STUDY OF THERMAL DECOMPOSITION AND IGNITION TEMPERATURE OF BAGASSE, COAL AND THEIR BLENDS

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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 is important features in boilers projects and in the stability of the combustion process control. The aim of this study is to investigate the thermal behavior of sugar cane bagasse, coal and their blends. The methodology proposed by Tognotti et al. (1985) was applied to determine the ignition temperature for all samples. Ignition temperatures were 256°C for neat bagasse and 427°C for neat coal, and 275°C for both blends (50-50% and 25-75%). The *Model-Free Kinetics* was applied to determine the apparent activation energy (E_α) 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 and lignin), average values of E_α were obtained for both combustion and pyrolysis processes. In synthetic air atmosphere, the E_α were 170.8±26.3 $kJ\cdot mol^{-1}$ and 277.8±58.6 $kJ\cdot mol^{-1}$, while in nitrogen atmosphere, the E_α were 185.0 ± 11.4 $kJ\cdot mol^{-1}$ and 82.1±44.4 $kJ\cdot mol^{-1}$. The results obtained can be explained by synergistic effects when both bagasse and coal were blended, changing the fuel reactivity.

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

NOMENCLATURE

A	pre-exponential factor of Arrhenius, s^{-1}
E	activation energy of Arrhenius, $kJ\cdot mol^{-1}$
$f(\alpha)$	reaction model
$k(T)$	rate constant of Arrhenius, s^{-1}
m	sample mass that varies with time, mg
m_∞	final sample mass, mg
m_0	initial sample mass, mg
R	universal gas constant, $kJ\ mol^{-1}\cdot K^{-1}$
T	temperature, K
T_0	initial temperature, K
t	time, s

Greek symbols

α	extent of conversion,
β	heating rate, $K\cdot s^{-1}$

INTRODUCTION

Brazil is one of the largest producers of sugar and alcohol in the world. However, a large number of by-products are generated during processing. Sugar cane bagasse is obtained after crushing 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 CO_2 decreasing, one of than is oxy-combustion, which can be combined with biomass and then providing a sink of CO_2 and then reducing the environmental effect of greenhouse gas (Arias et al., 2008).

The electricity generation from sugar cane bagasse in Brazil is quite practicable under economic point of view. In south-central region the available area to sugar cane harvest in the season 2008-2009 was estimated at 6.53 million ha, representing an increase of 15.7% 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, representing about 66% of the total area in south-central region available. In addition, in 2010 there was an increase of 12.2% of planting area compared to the previous harvest. One third of this production generates sugar and alcohol and the remaining two third are waste. This process generates 190 million ton of bagasse which supply 3% of energy matrix demand of Brazil and an increase of 14% in 2020 is estimated, which corresponds, on average, 13,159 MW (Unica, 2010).

The use of coal and biomass blends as a fuel applied in power station is increasing and gaining importance as a source of renewable energy and also to reduce CO_2 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 in co-firing presents also a low cost and it is an option for renewable energy with reduction of CO_2, SO_x and NO_x emissions (Sahu et al., 2010).

The knowledge of ignition behavior, as well as the chemical kinetics, in fuel combustion processes, are important features in different practical situations related to the technological use of fuels. In addition, studies as those mentioned are important for flame and combustion stability, boiler designs, 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 and Bhaduri, 1972; Karcz et al., 1980) and direct (Fuertes et al., 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 by 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, are still very scarce (Sahu et al., 2010).

There are different 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 to obtain the ignition temperature employing TGA was proposed by Tognotti et al. (1985) and has been used in several works. 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.

Ignition temperature and kinetic parameters are important data 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, which is a process that occurs 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 et al., 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 et al., 2008).

The aim of this study is to investigate the thermal behavior of sugar cane bagasse, coal and their 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 activation energy determination and the methodology proposed by Tognotti et al., (1985) to determine the ignition temperature of the samples, was applied.

EXPERIMENTAL

Materials

A Brazilian bituminous coals called CE4500 (energetic coal with higher calorific value up to 4500 kcal kg^{-1}) from Criciúma, Santa Catarina State and a Brazilian biomass (sugar cane bagasse) from a mill located in São Paulo State were used in this work. Table 1 shows the chemical composition of the samples.

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

Analysis (wt%)	*Sugar cane Bagasse*	*Coal (CE-4500)*
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$^{(i)}$	45.5	7.93

$^{(i)}$ by difference

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^{o}C·min^{-1} in two different atmospheres: synthetic air (combustion process) and nitrogen (pyrolysis process) from room temperature up to 950^{o}C.

The *Model-Free Kinetics* method was used to calculate the effective activation energy as a function of the thermal decomposition conversion. For this, non-isothermal TG tests from room temperature up to 900^{o}C with three heating rates at 10, 15 and 20^{o}C·min^{-1}, and synthetic air and nitrogen atmospheres 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}.

Kinetic Method

The *Model-Free Kinetics* method applies an isoconversional technique to calculate the effective activation energy as a function of the conversion extent of a chemical reaction (Vyazovkin and Dollimore, 1996; Vyazovkin and Wight, 1999)

The concept of activation energy as a function of conversion is interesting since it provides an activation energy variable for each conversion value (α) normalized between 0 and 1, that is, its value is obtained for each physical and chemical processing that occurs in the process.

The approach considers conversions measured in multiple experiments, thereby avoiding the uncertainty that results from a single experiment (Crnkovic et al., 2007). The kinetics of heterogeneous reactions in solids is usually described in terms of a single step kinetic correlation as follows (Vyazovkin and Dollimore, 1996):

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

Under nonisothermal conditions, the temperature varies with a constant heating rate (β=dT/dt), Equation 1 gives

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

The explicit temperature dependence of the rate constant is introduced by replacing k(T) with the well-known Arrhenius equation into Equation 2:

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

From Equation 3 one obtains

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

The integration of Equation 4 from the initial temperature T_0, at which conversion is zero, up to a given temperature T, where conversion is α, gives

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

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)

$$\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)dT \approx \frac{R}{E}T^2\exp\left(-\frac{E}{RT}\right). \tag{6}$$

Substituting Equation 6 into Equation 5, and applying the natural logarithm operator, one has

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha}, \tag{7}$$

where subscript α represents the value related to a given conversion (α). Therefore, the activation energy (E_α) is obtained as a function of the conversion.

In Equation 7, there is still a dependence from model g(α) but one of the main advantages of this method is that it isolate the function g(α) in the linear coefficient and estimating E_α as a function of α without choosing the reaction model. Therefore, the determination of this function in a complex process is very difficult (Vyazovkin and Sbirrazzuoli, 1997) and when assumed incorrectly, it may lead to errors in determining the kinetic parameters (Ersoy-Meriçboyu et al., 1993).

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

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

where m is the sample mass that varies with time, m0 is the initial sample mass, and m_∞ is the remaining mass of the sample after calcination.

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

RESULTS AND DISCUSSION

Thermal behavior of the neat bagasse and neat coal

Figure 1 shows the TG and DTG curves obtained for thermal decomposition of the bagasse in air atmosphere.

Through DTG curves, four distinct events can be observed. These events correspond to the thermal decomposition of lignocellulosic materials, including moisture content [A] at the beginning of the curves. Hemicellulose [B] and cellulose [C] decomposition (between 200 and 350°C) are the dominant events for the rate of mass loss. According to Klass (1998) the most part of volatile content in the biomass are generated from the decomposition of hemicellulose and cellulose. After their decomposition, the lignin content [D] is more difficult to decompose due to its structural chemical complexity and it is responsible for the char formation (Quensanga and Picard, 1988; Aiman and Stubington, 1993; Byrne and Nagle, 1996; Guimarães et al., 2009).

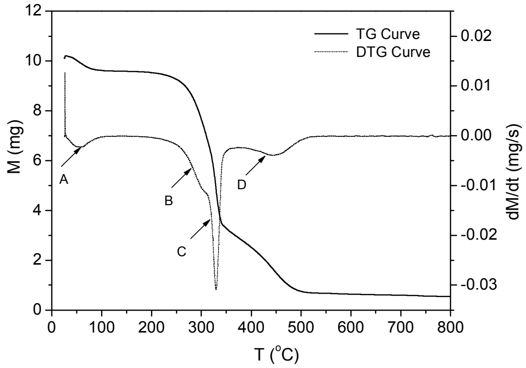

Figure 1. TG and DTG curves of the neat bagasse in air atmosphere (100 mL·min^{-1}) with heating rate of 10°C·min^{-1}.

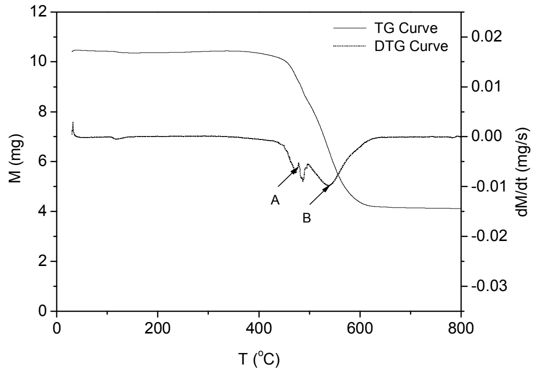

Figure 2. TG and DTG curves of the neat coal in nitrogen atmosphere (100 mL·min^{-1}) with heating rate of 10°C·min^{-1}.

Through TG/DTG curves (Figure 2) it can be observed the occurrence of two distinct events of mass loss for neat coal at temperatures between 400°C and 750 ° C. These events are identified as primary combustion or combustion of volatile [A] and secondary combustion or combustion of char [B] (Crelling et al., 1992).

Figures 3 and 4 show the TG and DTG curves, respectively, for all samples (neat bagasse, neat coal and two blends).

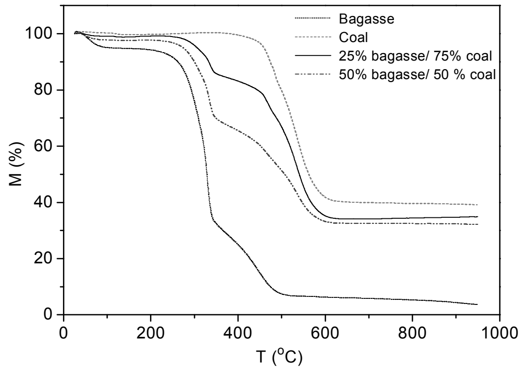

Figure 3. TG curves of the samples obtained under air atmosphere (100 mL·min^{-1}), heating rate of 10°C min^{-1}, mass of 10± 0.5 mg.

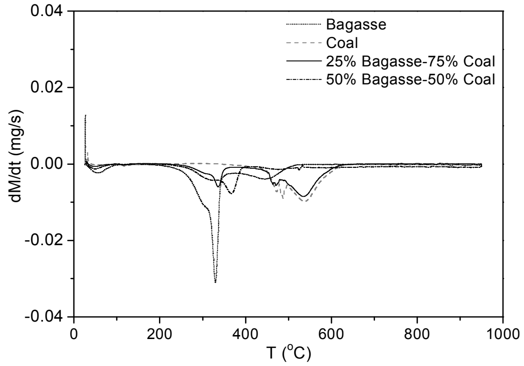

Figure 4. DTG curves of the samples obtained under air atmosphere (100 mL·min^{-1}), heating rate of 10°C·min^{-1}, mass of 10± 0.5 mg.

For all samples, the initial and final temperatures for each mass loss event, except for the moisture, are shown in Table 2.

Table 2. Temperature range of mass loss for all samples (100 mL·min^{-1}, heating rate of 10°C·min^{-1}, mass of 10± 0.5 mg).

Samples	*Temperature range (T±5°C)*		
	1ª Event	*2ª Event*	*3ª Event*
Neat Bagasse	230-315	315-340	340-525
Neat Coal	380-495	495-665	-
25% Bagasse and 75% Coal	260-360	410-490	490-640
50% Bagasse and 50% Coal	260-315	315-435	435-640

The initial decomposition of these four samples is between 225°C and 380°C. After this initial step, a high rate decomposition reaction takes place and it is related to evolution of volatiles present in the samples. This rate of mass loss can be observed in the DTG curves and for bagasse, the rate of the first step is the highest among all samples.

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

Determination of the ignition temperature of the bagasse, coal and their blends

Ignition temperatures for all cases were determined using TG curves in both air and nitrogen atmospheres. Figures 5, 6, 7 and 8 show these curves for neat bagasse, neat coal, 25%-75% and 50%-50% bagasse-coal blends, respectively.

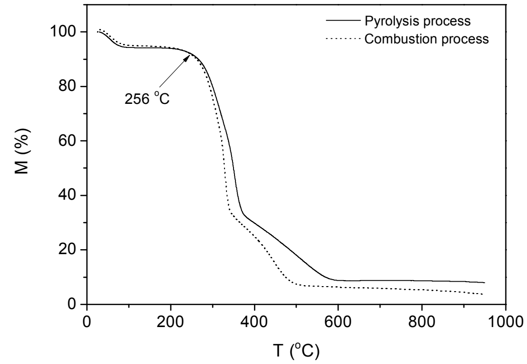

Figure 5. TG curves in air and nitrogen atmospheres for ignition temperature determination of the neat bagasse.

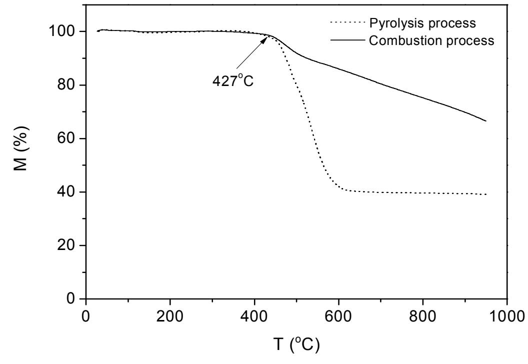

Figure 6. TG curves in air and nitrogen atmospheres for ignition temperature determination of the neat coal.

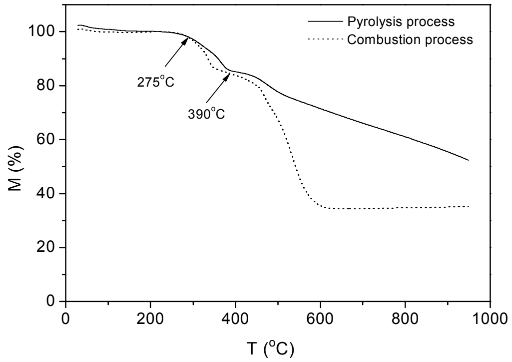

Figura 7. TG curves in air and nitrogen atmospheres for ignition temperature determination of the 25%-75% bagasse-coal blend.

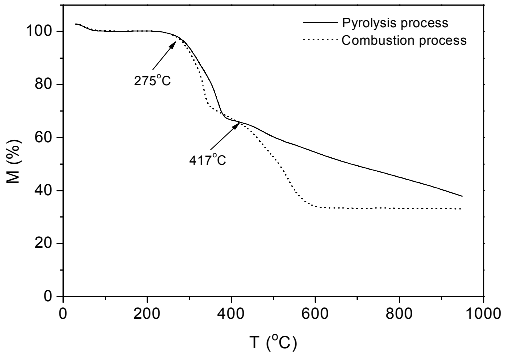

Figure 8. TG curves in air and nitrogen atmospheres for ignition temperature determination of the 50%-50% bagasse-coal blend.

Through Figures 5 and 6, it can be noted that there is only one meeting point, i.e., the ignition temperature, for neat bagasse (256°C) and neat coal (427°C). However, for the both blends there are two meeting points between pyrolysis and combustion TG curves. The first joint occurs at 275°C for both blends and the second joint point occurs at 390°C and 417°C for 25%-75% and 50%-50% bagasse-coal blend, respectively, which is closer to ignition temperature of the neat coal than neat bagasse.

For the blends the ignition temperature is considered at the first joint point, because from this temperature region the combustion process remains. Thus, ignition temperatures are as follows: 256°C for neat bagasse, 427°C for neat coal, and 275°C for both bagasse-coal blends (25%-75% and 50%-50%).

From the results presented in Table 2 and the ignition temperature values obtained for all samples, it is concluded that there is a synergistic effect when bagasse and coal are blended. This effect is observed through the temperature displacement of 30°C and 20°C higher in the results of the initial decomposition and the ignition temperature, respectively, obtained for the blends compared to neat bagasse.

Synergistic effects between biomass and coal were also investigated by Chen and Wu (2009). The authors used a thermogravimetric analyzer (TGA) and a drop tube furnace (DTF) in the pyrolysis of biomass-coal blends (rice husks and anthracitic). The TGA curves of the blends exhibited a linear correlation between the char yield and the biomass blending ratio, showing that synergistic effects in the pyrolysis processes were absent. However, the TGA curves of the unburned char showed that the char yield with respect to the biomass blending ratio followed a second order polynomial relationship, indicating that the unburned char was significantly characterized by synergistic effects. The authors concluded that biomass can be added to coal according to the need of volatiles necessary for the combustion or pyrolysis processes.

Activation energy determination for combustion and pyrolysis of the bagasse

In order to understand the thermal decomposition behavior of the bagasse from the kinetic point of view, this part of the study aims to determine the activation energy for the three decomposition events in two atmospheres, air and nitrogen. These three events correspond to the B, C and D regions, as presented in the Figure 1.

Model Free Kinetics was applied and values of activation energy (E) as a function of conversion (α) - E(α) or - were obtained to α between 0 and 1. The results are presented in Figures 9 and 10, for air and nitrogen atmospheres, respectively.

In Figures 9 and 10 two main regions can be observed. The first region (for α ranging from 0 to 0.6), related to the B and C regions (Figure 1), a stable value for activation energy is observed for both environments. The E_α values were 185.0±11.4 kJ mol^{-1} and 170.8± 26.3 kJ mol^{-1} for nitrogen and air atmospheres, respectively, in this region (1st step).

After this stage, i.e., for $\alpha > 0.6$ (2nd step), related to the D region, there is a changing of the behavior and then the activation energy was determined. E_α values were 277.8 ± 58.6 kJ mol^{-1} in nitrogen and 82.1 ± 43.4 kJ mol^{-1} in air atmosphere.

It also is observed that for air atmosphere, negative values were obtained. Thus, the model used was not well fit for this atmosphere. Only positive values were considered in the calculus of average and standard deviation in air atmosphere.

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

It is well known that thermal degradation is influenced by the nature of the atmosphere. For hemicellulose and cellulose (1st step), activation energy values showed no significant differences for nitrogen and air, considering the standard deviation, but for lignin decomposition (2st step), the influence of atmosphere were more evident comparing 277.8 ± 58.6 kJ mol^{-1} in nitrogen and 82.1 ± 43.4 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.

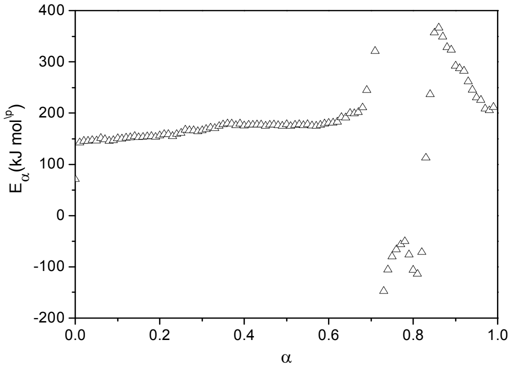

Figure 9. Activation energy versus conversion for the thermal decomposition of the bagasse in air atmosphere.

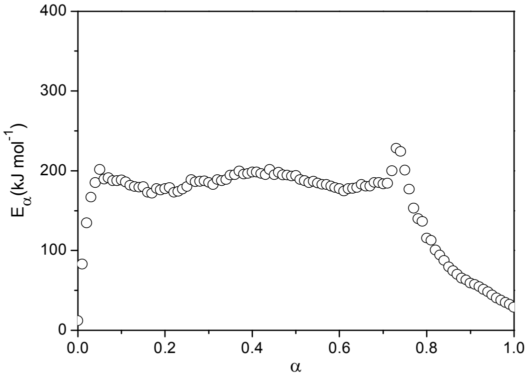

Figure 10. Activation energy versus conversion for the thermal decomposition of bagasse in nitrogen atmosphere.

This kinetic study was carried only for bagasse because for the coal, activation energy in air was previously presented elsewhere (Ávila et al., 2007). Activation energy values for the two steps of the thermal decomposition in air for both samples are presented in the Table 3.

Table 3. Activation energy obtained for bagasse and coal samples in air atmosphere.

Regions	E_α (kJ mol^{-1})	
	Bagasse	Coal(1)
1st Step	170.8± 26.3	183.5± 39.9
2nd Step	82.1± 43.4	101.3± 12.3

(1) Ávila et al. (2007).

From the activation energy, it is noted that the first and second steps for the bagasse is lower than coal, and this can explain by the synergistic effect that was observed when both samples were blended, i.e., the displacement in the both initial decomposition temperature and ignition temperature occurs due to the influence of the bagasse on the coal leading to the changes in the fuel reactivity.

CONCLUSIONS

This study investigated the thermal decomposition of biomass (sugar cane bagasse) and coal by TGA in order to evaluate the synergistic effects in their blends (50%-50% and 25%-75% bagasse-coal blends).

The decomposition temperatures values ranged between 230-525°C, 380-665°C, 260-640°C and 260-640°C for neat bagasse, neat coal, 25%-75% bagasse-coal blend and 50%-50% bagasse-coal blend, respectively. For the two blends, in the first decomposition region there were no changes of the initial temperatures when compared to the decomposition of the neat bagasse. However, changes were observed for the second decomposition region.

It was shown that there was only one meeting point, i.e., the ignition temperature, for neat bagasse (256°C) and neat coal (427°C). However, for the both blends two meeting points between pyrolysis and combustion TG curves were obtained. The first joint occurred at 275°C for both blends and the second joint point occurred at 390°C and 417°C for 25%-75% and 50%-50% bagasse-coal blend, respectively, which is closer to ignition temperature of the neat coal than neat bagasse.

Moreover, *Model-Free Kinetics* was applied to determine the activation energy as a function of conversion (E_α) of the decomposition process in both nitrogen and air atmospheres. The values obtained showed that, only for the second decomposition region (related do lignin degradation) presented significant differences between nitrogen and air conditions. May be this difference is related to the sensibility of lignin with oxygen during its decomposition and the high oxygen content in the bagasse enhances the decomposition promoting the char residue combustion.

Findings from the present work show synergistic effects that occur when biomass and coal were blended. In addition, the determination of the correct activation energy values is important to understand the decomposition behavior of the bagasse, coal and their blends. Such knowledge allows for a more complete assessment of related technologies, such as Carbon Capture and Storage (CCS).

ACKNOWLEDGEMENTS

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