

STUDY OF THERMAL DECOMPOSITION OF SUGARCANE BAGASSE AND IGNITION TEMPERATURE OF COAL/BAGASSE BLENDS USING THERMOGRAVIMETRY

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Abstract. In Brazil, due to its availability, sugar cane bagasse has a high potential for power generation. The knowledge of ignition behavior, as well as the knowledge of the chemical kinetics, in of fuels combustion process are important features in boilers projects and in the stability of the combustion process control. Vyazovkin's model-free kinetics algorithms were applied to determine the apparent activation energy (E_a) of the thermal decomposition of sugar cane bagasse. For the two major events of mass loss of bagasse, which correspond to the thermal decomposition of organic matter (mainly hemicellulose, cellulose), average values of E_a were obtained for both combustion and pyrolysis processes. In synthetic air atmosphere, the E_a were $170.8 \pm 26.3 \text{ kJ mol}^{-1}$ and $277.8 \pm 58.6 \text{ kJ mol}^{-1}$, while in nitrogen atmosphere, the E_a were $185.0 \pm 11.4 \text{ kJ mol}^{-1}$ and $82.1 \pm 44.4 \text{ kJ mol}^{-1}$. The methodology proposed by Tognotti *et al.* (1985) was applied to determine the ignition temperature of coal and bagasse considering blends of coal/bagasse in proportions of 100/0, 75/25, 50/50 and 0/100 (% mass). Ignition temperatures of 427 °C, 256 °C, 275 °C, were obtained for neat coal, neat bagasse and bagasse/coal blends (50/50, 25/75), respectively.

Keywords: coal, biomass, sugar cane bagasse, ignition temperature, activation energy.

1. INTRODUCTION

Brazil is one of the world's largest producers of sugar and alcohol. However, a number of by-products are generated during processing. Sugar cane bagasse is obtained after the pressing of the sugar cane and it is usually burned to supply electric energy and steam for the process. Furthermore, about 10% of bagasse generated remains as by-products. Several alternatives have been proposed to increase the fraction of biomass in energy production. The direct co-firing of biomass with coal is one of the most promising technologies in the short term. Other technologies have been developed in order to contribute with CO₂ decreasing, one of them is oxy-combustion, which can be combined with biomass and then providing a sink of CO₂ and then reducing the environmental effect of greenhouse gas (Arias *et al.*, 2008)

The electricity production using sugar cane sugar bagasse in Brazil is quite practicable from economic point of view. In south-central region, the available area to sugar cane harvest in the season (2008/09) was estimated at 6.53 million hectares (ha), representing an increase of 15.7% (917,900 ha) in relation to previous harvest. In Brazil, the Sao Paulo State is the largest producer of sugar cane with an available area of 4.45 million ha for sugar cane harvest. This area represents about 66% of total area in south-central region available to sugar cane production. In addition, in 2010 there was an increase of 12.2% (483,300 ha) of planting area compared to the previous harvest. One third (1/3) of this production produces sugar and alcohol and two third (2/3) are waste generated. This process generates 190 million tons of bagasse, which currently supply 3% of energy matrix demand of Brazil and it is estimate an increase to 14% in 2020, which corresponding on average of 13,159 MW (Unica, 2010).

The use of coal/biomass blends as a fuel applied in power station is increasing and gaining importance as a source of renewable energy and also to reduce CO₂ emissions. This is considered a neutral carbon fuel because the carbon dioxide released during its utilization is an integral part of the carbon cycle (Arias *et al.*, 2008). Besides its sustainability, biomass used as a co-fuel presents also a low cost and it is an option for renewable energy with reduction of CO₂, SO_x and NO_x emissions (Sahu *et al.*, 2010).

The knowledge of ignition behavior, as well as the knowledge of the chemical kinetics, in fuel combustion processes, is important features in different practical situations related to the technological use of fuels such as boilers designs, flame and combustion stability, pollutant formation and in the stability of the combustion process control (Crelling *et al.*, 1992; Huang *et al.*, 2008).

Related to practical determination of ignition temperature, several techniques have been described for indirect (Bandyopadhyay, 1972; Karcz, 1980) and direct (Fuertes, 1993) measurements. With respect to determinations of kinetics parameters, thermal analysis is considered an important technique for such studies.

According to Shen *et al.* (2009), the knowledge of biomass decomposition thermogravimetric analyzer (TGA) has been extensively used to investigate combustion basic properties of solid fuels. There are many researches that employ TGA on biomass combustion study. However, the knowledge on co-firing of both coal and biomass, as well as the use of their blends of char/biomass, are still very little (Sahu *et al.*, 2010).

There are several methods to determining ignition temperature for coals according to TG/DTG curves (Tognotti *et al.*, 1985; Crelling *et al.*, 1992; Huang *et al.*, 2008). An important methodology that it been used in TGA was that proposed by Tognotti *et al.* (1985). In this method the ignition temperature is taken as the temperature at which TG curves in the combustion (oxidant atmosphere) and pyrolysis (inert atmosphere) experiments diverge.

In addition to ignition temperature, kinetics study is also very important for the development of efficient technological processes during the thermochemical conversion of both neat biomass and biomass/coal blends. Most studies on the kinetics decomposition of biomass are focused on pyrolysis process in inert atmosphere. However, recently more attention has been directed to the biomass decomposition in oxidative environments (Safi *et al.*, 2004; Shen *et al.*, 2009; Yorulmaz and Atimtay, 2009).

There are several studies in the literature that focus on the determination of kinetic parameters, such as activation energy and constant of reaction in fuels combustion processes. Kinetic studies employing thermal analysis can be achieved by isothermal or non-isothermal methods, but this issue is still controversial. Non-isothermal methods have been extensively applied to complex heterogeneous reactions (Smith *et al.*, 1981; Cumming, 1984; Ozawa, 1957; Morgan, 1986; Williams and Besler, 1993; Williams and Besler, 1995; Tanaka, 1995; Wu *et al.* 1997; Conesa *et al.*, 1998; Senneca *et al.*, 1999; Silva Filho, 2008).

The aim of this study is to investigate the thermal behavior of sugar cane bagasse and bagasse/coal blends. Activation energy on the thermal decomposition process and ignition temperature of these fuels were determined using thermogravimetric techniques in different atmospheres: oxygen (combustion process) and nitrogen (pyrolysis process), Vyazovkin's model-free kinetics was used for kinetic study and the methodology proposed by Tognotti *et al.*, (1985) was applied to determine the ignition temperature of the samples.

2. EXPERIMENTAL

2.1. Materials

A Brazilian bituminous coals called CE4500 (energetic coal with higher calorific value up to 4500 kcal kg⁻¹) from Criciúma-SC and a Brazilian biomass (sugar cane bagasse)- collected directly from a mill (alcohol plant - COSAN Group located in Brazil – São Paulo State) were used in this work.

Samples of both biomass and coal were selected between two subsequent ASTM sieves with average size of 142 µm (e.g., the average size of 142 µm results from passing through a sieve with 210 µm aperture and retention in a sieve with 74 µm aperture) and the samples of 5.0 ± 0.5 mg. Two blends of coal/bagasse were prepared in proportion of 75/25 and 50/50 (% mass). Table 1 shows the chemical composition of the samples.

Table 1: Chemical composition (wt %) of the Coal CE 4500 and bagasse.

Analysis (wt%)	<i>Sugar cane Bagasse</i>	<i>CE-4500</i>
Moisture	4.4	0.81
Ash	4.0	34.64
Ultimate Analysis		
Carbon	44.3	49.38
Hydrogen	5.7	3.66
Nitrogen	0.2	1.06
Sulfur	0.07	2.35
Chlorine	-	0.17
Oxygen (by difference)	45.5	7.93

2.3. Thermogravimetric Experiments

Thermogravimetric experiments (TGA) were performed in a Shimadzu TGA-51H analyzer with sample mass of 10± 0.5 mg.

For the determination of the ignition temperature, the methodology used was that proposed by Tognotti *et al.*,

(1985). Experiments were carried out under non-isothermal conditions applying a heating rate of 10 °C min⁻¹ in two different atmospheres: synthetic air (combustion process) and nitrogen (pyrolysis process) from room temperature up to 950 °C.

The Model-Free Kinetics method was used to calculate the effective activation energy as a function of the extent of conversion of the thermal decomposition in air condition. For this, non-isothermal TG tests from room temperature up to 900 °C with three heating rates at 10, 15 and 20 °C min⁻¹, and atmosphere of synthetic air were used.

For all TGA tests the reacting atmosphere (synthetic air or nitrogen) was continuously blown over the samples through the TGA furnace at a volumetric rate of 100 mL min⁻¹.

2.1. Kinetic Method

The Model-Free Kinetics method based on a Vyazovkin method (Vyazovkin and Dollimore, 1996; Vyazovkin and Sbirrazzuoli, 1997; Vyazovkin and Wight, 1999) applies an iso-conversional technique to calculate the effective activation energy (E) as a function of the conversion level (α) of a chemical reaction.

The approach follows all points of conversion from multiple experiments instead of a single one. The kinetics of reactions in solids is usually described by Eq. (1) (Vyazovkin and Dollimore, 1996).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Dividing Eq. (1) by the heating rate β=dT/dt one obtains

$$\frac{d\alpha}{dt} \cdot \frac{dt}{dT} = \frac{1}{\beta} k \cdot f(\alpha), \quad (2)$$

where α is the conversion, f(α) represents the reaction model and k is the constant of reaction rate.

From Eq. (2) it has

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \left[A \exp\left(-\frac{E}{RT}\right) \right] f(\alpha), \quad (3)$$

where, A is the pre-exponential factor, E is the activation energy, T is the temperature and R is the universal gas constant.

From Eq. (3) one obtains

$$\frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

From Eq. (4), as well as a numerical approximations of their integral form, gives

$$\int_0^\alpha \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT, \quad (5)$$

Provided that the term E/2RT >> 1, the temperature integral on the right hand side can be approximated by (Vyazovkin and Wight, 1999; Majchrzak-Kuceba and Nowak, 2004)

$$\int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \approx \frac{R}{E} T^2 \exp\left(-\frac{E}{RT}\right). \quad (1)$$

Substituting the temperature integral, rearranging and logarithming, one has

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{RT_\alpha}, \quad (7)$$

where subscript α represents the values related to a given value of conversion.

Equation (7) is defined as a dynamic equation, and is used for the determination of the activation energy for all of the conversion values.

One of the main advantages of this method is the possibility of isolating the function $g(\alpha)$ in the linear coefficient, therefore the determination of this function in a complex process is difficult (Vyazovkin and Wight, 1999).

To apply the Model-Free Kinetics method it is necessary to obtain at least three different heating rates (β) and respective conversion curves being evaluated from the measured TG curves (Vyazovkin, 1999). The conversion (α) is given by

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (8)$$

where m is the sample mass that varies with time, m_0 is the initial sample mass, and m_∞ is the remaining mass of the sample after calcination.

For each conversion value (α), $\ln(\beta/T_\alpha^2)$ is plotted against $1/T_\alpha$. Then, the method of least squares (linear regression) is applied establishing the straight lines whose slopes ($-E_\alpha/R$) provide the values of activation energy.

3. RESULTS AND DISCUSSION

3.1. Determination of the ignition temperature of bagasse and bagasse/coal blends

TG and DTG curves for the samples are presented in Fig. 1 and 2 respectively.

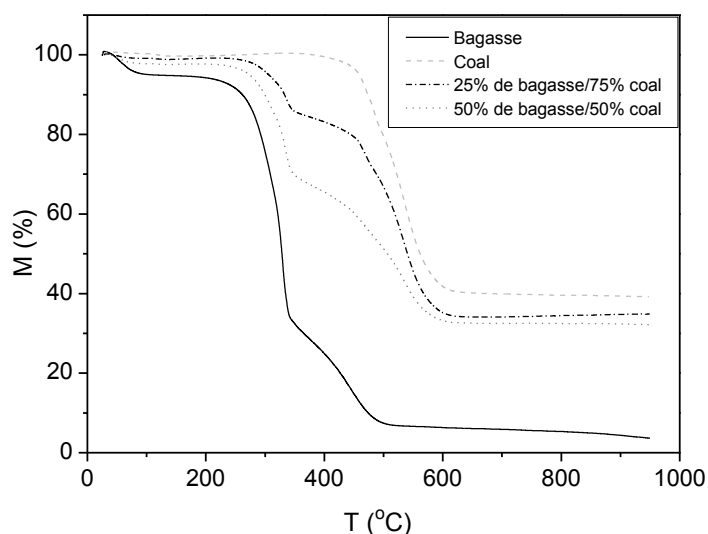


Figure 1: TG curves of the samples obtained under air atmosphere (100 mL/min), heating rate of 10°C/min, mass of 10±0.5 mg

From DTG curve of neat coal (Fig. 2), it can be clearly observed that there are at least two regions of mass loss, from 367°C. According to Crelling *et al.*, 1992, this process is identified as primary and secondary combustion.

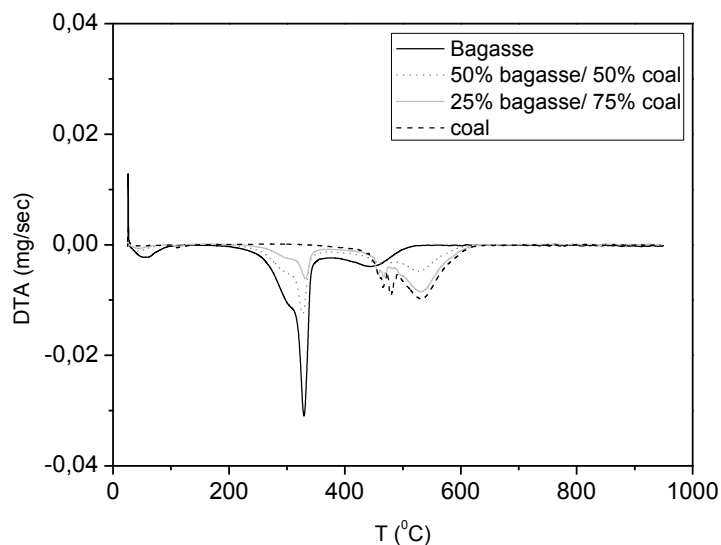


Figure 2: DTG curves of the samples obtained under air atmosphere (100 mL/min), heating rate of 10°C/min, mass of 10± 0.5 mg

It is evident from both TGA and DTG thermogram that two overlapping reactions place between 200 and 350°C for neat bagasse and for the two bagasse/coal blends. This behavior is characteristic of lignocellulosic materials (Quensanga e Picard, 1988; Aiman e Stubington, 1993; Byrne e Nagle, 1996; Guimarães *et al.*, 2009).

The initial decomposition of these three samples started at around 210°C, whereas the final temperature for the first region zones were 200, 220°C and 246°C for the neat bagasse, 75/25% and 50/50 % blends, respectively. Very rapid decomposition took place above the initial decomposition due to the rapid evolution of volatiles present in the samples. Through DTG curves, two events are showed, which are related to hemicellulose and cellulose materials. Whereas, the pyrolysis of lignin occurs very slowly from 400°C, and similar results were obtained by Quensanga e Picard, 1988; Byrne e Nagle, 1996..

According to Brown and Tang (1962), the rapid thermal degradation of cellulose within a narrow range of temperature and the slower disintegration of lignin over a large broad band or temperature are explicable by the fact that cellulose is a repeating polymer as a single monomer while lignin is a more intricate macromolecule.

For the two blends, in the first decomposition region there are no changes of the initial temperatures when compared to the decomposition of the neat bagasse. However, changes can be observed for the second decomposition region (from 480°C).

Several peaks can be observed through DTG curves for the two blends, and they are related to the volatiles present in the coal that, after releasing, interfere in the bagasse present in the blend.

Ignition temperatures for all cases were determined using TG curves in both air and nitrogen atmospheres. Fig. 3, 4, and 6 show these curves for neat coal, neat bagasse, 50/50 % and 75/25% coal/bagasse blends respectively.

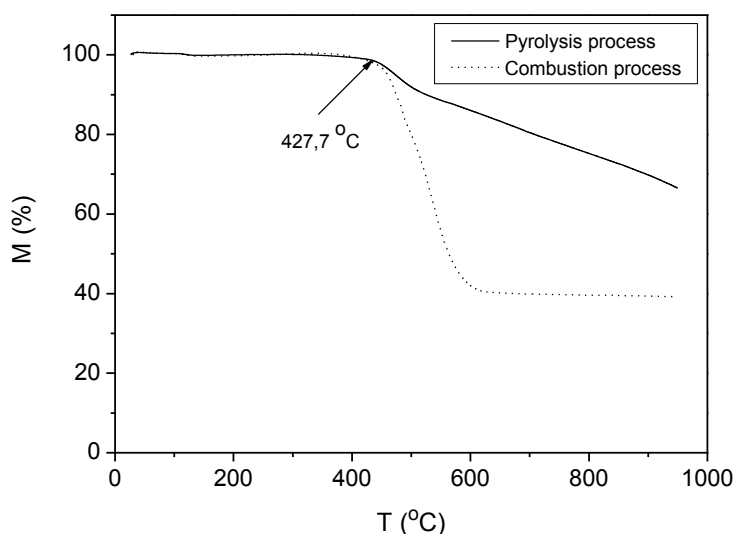


Figure 3: TG curves in air and nitrogen atmospheres for ignition temperature determination of the neat coal

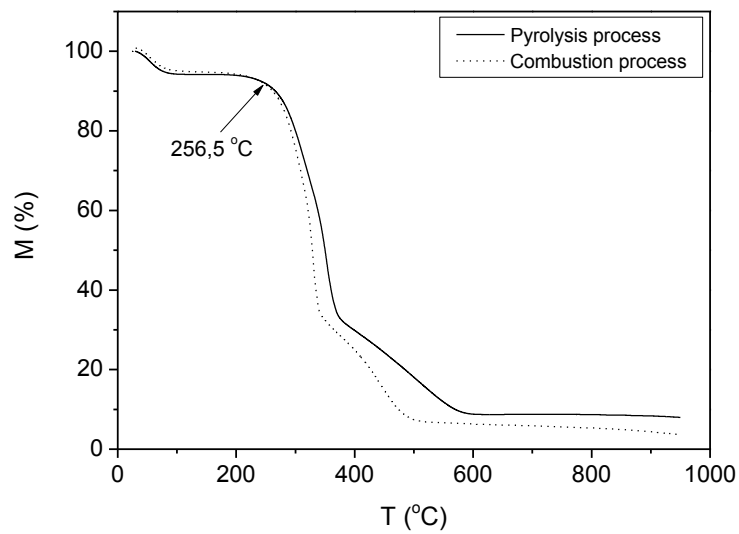


Figure 4: TG curves in air and nitrogen atmospheres for ignition temperature determination of the neat bagasse.

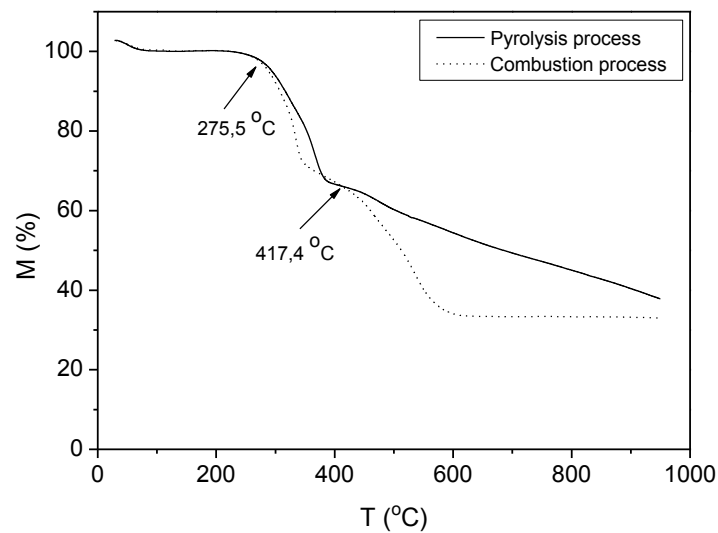


Figure 5: TG curves in air and nitrogen atmospheres for ignition temperature determination of the 50/50% coal/bagasse blend.

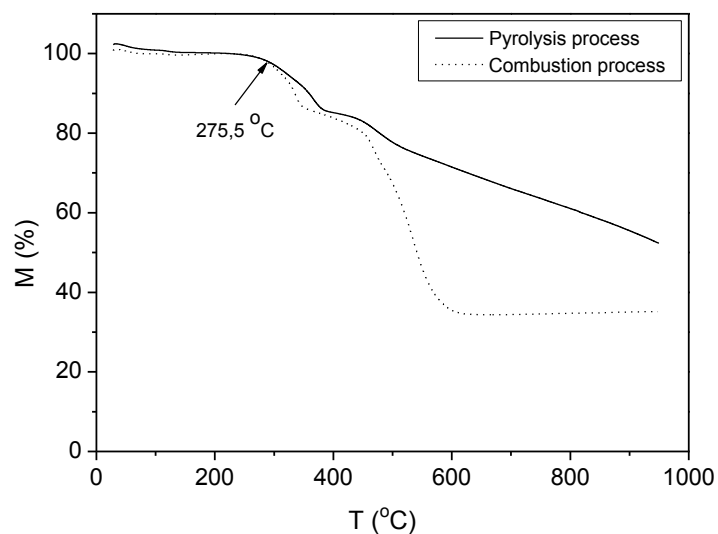


Figure 6: TG curves in air and nitrogen atmospheres for ignition temperature determination of the 75/25% coal/bagasse blend.

Through Fig. 5, it can be noted that there is two meeting points between pyrolysis and combustion TG curves. The second joint occurs at 417°C, which is near to ignition temperature of the neat coal (427°C), but for the blends the ignition temperature is considered the first joint point.

Through Fig. 6, it can be noted that there is one meeting point between pyrolysis and combustion TG curves at 275,5°C and the second meeting point is near to 350°C.

Ignition temperatures were 427°C for neat coal, 256°C for neat bagasse, and 275°C for both blends (50/50% and 75/25%).

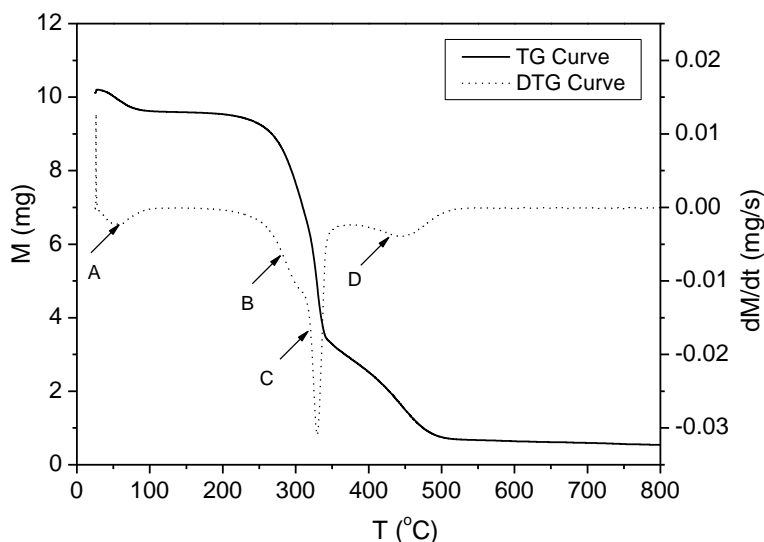
Chen and Wu (2009) used TGA and drop tube furnace (DTF) for evaluating the synergism effect in blends in the proportion from 25 to 75% of biomass with coal. The authors focused the effect of biomass (rice husk) in the combustion of anthracitic coal. The choice of this coal was due to its low volatile content. TGA studies showed three steps of mass loss, being that the first corresponds to the moisture and volatile contents, the second to the hemicelluloses and cellulose decompositions and the third stage, correspond to the lignin decomposition. Results showed a linear correlation between the first stage of mass loss and the percentage of the biomass present in the blend, from this observation the authors concluded that there was no synergism between biomass and coal. On the other hand, after the DTF experiments, ashes were collected and analyzed in TG balance and the thermograms showed that there wasn't a linear correlation, showing that there is a synergism between ashes from pyrolysis and biomass. The authors concluded that biomass can be added to coal according to the need of volatiles necessary for the combustion or pyrolysis processes.

3.2. Activation energy determination for combustion and pyrolysis of bagasse

Figures 7 and 8 show the TG and DTG curves obtained for thermal decomposition of the bagasse in both air and nitrogen atmospheres. Through DTG curves, four distinct events can be clearly observed. As previously described, these events correspond to the thermal decomposition of lignocellulosic materials, including moisture content at the beginning of the curves.

Hemicellulose and cellulose decomposition (between 200 and 350°C) are the dominant events for the rate of mass loss. In this study, the kinetic model was applied for the region of hemicelluloses and cellulose decomposition, i.e., $\alpha = 0$ at 200°C and $\alpha = 1$ at 350°C.

According to Klass (2006), in the hemicellulose and cellulose there is the most part of volatile content in the biomass and after their decomposition, the lignin content is relatively less reactive and it is responsible for the char formation.



A refers to moisture; B, hemicelluloses; C, cellulose and D, lignin.

Figure 7: TG and DTG curves of the bagasse in air atmosphere (100 mL/min).with heating rate of 10 °C min⁻¹).

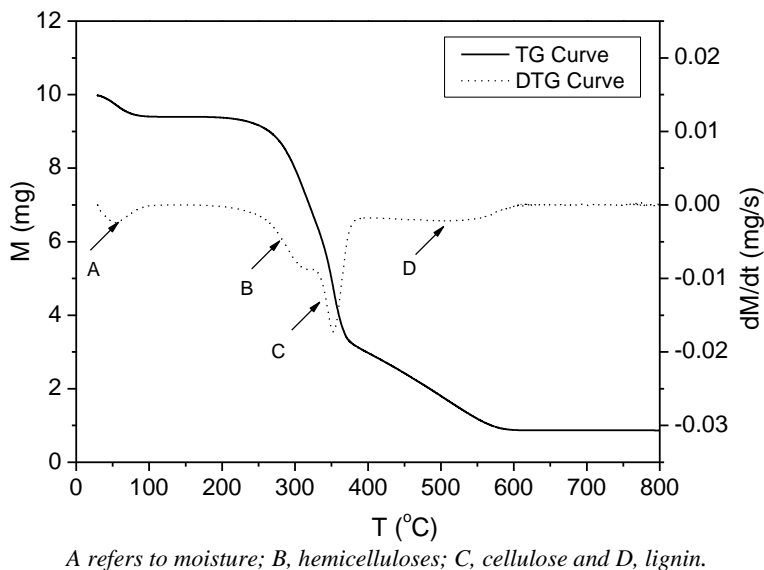


Figure 8: TG and DTG curves of the bagasse in nitrogen atmosphere (100 mL/min).with heating rate of 10 °C min⁻¹

Activation energy was obtained for two events and the “*Model Free Kinetics*” were applied. 1000 points were considered for conversion (α) between 0 and 1 and the results are showed in Fig. 9 and 10.

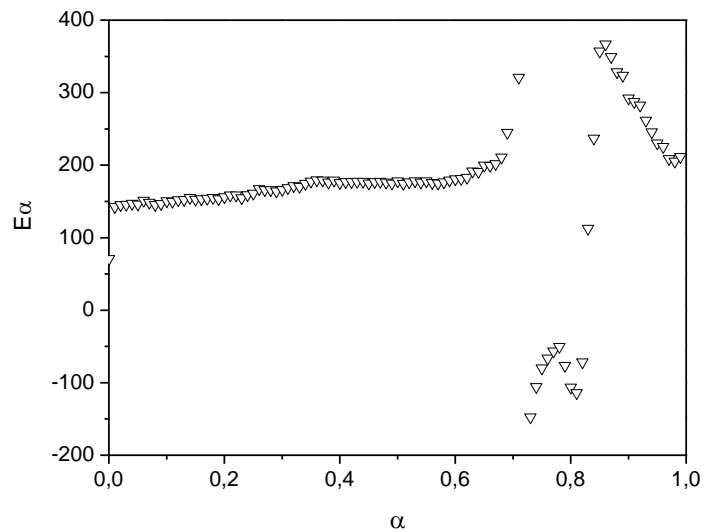


Figure 9: Activation energy versus conversion for the thermal decomposition of bagasse in air atmosphere.

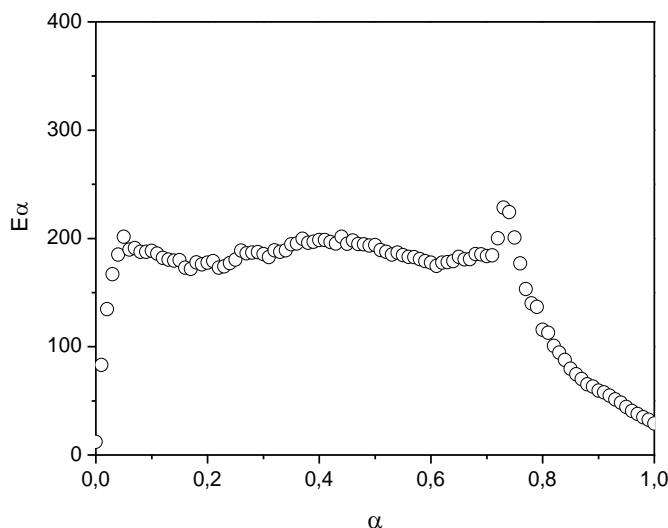


Figure 10: Activation energy versus conversion for the thermal decomposition of bagasse in nitrogen atmosphere.

In Fig. 9 and 10 two main regions can be observed. The first region (for α from 0 up to 0.6), a stable value for activation energy is observed for both environments. For nitrogen atmosphere, $E_a = 185.0 \pm 11.4 \text{ kJ/mol}$ and for air $E_a = 170.8 \pm 26.3 \text{ kJ/mol}$.

After this stage, i.e., for $\alpha > 0.6$, there is a changing of the behavior and then the activation energy was determined as a $277.8 \pm 58.6 \text{ kJ mol}^{-1}$ in nitrogen and $82.1 \pm 43.4 \text{ kJ mol}^{-1}$ in air atmosphere. As in air atmosphere negative values were obtained, only positive values were considered in the calculus of average and standard deviation.

For air condition, as negative values were obtained, it can be said that the model used wasn't well fit for this atmosphere and it is an indicative that the decomposition of hemicelluloses and cellulose must be considered separated.

The values of activation energy before and after $\alpha = 0.6$, can be explained by the fact that there is a changing of mechanism of the hemicelluloses and cellulose decomposition, but these events in the TG and DTG curves is difficult to be distinguished due to an overlapping of these materials during their thermal decomposition.

It is well known that thermal degradation is influenced by the nature of the atmosphere, for hemicelluloses decomposition, activation energy values didn't present substantial difference for nitrogen and air, considering the standard deviation, but for cellulose, the influence of atmosphere were more evident comparing $277.8 \pm 58.6 \text{ kJ mol}^{-1}$ in nitrogen and $82.1 \pm 43.4 \text{ kJ mol}^{-1}$ in air atmosphere. This difference can be understood based on oxygen content in the sample. Since biomass has high oxygen content (more than 45%), after volatilization step the oxygen released enhances the decomposition promoting the char residue combustion.

4. CONCLUSIONS

Results showed that there wasn't substantial variation on decomposition temperature of the blends when compared to neat bagasse. The initial decomposition temperature for 50/50% and 25/75 % blends were $220 \text{ }^\circ\text{C}$ and $246 \text{ }^\circ\text{C}$, respectively.

Ignition temperatures were 427°C for the neat coal and $256,5 \text{ }^\circ\text{C}$ for the neat bagasse, for the blends ignition temperatures were $275 \text{ }^\circ\text{C}$, indicating that the proportion of either 50% or 25% of bagasse with coal, doesn't interfere in the ignition temperature, but the values are different than the original fuels. The lowest ignition temperature determined for neat bagasse can be understood based on the higher volatile content in bagasse than coal and blends.

As a linear correlation was detected between the proportions of the bagasse in the coal with the position of the DTG peaks, no synergism could be confirmed in this study.

Moreover, activation energies were determined for neat bagasse als in both nitrogen and air atmospheres. The values obtained showed that, only for the second decomposition region (related do cellulose degradation) presented differences between nitrogen and air conditions. May be this difference is related to the sensibility of cellulose with oxygen during its decomposition and the high oxygen content in the bagasse enhances the decomposition promoting the char residue combustion.

It can be concluded that important parameters such as ignition temperature and activation energy can be determined using TGA experiments and they are different for neat fuels and their blends, but it is important to realize that while the absolute value of the ignition temperature and activation energy may be debatable, the relative values can be used in the evaluation of the thermal decomposition of the samples.

3. ACKNOWLEDGEMENTS

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