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Correlation Between Activation Energy and Thermal Decomposition Yield of Sugar Cane Bagasse under CO_2/O_2 and N_2/O_2

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Brazil is the largest producer of sugar cane bagasse in the world and the combination of this biomass with oxy-fuel combustion has become a promising technology from environmental and energetic points of view. Fundamental knowledge on the thermal behavior of biomasses is important in the development and optimization of efficient processes. This study compares the effects of both oxy-fuel (CO_2/O_2) and conventional (N_2/O_2) atmospheres of combustions on the thermal decomposition of sugar cane bagasse. An electrically heated Drop Tube Furnace (DTF) of 60 X 400 mm internal dimensions and a thermogravimetric analyser (TG) were used to evaluate the thermal decomposition yield and the activation energy (E_α) of the bagasse. Thermogravimetric tests using a sample mass of 7.0 ± 0.5 mg were performed. Three heating rates (10, 15 and 25 $^oC\cdot min^{-1}$) from room temperature up to 650 ^oC and a "Model Free" isoconversional model were used to determine the activation energy for the combustion of sugar cane bagasse under both atmospheres. The results show that when N_2 is replaced by CO_2, the activation energy value increases on average 90 %. From DTF, the TG experiments of ashes showed that the highest yield was obtained under CO_2/O_2 environment.

1. Introduction

Currently the use of biomasses is of great interest in thermal processes because it is renewable, sustainable, economically viable and enables lower emissions of pollutants. It is a source of neutral carbon, since the carbon dioxide released is further returned into the geochemical carbon cycle.

In Brazil sugar cane bagasse is abundant and its application coupled with the oxy –fuel combustion to produce energy is a promising strategy for the carbon dioxide (CO_2) sink (Arias et al., 2008). However, oxy-fuel combustion is still a relatively new area and many technical aspects need to be clarified.

Several studies have reported on the replacement of N_2 by CO_2 in thermal processes. However, the results are controversial. Some authors affirm that CO_2 negatively interferes in the combustion process due to its physicochemical characteristics and others state that the results obtained under N_2 and CO_2 atmospheres are very similar. Rathnam et al 2009 investigated the combustion of single coal particles under O_2/N_2 and O_2/CO_2 atmospheres. In bituminous coals the replacement of N_2 by CO_2 reduced the volatile flame temperatures and coal char surface temperature. According to Munir et al 2009, fundamental knowledge on the thermal behavior and kinetics of biomass combustion under CO_2 atmosphere is inherent to the development of efficient technological processes.

This study aims to compare the behavior of thermal decomposition of sugar cane bagasse under two different atmospheres: (CO_2/O_2) to simulate oxy-fuel combustion and (N_2/O_2) to simulate conventional combustion. For these purpose, the studies were conducted in a TG balance and DTF reactor.

2. Materials and method

2.1 Samples

The biomass studied is sugar cane bagasse from the central region of São Paulo State (Brazil).

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The chemical composition of the material is shown in Table 1 and the morphological structure obtained by Scanning Electron Microscopy (SEM), is provided in Figure 1, in which elongated fibers bundles in tube shape can be observed.

Table 1: Chemical composition of sugar cane bagasse ,(dry basis)

Proximate Analysis	
moisture (%)	4.4
volatile matter (%)	83.9
fixed carbon (%)	7.7
ash (%)	4.0
Ultimate Analysis	
Carbon (%)	44.3
Hydrogen (%)	5.7
Oxygen (%)*	45.5
Nitrogen (%)	0.2
Sulfur (%)	0.07
Ash (%)	4.2

by Kazanc et al., 2011.

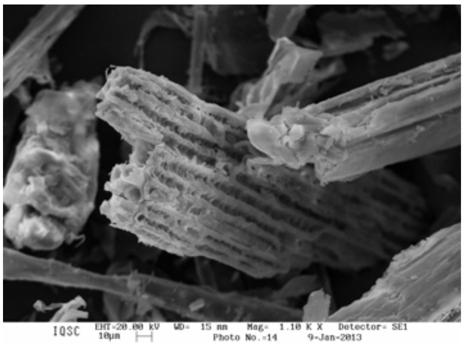


Figure 1: Morphological structure of sugar cane bagasse obtained by Scanning Electron Microscopy (SEM) with magnitude of 1000 x

Prior to thermogravimetric (TG) experiments, the samples were crushed and sieved to provide the average particle size of 89.5 µm, i.e, the chosen fraction was that obtained from sieves 105 and 74 µm. Before being crushed, the bagasse was washed in water during 5 min and dried in an oven at 80 °C for 24 hours. Although the bagasse was dried, the moisture content in the sample, as presented in Table 1, is due to the hydrophilic nature of the fibers, which is present even as structurally bound water molecules.

2.2 Thermogravimetric experiments

TG experiments were performed in a Shimadzu TGA-51 and were conducted for three different purposes: characterization of sugar cane bagasse, kinetic study and, evaluation of ashes from the combustion processes carried out in the DTF (Drop Tube Furnace).

In all TG experiments, a sample mass of 7.0 ± 0, 5 mg, an alumina crucible and flow rate of 100 mL min^{-1} were used. The temperature program was set from room temperature up to 650 ^{o}C. Other experimental conditions for each purpose are depicted in Table 2.

Table 2. Experimental conditions for the characterization of sugar cane bagasse; kinetic study and evaluation of ashes from the combustion

Purposes	Heating rates (^{o}C min^{-1})	Atmosphere
Characterization	20	80 % N_2/20 %O_2 and 80 %CO_2/20 %O_2
Kinetic study	10,15 and 25	80 % N_2/20 %O_2 and 80 %CO_2/20 %O_2
Evaluation of ashes	20	80 % N_2/20%O_2

2.3 Kinetic study

Activation energy determinations were obtained based on Model-Free kinetics theory, which applies isoconversional techniques to obtain the activation energy (E_α) as a function of conversion (α). This method is based on Arrhenius Equation, which can be described by Equation 1:

$$K(T) = A\exp\left(\frac{-E}{RT}\right) \tag{1}$$

Where A and E are kinetic parameters (the preexponential factor and the acivaton energy, respectively), R is the universal gas constant. *K* (T) is the temperature - dependent constant and it is related to the rate of conversion (dα/dt) and the reaction model f (α). The conversion rate (α) is defined as (initial mass – mass of the sample at time divided by initial mass – final mass).

The “Model Free Kinetics” comprises the use of at least three TG curves with different heating rates (β). The fundamental expression to calculate kinetic paramenter on the basis of TGA data is based on that proposed by Vyazovikin. This is an iso-convertional method and directly leads to (-E/R) for a given value of α by plotting the $\ln(\beta/T_\alpha^2)$ against 1/T (Equation 2) (Vyazovkin and Wight, 1999).

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

where E_α [kJ mol^{-1}] is the activation energy related to each conversion value (α), β is the heating rate [K/min], T_α is the temperature [K] related to each α value and g(α) is the integral form of the inverse function f(α), which is the model reaction.

In this study we considered two approaches, namely one-step and three-steps. One-step approach corresponds to the evaluation of the entire process of thermal decomposition (between 170 and 570°C) whereas the three-step approach corresponds to the evaluation of the thermal decomposition of three independent events.

2.4 Laboratory furnace and procedure

An electrically heated drop tube furnace (DTF) (3.5 kVA maximum power) with outer diameter of 6 cm and radiation zone of 40 cm length (Figure 2) was used for the combustion processes. To introduce particles into the reactor we used a vibratory feeder, with mass flow rate of 0.5 g min^{-1} (downward flow) and two different environments (CO_2/O_2 and N_2/O_2 gas mixtures with oxygen molar fractions of 20%) with gas flow rate of 5L min^{-1} (upward flow) were applied. The feed moves downwards while the gas is introduced from the bottom of the equipment.

The gas flow was previously calculated based on the stoichiometric ratio (considering O_2 excess of 20%). Before starting the tests, the reactor was heated up to 900 ° C, remaining in this temperature for 30 min. Then was activated gas flow and again waited for the reestablishment of temperature. The experiments were carried out at 900 °C for ten minutes. The purpose of using DTF was to collect the ashes after samples have been burnt under different atmospheres. After the combustion, the ashes were collected and analysed by means of TG curves in order to evaluate the performance and yield of the combustion processes.

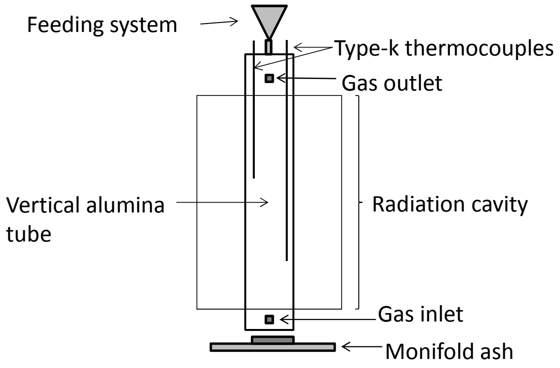


Figure 2: Scheme illustrating the furnace electrically heated.

3. Results and discussion

3.1 Thermogravimetric experiments

The effect of CO_2 atmosphere and kinetic behavior were analyzed by using the thermogravimetric results. Figure 3 shows the TG and DTG curves related to the thermal decomposition of the sugar cane bagasse. The three events considered for the kinetic study of the three-step approach are indicated in the figure.

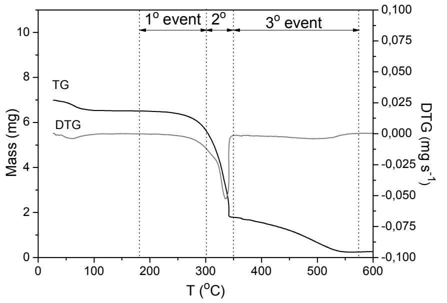
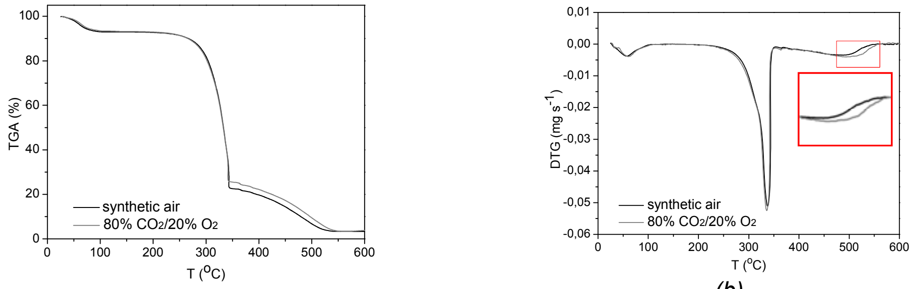


Figure 3: TG and DTG curves of the thermal decomposition of the sugar cane bagasse. Conditions: synthetic air atmosphere - 100 mL min^{-1} and heating rate - 20°C min^{-1}

The three events that occur between 170 and 550 °C are related to the decomposition of lignocellulosic materials whose main compounds are hemicellulose, cellulose and lignin. Hemicelulose e cellulose decompositions occur between 170 and 350 °C. The lignin decomposition occurs between 170 and 550 °C. The decomposition of three compounds occurs sequentially, and is not clearly distinguished in the curves TG/DTG. Hemicellulose is degraded at low temperatures because it consists of several saccharides, which are amorphous structures rich in branching and easy to be removed. Cellulose consists of long unbranched glucose polymers, which have an ordered and strong structure, and high thermal stability. Lignin is composed of aromatic rings with multiple branches, whose degradation occurs in a broad temperature range.The decomposition of three compounds occurs sequentially, and is not clearly distinguished in the curves TG/DTG. Hemicellulose is degraded at low temperatures because it consists of several saccharides, which are amorphous structures rich in branching and easy to be removed. Cellulose consists of long unbranched glucose polymers, which have an ordered and strong structure, and high thermal stability. Lignin is composed of aromatic rings with multiple branches, whose degradation occurs in a broad temperature range. According to Varhegyi e Antal Jr. 1989, bagasse is composed of 32% hemicellulose, 40% cellulose, 20% lignin, 6% of extractives and 2% ash.

Figure 4 shows the TG and DTG curves of the thermal decomposition of the sugar cane bagasse comparing both $80\%CO_2/20\%O_2$ and $80\%\ N_2/20\%\ O_2$ atmospheres at a heating rate of 20^oCmin^{-1}. The presence of CO_2 causes a displacement of the degradation to higher temperatures, especially in the decomposition step from 350° C. The delay of the decomposition under $80\%\ CO_2/20\%\ O_2$ atmosphere is probably caused by the increase of the CO_2 partial pressure. The CO_2 partial pressure interferes in the equilibrium of the auto-oxidation reaction of biomass, which is explained because bagasse has oxygen in their composition. This behavior can be explained by the differences in the properties of CO_2, such as higher density (the molecular weight of CO_2 is 44 while N_2 is 28), higher heat capacity, lower oxygen diffusivity (the O_2 diffusion rate in CO_2 is 0.8 times that in N_2) and higher emissivity in comparison to N_2 (Wall et al. 2009).



(a) *(b)*

Figure 4: TG (a) and DTG (b) curves of sugar cane bagasse under synthetic air and $80\%CO_2/20\%O_2$ atmospheres

3.2 Kinetic study

Figure 5 shows the E_α versus α curves for the thermal decomposition of the sugar cane bagasse (between 180 and 570°C) under synthetic air (N_2/O_2) and CO_2/O_2. In both cases the entire process, named here one-step approach, was considered for the calculations.

The curves show negative values of activation energy at conversion around 0.7. This behavior indicates a change in the mechanism during the thermal decomposition of the sugar cane bagasse. The values of E_α are provided in the fifth line of Table 3.

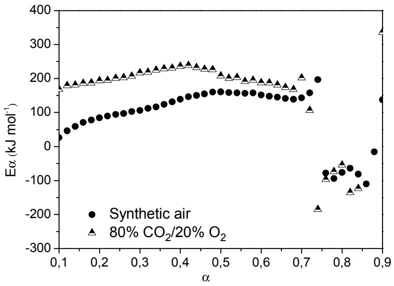
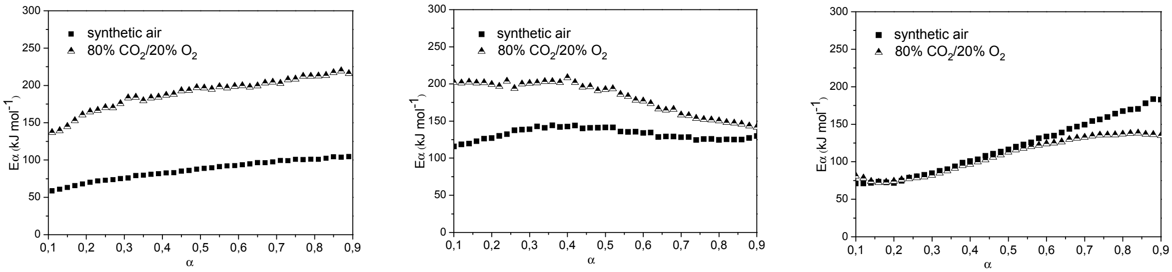


Figure 5: E_α versus α curves under synthetic air and $80\%CO_2/20\%O_2$ atmosphere considering all the events during the thermal decomposition of sugar cane bagasse

In order to better evaluate the processing of the sugar cane bagasse, the kinetic model was also applied to the three separate regions of the decomposition (according to Figure 3).
Figure 6 shows the profiles of the E_α *versus* α curves.



(a) (b) (c)

Figure 6: E_α versus α curves under synthetic air and 80%CO_2/20%O_2 atmosphere during the thermal decomposition of the sugar cane bagasse. (a) first event; (b) second event and (c) third event.

The comparison of Figure 5 and 6 shows the profile of the curve for the one-step approach is very close to the sum of the three independent events. The main difference between the two approaches is related to the variation of the E_α values. For the one-step approach this variation is higher and an abrupt change can be observed in the mechanism. On the other hand, when three events are considered separately, a slight variation in the activation energy is observed. Both approaches yield several activation energy values. The one-step approach provides a higher range between minimum and maximum values, whereas the standard deviation shows this range is lower for the three-steps approach. All these values are illustrated in Table 3.

Table 3: Minimum, maximum and average values of E_α for both one-step and three-steps approaches under two atmospheres (N_2/O_2 and CO_2/O_2).

		Activation energy values (kJ mol^{-1})							
Approaches		**80% N_2/20% O_2**				**80% CO_2/20% O_2**			
		Min.	Max.	Average	SD*	Min	Max.	Average	SD
Three-steps	First	58	106	**86**	13	134	220	**189**	22
	Second	116	145	**132**	8	142	208	**181**	22
	Third	71	183	**119**	36	79	132	**110**	19
One step		-120	200	**91**	84	-274	576	**171**	145

**SD: Standard deviation.*

Sugar cane bagasse is a heterogeneous material which shows high complexity in its thermal decomposition. This complexity is evidenced by means of E_α versus α curves profile, in which strong variations can be observed and understood in terms of changes in the reaction mechanism, resulting in negative values of activation energy. This trend is not typically expected from the activation energy barrier, but in this case, the reaction rate decreases by increasing the temperature.

In the three-step approach and comparing both atmospheres, there was an increase in the average activation energy values, on both first and second steps when N_2 was replaced by CO_2 (120% and 37%, respectively). However, on the third step there was an 8% decrease in the E_α. This trend can be observed in the profiles of the E_α versus α curves (Figure 6) and the values in Table 3. The first step of the thermal degradation is related to the ignition process and our findings show that under CO_2/O_2 atmosphere, this biomass ignites more easily than under N_2/O_2.

3.3 Furnace results

The ashes produced in the DTF under both atmospheres were collected and analyzed through TG experiments. The results are presented in Figure 7. To evaluate the ash yields, we used the TG curve for biomass *in natura,* which shows approximately a 95% mass loss. Under CO_2/O_2 atmosphere the profile of the TG curve indicates no mass loss events, which means that there is neither volatile matter nor fixed carbon in the ash. In this case we considered a high yield of burning. However, the TG curve for N_2/O_2 atmosphere shows approximately a 20% mass loss due to unburnt biomass particles in the ash.

The ash formation depends on the combustion conditions and according to the literature few studies have been published on ash formation under CO_2/O_2 atmosphere. Fryda et al. 2012 reported that a higher carbon-in-ash amount was observed in both air and oxy-fuel cases. Based on these results, the authors could not conclude which atmosphere presents higher yields.

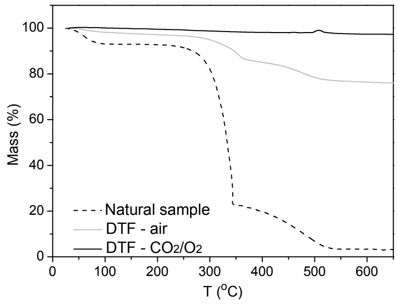


Figure 7: TG curves of ashes produced in the combustion process under N_2/O_2 and CO_2/O_2 atmospheres.

4. Conclusions

This study has reported on the behavior of the thermal decomposition of sugar cane bagasse in two different atmospheres based on two strands: activation energy and evaluation of the ashes collected from the DTF.

The thermal behavior of the biomass was also evaluated and the TG curves showed that under CO_2/O_2 atmosphere there was a displacement of the third decomposition step to higher temperatures in comparison to the thermal decomposition under N_2/O_2. This behavior can be understood as a delay caused by the increase in the CO_2 partial pressure in the combustion environment.

Concerning activation energy, lower values were determined for the first step of degradation, which is related to the ignition process. Our findings show that under CO_2/O_2 atmosphere, this biomass ignites more easily than under N_2/O_2.

Comparing the results obtained in the DTF under different combustion environments, higher yields are found in CO_2/O_2. This statement could be verified by means of TG curves profile. The curves showed that the ashes produced under CO_2/O_2 do not present mass loss events, while those produced under N_2/O_2 present 20% mass loss.

Acknowledgment

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