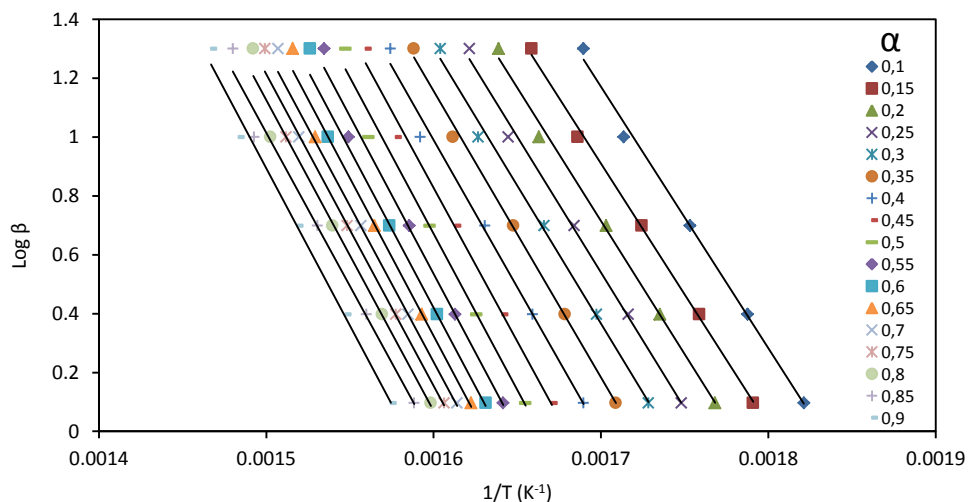


Figure 4. Obtained curves with Ozawa-Flynn-Wall method

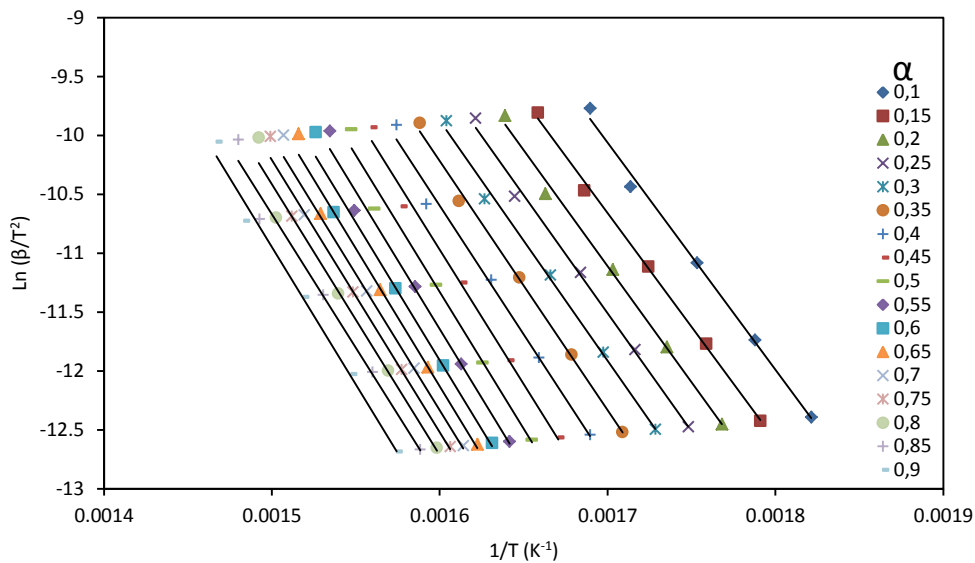


Figure 5. Obtained curves with Coats-Redfern modified method.

Apparent activation energy as a function of conversion (0.1 to 0.9), obtained by both methods is presented in Fig. 6. The apparent activation energy values obtained by the Ozawa-Flynn-Wall method are in the range of 161.6 – 195.2 kJ/mol, whereas the obtained values by the Coats-Redfern (modified) method are in the range of 160.5– 194.7 kJ/mol. The variation between values obtained with both methods is low (less than 1%)

For conversion values less than 0.45 it was observed a large variation in the apparent activation energy values obtained (161.6 – 190.0 kJ/mol); as commented before this conversion range corresponds to hemicellulose decomposition. This behavior is due to the structure of this biomass component, which is formed mainly by xylan and mannan (Levan, 1989; Di Blasi and Lanzetta, 1997; Shen *et al.*, 2010). The xylan is the hemicellulose component most thermally unstable (Levan, 1989), facilitating the thermal decomposition.

For conversion values higher than 0.45, the apparent activation energy remained stable (variation less than 3.5%), between 188.7 e 195.2 kJ/mol, corresponding to cellulose decomposition. This biomass component is formed by links of β (1-4)-glucose (Liu *et al.*, 2009), very stable links, thus requiring more energy for the breaking and decomposition.

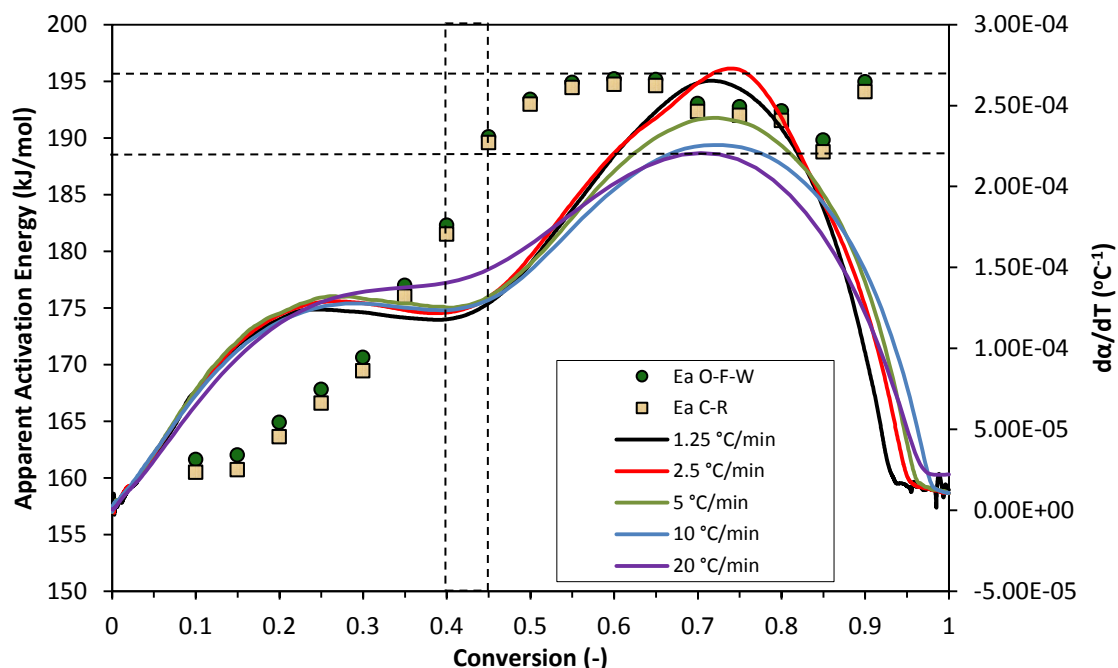


Figure 6. Apparent activation energy and non-isothermal reaction rate as a function of conversion

5. CONCLUSIONS

Thermogravimetric analysis TG was used to investigate the thermal decomposition process of sugarcane straw at different heating rates. The Ozawa-Flynn-Wall and Coats-Redfern (modified) methods were used to determine the apparent activation energy of this biomass.

The main thermal decomposition process occurred in the temperature range of 150 - 450°C. Were observed two peaks in the DTG curve, concerning mainly to the hemicellulose and cellulose decomposition. The temperature of maximum thermal decomposition (peak temperature) of biomass was affected by the heating rate, whereas the lower the heating rate, the lower is the temperature of maximum decomposition.

The reaction velocity in the conversion range of 0 to 0.45 is not affected by heating rate; this range of conversion corresponds to the hemicellulose thermal decomposition. For higher conversion values (>0.45), where the main decomposition is attributed to cellulose, the reaction velocity decreases with increasing the heating rate.

The apparent activation energy of sugarcane straw is in the range of 160.5 – 195.2 kJ/mol. Whereas for conversion values less than 0.45, the apparent activation energy was in the range 161.6 – 190.0 kJ/mol and for conversion values higher than 0.45, were obtained values between 188.7 and 195.2 kJ/mol. The knowledge of this kinetic parameter allows a better understanding of the thermal decomposition behavior of sugarcane straw.

6. ACKNOWLEDGEMENTS

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