

# Comparative study on combustion and oxy-fuel combustion environments using mixtures of coal with sugarcane bagasse and biomass sorghum bagasse by the thermogravimetric analysis



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## ARTICLE INFO

### Article history:

Received 27 November 2017

Received in revised form

14 February 2018

Accepted 19 February 2018

Available online 1 March 2018

### Keywords:

Coal

Biomass

Sugarcane

Biomass sorghum

TGA

## ABSTRACT

Biomass and coal have different physicochemical properties and thermal behavior. During the co-combustion of coal-biomass mixtures, their thermal behavior varies according to the percentage of each fuel in the mixture. Thereby, this research aims to characterize the thermal behavior of mixtures of coal, sugarcane bagasse, and biomass sorghum bagasse as biomass in simulated combustion (O<sub>2</sub>/N<sub>2</sub>) and oxy-fuel combustion (O<sub>2</sub>/CO<sub>2</sub>) environments. Experiments have been performed in duplicate on a thermogravimetric analyzer at heating rate of 10 °C/min. A uniform granulometry was considered for all materials (63 μm) in order to ensure a homogeneous mixture. Four biomass percentages in the mixture (10, 25, 50 and 75%) have been studied. Based on thermogravimetric (TG) and thermogravimetric (DTG) analyses, parameters such as combustion index, synergism, and activation energy have been determined, as well as the combustion environment influence on these parameters. The results indicate that, although sugarcane bagasse has the lowest activation energy, the thermal behavior of both types of biomass is similar. Thus, biomass sorghum bagasse can be used as an alternative biomass to supply the power required during sugarcane off-season. For both mixtures, optimal results were obtained at 25% of biomass. By analyzing the environment influence on combustion behavior, the results indicate that when N<sub>2</sub> is replaced with CO<sub>2</sub>, it is observed an increase in reaction reactivity, a higher oxidation rate of materials and an improvement in evaluated parameters.

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## 1. Introduction

Fossil fuel combustion to generate energy increases greenhouse gas (GHG) emissions, mainly carbon dioxide (CO<sub>2</sub>), which is directly linked to global warming [1]. The demand for alternative fuels that reduce emissions of greenhouse gases tends to increase in the upcoming years. Thus, biomass has enormous potential to meet this energy demand due to being the object of several studies in the literature [2–4]. In March 2017, atmospheric CO<sub>2</sub> concentration reached a global average of 404.70 ppm, i.e. the highest level recorded in the latest 20 years [5]. In comparison with other fossil fuels, such as oil and natural gas, coal has the largest reserves available in the world, thus making it a low-cost fuel. The reserves available in the world registered in 2014 are enough to meet the global production demand for the next 110 years [6].

In Brazil, coal reserves are in the order of 32 × 10<sup>9</sup> tons, which are composed mainly of lignite and sub-bituminous coal and largely located in southern Brazil [7,8]. The co-combustion of coal and biomass tends to increase in the upcoming years due to a large demand for fuels that reduce emissions of CO<sub>2</sub>, nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) [4,9].

Due to natural and geographical conditions, Brazil possesses a significant variety of renewable energy sources, in which biomass is one of the most promising. According to the National Energy Balance of 2016 (based on 2015), 41.2% of Brazil's energy supply is produced from renewable sources, and 16.9% of it is from sugarcane [10]. Brazil has a significant variety of biomass, among which sugarcane bagasse/straw and, most recently, a variety of biomass sorghum has been recently developed and introduced by EMBRAPA to be used for electricity

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generation. Sugarcane bagasse is an important solid residue that can be easily converted into bioenergy by direct combustion in an electricity generation system [11]. Brazil comprises an area of 8.84 million hectares with sugarcane to be harvested and used for sugar-alcohol activities in 2017/18, in which the state of São Paulo is the largest national producer [12].

Biomass Sorghum bagasse has similar physico-chemical characteristics to sugarcane bagasse and is a very versatile crop that can be used for animal and human food, as well as alcohol and sugar production, being the fifth most produced cereal worldwide. The largest producers of sorghum are the United States and Mexico [13]. Brazilian biomass sorghum has been developed by EMBRAPA Milho e Sorgo to be used to produce second generation ethanol for electricity generation by burning biomass. It presents lower lignin content when compared to the varieties of sorghum, forage and saccharine. Lower lignin content facilitates cellulose and hemicellulose hydrolysis for ethanol fermentation and production [14]. Furthermore, it can be rapidly grown, its productivity is 2.5 times greater than that of sugarcane or corn and its heating value is similar to that of sugarcane bagasse. Harvesting sorghum planted between October and November occurs between March and April, thus it is an alternative to be used in sugarcane harvesting, during which there is a reduction in the quantity of sugarcane bagasse used for electricity generation [15].

Electricity generation from biomass also releases CO<sub>2</sub>, however, part of it is absorbed by the photosynthesis process of plants [16]. Using biomass also has some disadvantages, such as seasonal availability, high moisture content, low heating value and low density. One way to reduce these impacts of using coal and biomass is to use the co-combustion technique, i.e. using mixtures of coal and biomass [17]. If compared to burning pure coal, the presence of biomass reduces CO<sub>2</sub> and other GHG emissions, such as NO<sub>x</sub> and SO<sub>x</sub> [18]. It should be noted, however, that even in smaller proportions, GHGs are still released into the environment during the co-combustion of coal and biomass mixtures. Thus, new technologies have been developed for industrial application in order to reduce CO<sub>2</sub> emissions into the environment, called as *Carbon Capture and Storage* (CCS). Among them, oxy-fuel combustion is a promising technique to further reduce emissions, since it allows capturing CO<sub>2</sub> from combustion processes [9,19–21].

In an oxy-fuel combustion process, fuel is burned with pure oxygen or a mixture of oxygen and captured CO<sub>2</sub> and reintroduced into the combustion process [22]. The concept of oxy-combustion was introduced in the 1980s with the aim of producing a gas with high CO<sub>2</sub> concentration to be used in oil recovery [21,23]. At the beginning of the 1990s, due to the growing concern about GHG emissions, the concept of oxy-fuel combustion was used in a coal combustion process aimed at capturing and reintroducing CO<sub>2</sub> from the burning process into the cycle [21]. Oxy-fuel combustion technology aims to make the burning process more efficient and reduce the impacts generated by the emission of pollutant gases [24]. The technology reduces environmental impacts because it allows capturing CO<sub>2</sub>, which is the main difference between combustion and oxy-fuel combustion [25]. Oxy-fuel combustion can be applied to any type of fuel for heat generation, but this research is mainly focused on coal because of its widespread availability.

According to data from 2014, reserves available worldwide are enough to meet the global production demand during the next 110 years [6]. In Brazil, the coal reserves are in the order of  $32 \times 10^9$  tons, which are composed mainly of lignite and sub-bituminous coal and mostly located in southern Brazil [7,8]. In the Brazilian energy grid, coal represents 5.7% of its domestic energy supply (EPE, 2015) [26]. CO<sub>2</sub> concentration in coal combustion gas in air (O<sub>2</sub>/N<sub>2</sub>) is only 14–16%, which makes the process of CO<sub>2</sub> sequestration costly and disadvantageous. However, in oxy-fuel combustion with recirculation of combustion gases, CO<sub>2</sub> concentration in the combustion gas can reach up to 95% and it can be directly sequestered and stored [27].

The gas generated from the oxy-fuel combustion process consists mainly of CO<sub>2</sub> and steam. Steam can be easily separated from CO<sub>2</sub> and its flow is captured, compressed and transported for suitable geological storage [28]. However, the presence of CO<sub>2</sub> in the oxy-fuel combustion process alters heat transfer processes and properties, such as ignition temperature and ash characteristics [29,30].

For evaluating the combustion and oxy-fuel combustion behavior of solid fuels, one of the most widely used techniques in the literature is the thermogravimetric analysis (TGA). Through it, it is possible to study and compare the thermal behavior of different samples and environments and to efficiently determine thermal parameters, such as ignition temperature, burning temperature, thermal reactivity [31,32].

The use of coal-biomass mixtures for energy generation through combustion and oxy-fuel combustion processes has the main advantage of reducing CO<sub>2</sub> emissions. On average, there is an 18% reduction in CO<sub>2</sub> emissions when 20% of biomass is added to the mixture, which may vary according to the type of coal being used in the process [33]. Studies on using different environments to investigate the influence of biomass percentage on the co-combustion process of coal in different environments can be found in the literature [34–39].

Gil et al. [34] conducted a study on thermal and kinetic behavior of mixtures of coal and biomass in a combustion environment using a non-isothermal thermogravimetric method, whose results have indicated the absence of a synergistic effect during the combustion process. However, 5–20% of biomass reduced activation energy, thus facilitating the processes of coal combustion and volatilization.

Zhou et al. [35] carried out a study on the thermal characteristics of co-combustion of biomass and mineral coal by using TGA, in which soybean stem and sawdust were used as biomass. The authors have observed that, for the used biomass, optimal results as regards ignition temperature reduction and thermal reactivity improvement were obtained when 20–30% of biomass was used in the mixture.

Buratti et al. [36] studied the thermal behavior of co-combustion of sub-bituminous coal and ethanol production waste through the TGA. The results indicated that combustion index reached optimal performance when 20% of waste was used and that the activation energy of the reaction was lower by using the same percentage of biomass.

Haykiri-Acma et al. [40] performed a study on combustion and thermal reactivity characteristics of mixtures of biomass and coal in an oxy-fuel combustion environment. The authors have concluded that in an oxy-fuel combustion environment, the exothermic reaction of coal can be controlled with up to 20% biomass, once oxy-fuel combustion is an alternative method to capture CO<sub>2</sub>.

Niu; Han and Lu [27] investigated the characteristics of bituminous coal oxy-fuel combustion through the TGA. The results showed that the combustion characteristics of coal are similar in O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub> environment at a concentration of 20% of O<sub>2</sub>. As O<sub>2</sub> concentration increases to 40%, the combustion properties of coal are improved. However, the authors concluded that this improvement in combustion parameters is not financially worth it.

López et al. [30] studied the thermal behavior of mixtures of four types of biomass in an oxy-fuel combustion environment by means of the TGA. The results demonstrated that the oxy-fuel combustion environment can either reduce or increase the activation energy of the reaction, depending on the physical-chemical composition of biomass. However, even though there is increased activation energy in an oxy-fuel combustion environment for some types of biomass, the benefit of reducing CO<sub>2</sub> emissions into the environment compensates for the loss of efficiency.

In order to estimate activation energy as a function of conversion rate ( $E\alpha$ ) of different biomasses in combustion and oxycombustion environments, different isoconversion methods can be used, such as Friedman (FD), Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Vyazovikin (VZ) [36,39,41,42].

By using corn harvest waste, López et al. (2014b) [39] obtained  $E\alpha$  values of 153.0 kJ ml<sup>-1</sup> and 150.1 kJ ml<sup>-1</sup> through KAS and FWO models, respectively, in a combustion environment. In oxicomustion conditions, the  $E\alpha$  values obtained for corn waste were 168.6 kJ ml<sup>-1</sup> and 169.1 kJ ml<sup>-1</sup> using KAS and FWO models, respectively.

LOPES; TANNOUS; RUEDA-ORDÓÑEZ (2016) [42] used FD, FWO, KAS, and VZ methods to determine kinetic parameters of guarana seed residue. The values of ( $E\alpha$ ) were determined for each conversion rate. In a combustion environment, the lowest  $E\alpha$  value was obtained by the FD method, which was 75.62 kJ ml<sup>-1</sup>. For these three integral methods (FWO, KAS and Vz), the authors observed that the activation energies have remained approximately constant in conversion rates ranging from 0.15 to 0.90 and that there was a similarity in the distribution of  $E\alpha$ , being 98.16 kJ ml<sup>-1</sup>, 90.65 kJ ml<sup>-1</sup> and 91.40 kJ ml<sup>-1</sup> for FWO, KAS and Vz, respectively.

XIE et al. (2018) [43] used the FWO and KAS methods to determine  $E\alpha$  values during sugar cane bagasse combustion. The results show that  $E\alpha$  values were similar for both methods on average, being 206.61 kJ.mol<sup>-1</sup> and 207.66 kJ.mol<sup>-1</sup> for FWO and KAS methods, respectively.

The analysis of works published in the literature so far shows that the results of co-combustion of coal and biomass mixtures and CO<sub>2</sub> influence on oxy-fuel combustion processes do not follow a trend, but rather depend on the physicochemical characteristics of each material. For an efficient implementation of co-combustion of coal-biomass mixtures in industrial systems, further studies are needed to define the most appropriate amount of biomass in combustion or oxy-fuel combustion processes.

Thus, the present research contributes to clarify some technical aspects of co-combustion of coal mixtures using two Brazilian types of biomass, and it also investigates the influence of the presence of CO<sub>2</sub> on the oxy-fuel combustion process. This research also contributes to determining the combustion behavior of biomass sorghum bagasse and its potential to be used in the sugarcane harvesting period. Biomass Sorghum is a recently introduced biomass that needs further research on its combustion behavior, so that it can be considered as fuel for energy generation.

## 2. Materials and methods

### 2.1. Sample preparation

This study uses a bituminous coal and two types of biomass, sugarcane bagasse (SB) and biomass sorghum bagasse (BSB). The coal was provided by Carbonífera Metropolitana S.A, located in Criciúma-SC, which comes from the Fontanella mine (28°29'16.3"S 49°27'42.4"W), located in Siderópolis-SC. Sugarcane bagasse was provided by Açucareira da Serra S.A., which belongs to the Cosan Group, located in the city of Ibaté-SP (22°00'44.6"S 48°00'03.3"W). The biomass sorghum bagasse was supplied by EMBRAPA Milho e Sorgo, located in the city of Sete Lagoas-MG (19°26'52.1"S 44°10'02.8"W). Table 1 provides the physicochemical characteristics of used fuels.

The concentrations of inorganic elements that constitute biomass were determined by X-ray Fluorescence (XRF) and are presented in Table 2. BSB has a higher concentration of inorganic elements than SB, mainly Cl and K, which indicates that BSB combustion has a greater tendency to generate problems, such as corrosion and incrustation.

Standards ASTM D346 and E1757-01 were followed for preparing the samples of coal and biomass, respectively. All materials were supplied with random particle size distribution. In order to standardize the particle size of materials, the samples were ground for about 3 h in a Solab SL-35 ball mill crusher with alumina balls of three different sizes. After grinding, standard ASTM sieves were used to obtain average particle size of 63 μm through a 75 μm sieve and retention in a 63 μm sieve in order to avoid coal decrepitation, i.e. microexplosions occurring inside coal particles (CRNKOVIC et al., 2004), and to ensure mixture homogenization.

### 2.2. Experimental setup

Thermogravimetry (TGA) and Differential Thermal Analysis (DTA) were used as thermal analysis techniques, which were performed on a simultaneous TA Instruments - SDT TGA-DSC Q600 system in an alumina crucible.

**Table 1**  
Physicochemical characteristics of the coal, sugarcane bagasse (SB) and biomass sorghum bagasse (BSB).

	Coal	SB	BSB
High Heating Value (MJ kg <sup>-1</sup> )	18.81	17.33	17.72
<i>Proximate analysis (% wt.)</i>			
Moisture	1.0	4.8	8.1
Volatile matter	24.6	78.5	75.4
Fixed carbon	36.9	9.8	14.2
Ash	37.5	6.9	2.3
<i>Ultimate analysis (% wt.)<sup>a</sup></i>			
C	54.96	43.53	44.12
H	3.36	5.09	4.95
N	1.07	0.43	0.93
O <sup>b</sup>	0.76	39.25	39.60
S	1.18	nd	nd
Cl	0.17	nd	nd

Note: n.d. Not detected.

<sup>a</sup> Dry basis.

<sup>b</sup> Calculated by difference.

**Table 2**  
Concentrations of inorganic elements of sugarcane bagasse (SB) and biomass sorghum bagasse (BSB).

Inorganic elements (% m/m)	SB	BSB
Al	0.569	–
Si	1.621	0.315
P	0.130	0.071
Cl	0.105	1.303
K	0.511	3.600
Ca	0.646	2.163
Ti	0.198	–
Fe	0.493	0.108

Conventional combustion environments with synthetic air (20% O<sub>2</sub> and 80% N<sub>2</sub>) and oxy-fuel combustion (20% O<sub>2</sub> and 80% CO<sub>2</sub>) were selected, both with volumetric flow rate of 100 mL min<sup>-1</sup>.

For tests in an oxy-fuel combustion environment, it was used an AALBORG® gas flowmeter coupled to a simultaneous TA system. Coal mixtures and both types of biomass were used with 10%, 25%, 50%, and 75% of biomass in the mixture. Samples of 5 ± 0.5 mg of mixtures were used in three different heating ratios (10, 15 and 20 °C/min) from 30 °C to 700 °C. Synergism, combustion parameters and activation energy of the thermal decomposition of fuels was determined through the TGA.

Prior to the tests, it was performed equipment calibration to set baseline and temperature for each experimental condition being evaluated. Baseline was calibrated according to standard weights and temperature according to Zinc standard. A series of preliminary tests with different stepwise heating programs, sample mass and volumetric flow rate were conducted in order to evaluate the influence of temperature, heating rate, and furnace conditions. It is worth emphasizing that all measurements were carried out in duplicate so as to ensure accuracy and reproducibility.

### 2.3. Synergism

Synergism is a term used to describe the interaction between distinct samples that make up a mixture. The difference between theoretical DTG (DTG<sub>th</sub>) and experimental DTG profiles may indicate an interaction between samples. Theoretical DTG curves of mixtures were calculated according to Eq. (1), wherein (DTG)<sub>Coal</sub> and (DTG)<sub>Biomass</sub> are mass loss rates of each of the components and x<sub>1</sub>, x<sub>2</sub> are the mass proportions of coal and biomass in the mixture, respectively.

$$DTG_{th} = x_{coal} \cdot DTG_{coal} + x_{biomass} \cdot DTG_{biomass} \quad (1)$$

In order to quantify the degree of synergism, the relative error Δm<sub>erro</sub> (Eq. (2)) was determined according to Oyedun et al. [44]. M and x refer, respectively, to the mass loss of pure components (m<sub>1</sub> and m<sub>2</sub>) or the mixture (m<sub>Blend</sub>) and to mass fractions (x<sub>1</sub> and x<sub>2</sub>) of each component in the mixture. The greater the relative error value is, the greater the interaction between the mixture components becomes.

$$\Delta m_{Error} = \left[ m_{Blend} - \left( \frac{x_1 \cdot m_1 + x_2 \cdot m_2}{m_{Blend}} \right) \right] \cdot 100 \quad (2)$$

### 2.4. Combustion and oxy-fuel combustion index

Combustion index (S) is a parameter used to evaluate combustion performance. The higher its value, the better the reactivity of the fuel or mixture becomes [30,36,45,46]. It [47] is calculated according to equation (3).

$$S = \frac{(DTG)_{max} \cdot (DTG)_{mean}}{T_i^2 \cdot T_b} \quad (3)$$

where (DTG)<sub>max</sub> and (DTG)<sub>mean</sub> are the maximum and mean mass loss rates, T<sub>i</sub> and T<sub>b</sub> are the ignition and burnout temperature in Kelvin (K). where (DTG) max and (DTG) are the maximum and mean mass loss rates, T<sub>i</sub> and T<sub>b</sub> are the ignition and burnout temperatures in Kelvin (K).

T<sub>i</sub> and T<sub>b</sub> are, respectively, initial and final mass loss temperatures measured through the TGA curves. The maximum mass loss point (DTG<sub>max</sub>) and average mass loss (DTG<sub>médio</sub>) as a function of temperature, both determined in (% min<sup>-1</sup>), were obtained through the DTG curve.

For both types of biomass, ignition and burnout temperatures were determined by the intersection method presented by Lu and Chen [47]. According to the authors, the intersection method is the most appropriate for evaluating biomasses.

With respect to coal, the most commonly used method is the one proposed by Tognotti et al. (TOGNOTTI et al., 1985) in which the ignition temperature is determined by the overlap of TGA curves obtained in synthetic air (combustion) and nitrogen (pyrolysis) environments. The temperature at which combustion and pyrolysis curves diverge was assumed as being the ignition temperature.

### 2.5. Determination of the activation energies

Activation energy is a kinetic parameter which represents the least energy required for a reaction to start, thus the lower the activation energy value is, the lower the energy consumption to start the reaction becomes and the process becomes better.

The model used to determine activation energy as a function of the degree of conversion (α) of a chemical reaction. It is based on isoconversional techniques to calculate activation energy (E<sub>α</sub>), which α is defined in terms of mass change in the sample (Eq. (4)), [48,49].

$$\alpha = \frac{m - m_0}{m_f - m_0} \quad (4)$$

Under non-isothermal conditions, temperature varies according to a constant heating ratio ( $\beta = dT/dt$ ). When it is not assumed or determined any particular form of reaction model, Isoconversional methods are used, which are also known as “model-free kinetics” [50]. The isoconversional method used herein is known as KAS (Kissinger-Akahira-Sunose), which is based on the approximation of Coats-Redfern method [51,52]. In order to determine activation energy as a function of the degree of conversion ( $\alpha$ ), Eq. (5) is used [48–52].

$$\ln \frac{\beta}{T_\alpha^2} = \ln \left[ \frac{RA}{E_\alpha g(\alpha)} \right] - \frac{E_\alpha}{R\alpha} \cdot \frac{1}{T\alpha} \quad (5)$$

where A and  $E_\alpha$  are the Arrhenius parameters, T is temperature, R is the universal gas constant and  $g(\alpha)$  is the overall reaction model.

$E_\alpha$  is determined from the TGA curve. To employ the KAS method, it is necessary to obtain at least three different heating ratios [48]. For each conversion value  $\alpha$ , it is plotted  $\ln(\beta/T_\alpha^2)$  versus  $1/T\alpha$  in order to obtain a straight line whose slope is  $-E_\alpha/R$ .

A kinetic analysis based on the isoconversional method allows determining activation energy for different conversion degrees, without previously determining a reaction model [53]. This method allows isolating function  $g(\alpha)$  of the angular coefficient, thus the  $E_\alpha$  is determined regardless of the reaction model. In complex processes, determining this function is rather difficult and, if assumed incorrectly, it can lead to errors in determining kinetic parameters.

### 3. Results and discussion

#### 3.1. Combustion behavior and influence of environment types

##### 3.1.1. Pure materials

The combustion behavior of raw fuels was evaluated through the TGA and DTG curves obtained in a conventional combustion (20% O<sub>2</sub> and 80% N<sub>2</sub>) and oxy-fuel (20% O<sub>2</sub> and 80% CO<sub>2</sub>) environments at heating rate of 10 °C/min.

Figs. 1–3 show the mass variation curves (TGA) and their derivatives (DTG) as a function of temperature in combustion and oxy-fuel combustion environments for samples of coal, sugarcane bagasse, and biomass sorghum bagasse, respectively. Both fossil and renewable fuels have very different decomposition profiles. The decomposition behavior of mineral coal is well known and has been the object of study in the literature [54,55].

Coal decomposition occurs in three stages (Fig. 1), in which the first one is the moisture loss of the material at around 100 °C. The second one is the primary combustion of the material and volatile material loss and the third one is the fixated carbon combustion [56].

Biomass is composed of hemicellulose, cellulose and lignin, and those used herein have similar thermal decomposition characteristics (Figs. 2 and 3). Hemicellulose has low thermal stability and decomposition occurs at lower temperatures. The peak followed by hemicellulose shoulder corresponds to cellulose decomposition which is the main component of the biomass cell wall [57,58]. After hemicellulose and cellulose thermal decomposition, residual lignin decomposition was observed in both types of biomass. Lignin is a reinforcing component of the biomass cell wall, which gradually decomposes between 137 °C and 667 °C [18]. It has a thermally more stable complex structure than hemicellulose and cellulose, thus its total degradation occurs at higher temperatures [15,57,58].

Sugarcane bagasse (SB) TG curves reveal that there is an extensive oxidation of the material, in which ash content was less than 7% in both environments. There were no significant differences in thermal degradation of the sugarcane bagasse sample between the environments. However, it should be noted that the events are more intense in an oxy-fuel combustion environment. Through DTG curves, three main mass loss events can be observed in both environments. The first one is associated with the sample moisture loss at up to approximately 100 °C. The second event is on account of the overlapping decomposition of hemicellulose and cellulose. In a

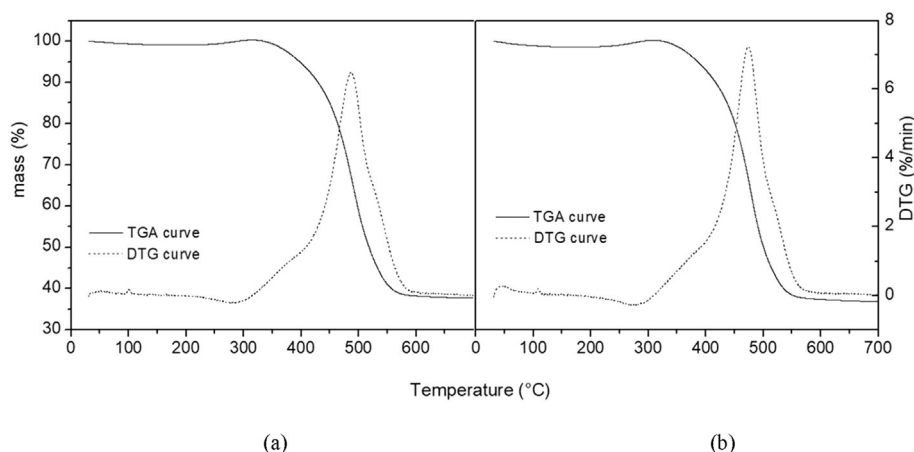


Fig. 1. TGA and DTG profiles for coal under atmospheres of (a) conventional combustion (20% O<sub>2</sub>–80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>–80% CO<sub>2</sub>).

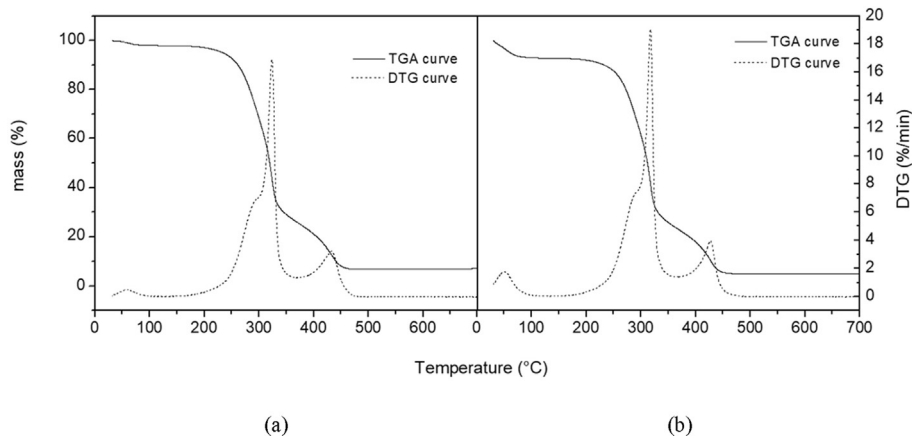


Fig. 2. TGA and DTG profiles for sugarcane bagasse (SB) under atmospheres of (a) conventional combustion (20% O<sub>2</sub>–80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>–80% CO<sub>2</sub>).

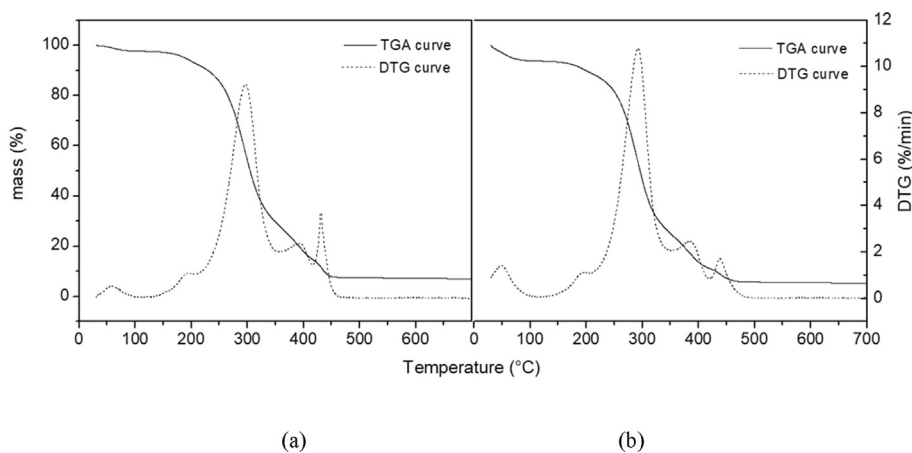


Fig. 3. TGA and DTG profiles for biomass sorghum bagasse (BSB) under atmospheres of (a) conventional combustion (20% O<sub>2</sub>–80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>–80% CO<sub>2</sub>).

combustion environment, the thermal decomposition of hemicellulose started at 200 °C and cellulose at 285 °C, the maximum decomposition rate of cellulose occurred at 325 °C. Residual lignin decomposition started at approximately 380 °C and a complete decomposition of the material occurred at 460 °C. In an oxy-fuel combustion environment, the material reactivity increases and a slight shift of events towards lower temperatures can be observed. The maximum temperature of the decomposition peak of cellulose occurs at 317 °C and a complete decomposition of the material at 440 °C. For the sorghum bagasse sample, TG curves allow concluding that approximately 93% of the material was totally oxidized in both environments. Through the DTG curves, at least four mass loss events in both environments can be observed. The first event is related to moisture loss of the sample at up to approximately 100 °C. The second and third events are due to hemicellulose and cellulose decomposition that occurred between 170 °C and 410 °C and the maximum rate of decomposition at approximately 290 °C. In an oxy-fuel combustion environment, the material reactivity increases in decomposition events of hemicellulose and cellulose. Residual lignin decomposition is more intense under a combustion environment and the maximum decomposition temperature rate occurred at 430 °C, i.e. a slightly lower temperature than that registered in an oxy-fuel combustion environment (440 °C).

Table 3 shows combustion parameters, as ignition and burnout temperatures, maximum mass loss rate (DTG<sub>max</sub> % min<sup>-1</sup>) and average mass loss rate (DTG<sub>average</sub> % min<sup>-1</sup>) of pure materials. In oxy-fuel combustion environment, there is an increase in mass loss rate, which can be associated with its reactivity, as well as a decrease in ignition, burnout and maximum temperatures. According to Lopez et al. (2014b), a reactivity increase in an oxy-combustion environment can be explained by the material porosity. According to the author, the CO<sub>2</sub> molecule has a larger volume than the N<sub>2</sub> molecule and, therefore, CO<sub>2</sub> has difficulty in filling the material micropores, thus favoring O<sub>2</sub> access. However, there are authors who report similar or inferior combustion performance when comparing the environment of combustion (O<sub>2</sub>/N<sub>2</sub>) with an oxy-fuel combustion environment (O<sub>2</sub>/CO<sub>2</sub>) [29,59,60]. A previous study [60], in which the behavior of sugarcane bagasse in different environments was evaluated, indicated that an oxy-fuel combustion environment increases the intensity of DTG peaks and shifts mass loss events towards higher temperatures, thus negatively affecting combustion parameters. Another study has demonstrated that the mass loss rate and reactivity of bituminous coal are greater in an oxy-fuel combustion environment. In contrast, for the biomass studied herein, the mass loss rate and reactivity were similar in both environments [29]. These different conclusions demonstrate that the environment influence depends more on the characteristics of each material than on experimental conditions.

**Table 3**

Combustion characteristics for coal and both biomass (SB and BSB), under conventional combustion and oxy-fuel combustion.

Material	Atmospheres	T <sub>i</sub> (°C)	T <sub>b</sub> (°C)	DTC <sub>max</sub> (% min <sup>-1</sup> )	T <sub>max</sub> (°C)	DTC <sub>médio</sub> (% min <sup>-1</sup> )
Coal	Combustion	382	601	6.5	487	1.06
Coal	Oxy-fuel combustion	366	574	7.25	474	1.12
SB	Combustion	285	479	16.88	324	2.03
SB	Oxy-fuel combustion	237	464	19.07	317	2.23
BSB	Combustion	168	470	9.23	295	2.04
BSB	Oxy-fuel combustion	170	486	10.8	291	2.13

### 3.1.2. Coal-biomass mixtures

TGA and DTG curves of the coal-sugarcane bagasse (coal-SB) mixtures in combustion (O<sub>2</sub>/N<sub>2</sub>) and oxyfuel (O<sub>2</sub>/CO<sub>2</sub>) environments are shown in Figs. 4 and 5. For mixtures of coal and biomass sorghum bagasse (coal-BSB), TGA and DTG curves in combustion and oxyfuel combustion environments are shown in Figs. 6 and 7, respectively. It is observed that mass loss increases as there is more biomass in the mixture for both mixtures and environments. It should also be observed a similar thermal behavior in combustion and oxy-fuel combustion environments.

DTG curves of coal-SB mixtures (Fig. 5) show two mass loss events in both environments for all biomass percentages in the mixture. For BSB-coal mixtures, DTG curves (Fig. 7) show two mass loss events with 10 and 25% of biomass and three events with 50 and 75% of biomass in the mixture in both environments.

Table 4 presents the combustion parameters for coal-SB and coal-BSB mixtures with 10, 25, 50 and 75% of biomass in combustion and oxy-fuel combustion environments.

For both coal-SB and coal-BSB mixtures, there is a reduction in ignition and burnout temperatures as the amount of biomass increases in the mixture. It can be observed that the difference between T<sub>b</sub> and T<sub>i</sub> ( $\Delta T = T_b - T_i$ ) is smaller when both mixtures were tested under an oxy-fuel combustion environment, which indicates a reduction in burning time in an oxy-fuel combustion environment. However, some authors report that an oxy-fuel combustion environment has affected the combustion parameters of coal and biomass mixtures.

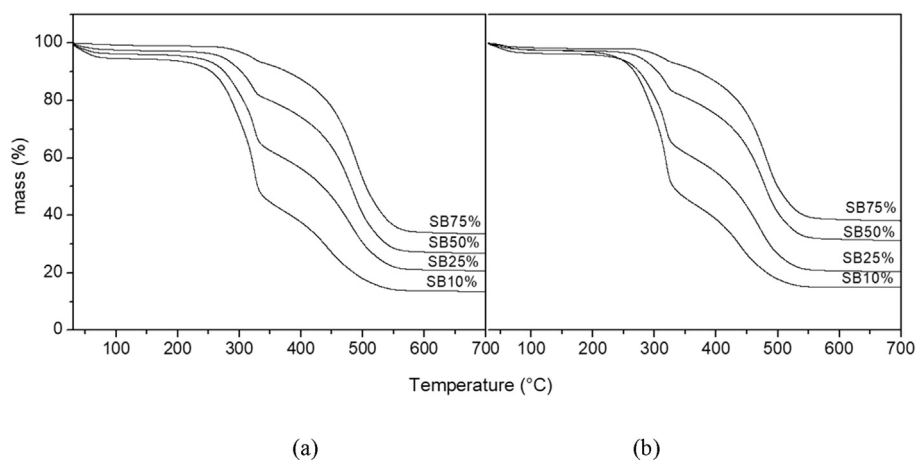
According to the results obtained by Riaza et al. (2012), by maintaining oxygen concentration at 21% and replacing N<sub>2</sub> with CO<sub>2</sub>, there was an increase in ignition temperature and a reduction in oxidation percentage of coal and biomass mixtures. However, when O<sub>2</sub> concentration is higher than 30%, ignition temperature values are lower than those recorded in air environment. The same behavior was observed by Arias et al. (2008) and Yuzbasi; Selçuk (2011). According to Arias et al. (2008), biomass ignites before coal in coal-biomass mixtures because it is more reactive than coal, thus reducing oxygen concentration in the medium. When oxygen concentration is above 30%, coal oxidation is less affected and an improvement can be observed.

### 3.1.3. Synergism

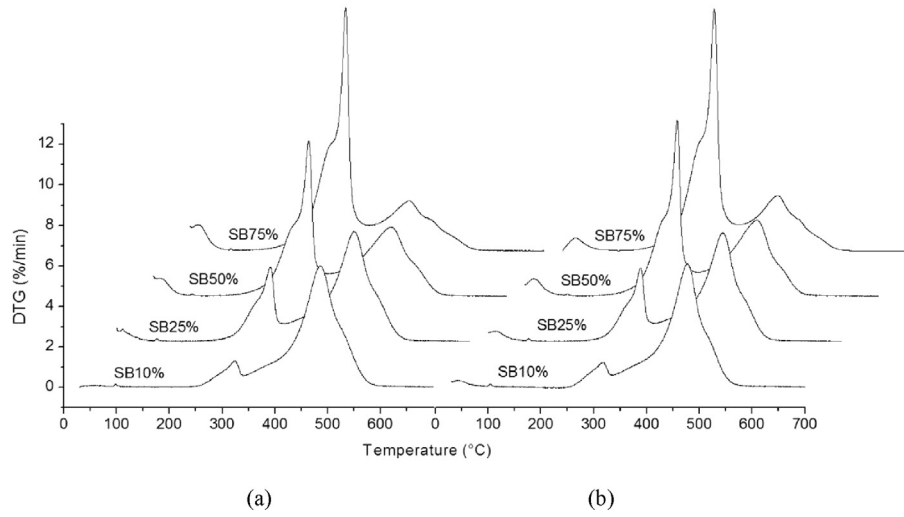
The differences between theoretical DTG and experimental DTG curves are the result of an interaction between coal and biomass, thus indicating a synergistic effect. Table 5 presents the values of the degree of synergism between experimental DTG and theoretical DTG curves. The results indicated that there was synergism in all mixtures, with a higher degree of synergism being observed in 75% of both biomasses in the mixture in both environments. Synergism during coal and biomass co-combustion has also been reported by other authors [61–63]. The synergism observed when the proportion of biomass is equal to or higher than coal can be attributed to an interaction between the volatile material released by burning biomass and coal [64,65].

### 3.1.4. Combustion and oxy-combustion index

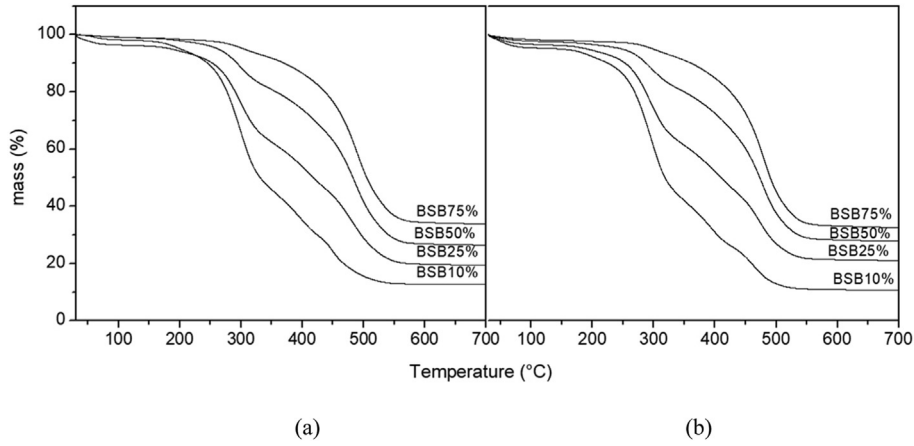
Combustion index (S) is a measure used to quantify the combustion performance by using TGA results. Biomass has a higher combustion index than coal. A superior performance of the biomass is attributed to a greater amount of volatile material present [66]. Higher S values indicate better ignition and burning performance. In coal and biomass co-combustion, combustion index increases as there is a larger



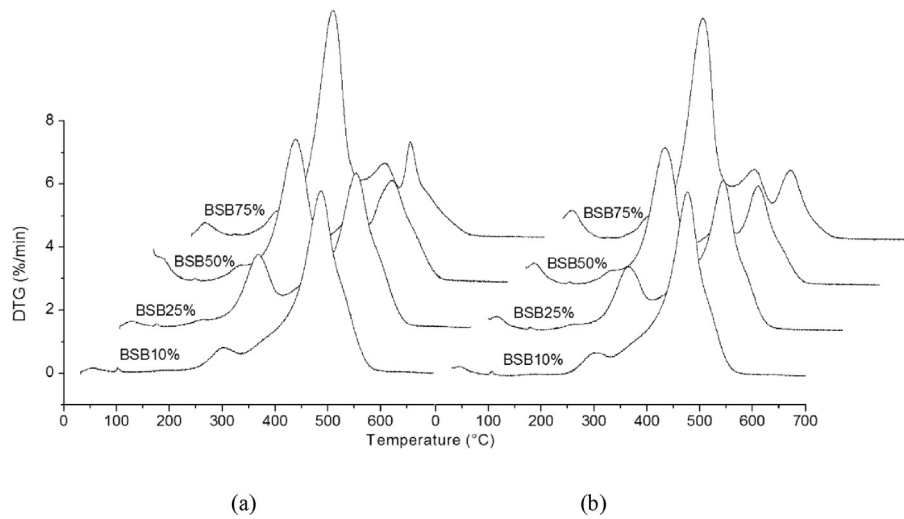
**Fig. 4.** TGA profiles for blends (SB/Coal in the proportion of 10/90, 25/75, 50/50 and 75/25 %wt), under atmospheres of (a) conventional combustion (20% O<sub>2</sub>–80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>–80% CO<sub>2</sub>).



**Fig. 5.** DTG profiles for blends (SB/Coal in the proportion of 10/90, 25/75, 50/50 and 75/25 wt%), under atmospheres of (a) conventional combustion (20% O<sub>2</sub>-80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>-80% CO<sub>2</sub>).



**Fig. 6.** TGA profiles for blends (BSB/Coal in the proportion of 10/90, 25/75, 50/50 and 75/25 (wt)), under atmospheres of (a) conventional combustion (20% O<sub>2</sub>-80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>-80% CO<sub>2</sub>).



**Fig. 7.** DTG profiles for blends (BSB/Coal in the proportion of 10/90, 25/75, 50/50 and 75/25 wt%), under atmospheres of (a) conventional combustion (20% O<sub>2</sub>-80% N<sub>2</sub>) and (b) oxy-fuel combustion (20% O<sub>2</sub>-80% CO<sub>2</sub>).



**Table 4**

Combustion characteristics for SB/Coal and BSB/coal blends in the proportion of, 75/25, 50/50, 25/75 and 10/90 (wt%) under atmospheres of conventional combustion and oxy-fuel combustion.

Mass Fraction	Atmosphere	T <sub>i</sub> (°C)	T <sub>b</sub> (°C)	DTG <sub>max</sub> (% min <sup>-1</sup> )	T <sub>max</sub> (°C)	DTG <sub>mean</sub> (% min <sup>-1</sup> )
SB10	Combustion	294.0	598.0	6.0	486.0	1.15
SB10	Oxy-fuel combustion	295.0	572.0	6.11	477.0	1.12
SB25	Combustion	286.5	585.0	5.5	485.0	1.33
SB25	Oxy-fuel combustion	286.4	587.0	5.4	475.0	1.26
SB50	Combustion	286.6	581.8	7.68	324.0	1.48
SB50	Oxy-fuel combustion	285.2	564.6	8.7	318.0	1.54
SB75	Combustion	286.0	566.0	12.0	324.0	1.69
SB75	Oxy-fuel combustion	284.0	563.0	11.94	319.0	1.66
BSB10	Combustion	283.0	596.0	5.8	487.0	1.15
BSB10	Oxy-fuel combustion	279.0	583.0	6.51	476.0	1.22
BSB25	Combustion	257.0	595.0	4.9	485.0	1.33
BSB25	Oxy-fuel combustion	258.0	582.0	5.31	474.0	1.35
BSB50	Combustion	255.0	593.0	4.53	300.0	1.5
BSB50	Oxy-fuel combustion	253.0	565.0	4.86	294.0	1.53
BSB75	Combustion	253.5	581.0	7.17	298.0	1.7
BSB75	Oxy-fuel combustion	251.0	555.0	7.82	296.0	1.82

**Table 5**

Degree of synergism for SB/Coal and BSB/Coal blends in the proportion of 75/25, 50/50, 25/75 and 10/90 (wt%) under conventional combustion and Oxy-fuel combustion.

Δm <sub>error</sub>	SB10	SB25	SB50	SB75	BSB10	BSB25	BSB50	BSB75
Combustion	1.44	5.53	3.13	6.03	2.04	6.02	5.76	5.76
Oxy-fuel combustion	5.71	3.05	1.91	11.48	6.33	4.57	3.56	15.12

amount of biomass in the mixture [67]. The combustion index value is determined by the combustion performance parameters presented in Tables 3 and 4.

The combustion index behavior for coal-SB coal and coal-BSB as a function of biomass mass fractions are shown in Fig. 8, respectively. It is observed that, in both environments being studied, combustion indexes (S) for the coal-SB and coal-BSB mixtures show an increasing behavior with larger amounts of biomass, which is represented by exponential functions with R<sup>2</sup> values that are higher than 0.99. This result indicates that the co-combustion using mixtures of coal with SB and BSB improves combustion performance, which is in agreement with Moon et al. (2013), Buratti et al. (2015) and Liu et al. (2015).

While carrying out the experiments, mineral coal had a lower combustion index when compared to the biomass being used herein. Biomass has a higher combustion index than coal because it has a higher volatile material content, consequently, it is more reactive than coal and oxidizes at lower temperatures [68]. In a combustion environment (N<sub>2</sub>/O<sub>2</sub>), the combustion index for coal was  $1.83 \times 10^{-8}$ . In an oxy-fuel combustion environment (CO<sub>2</sub>/O<sub>2</sub>), there was an improvement in combustion performance, whose value was  $2.34 \times 10^{-8}$ . This result is attributed to a reduction in ignition and burnout temperatures and to an increase in the material reactivity in an oxy-fuel combustion environment.

In a combustion environment, SB has a combustion index of  $14.51 \times 10^{-8}$ , which is higher than  $13.04 \times 10^{-8}$  obtained for SB. When tested in an oxy-fuel combustion environment, SB combustion index increased to  $22.15 \times 10^{-8}$  and to  $15.52 \times 10^{-8}$  for SB. As it occurs with coal, biomass combustion performance improvement is attributed to an increase in material reactivity and reduction in ignition and burnout temperatures when these types of biomass are tested in an oxy-fuel combustion environment.

For coal-SB mixtures, no significant differences were observed in the combustion index values between the two environments. In coal-SB mixtures, an improvement in performance is noted when they have been tested in an oxy-fuel combustion environment. A combustion performance improvement results from an increased combustion index.

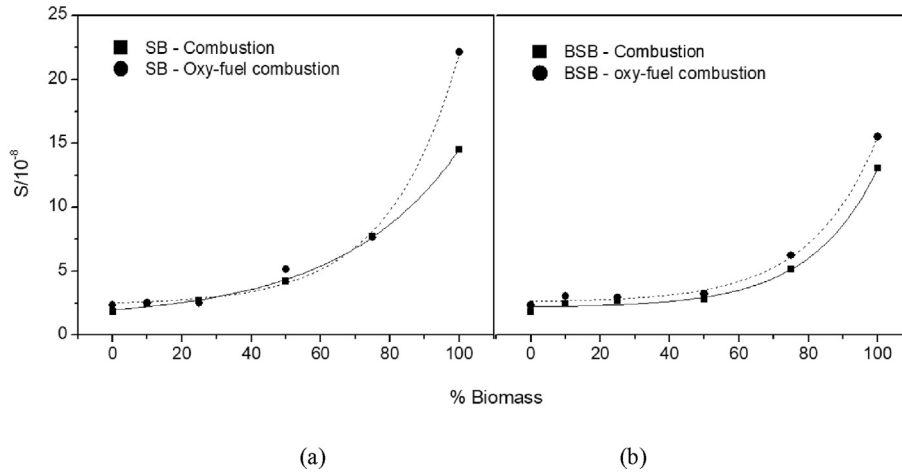
### 3.2. Combustion and oxy-fuel combustion activation energies

#### 3.2.1. Pure materials

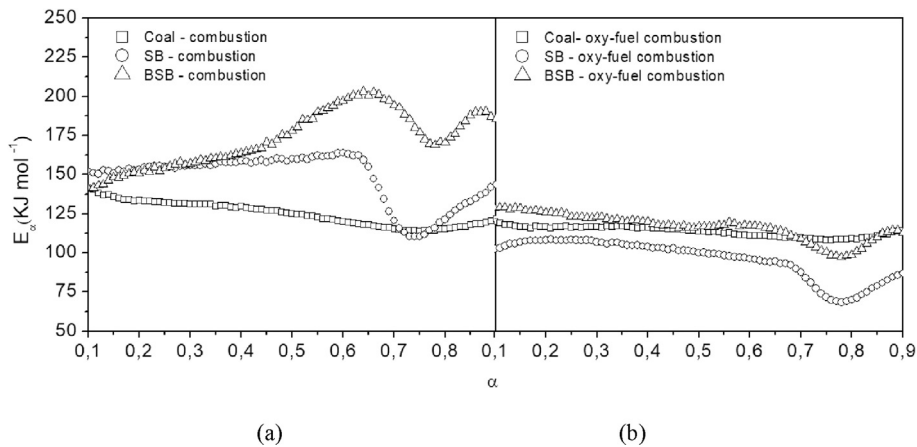
For the determination of activation energy values of biomass samples and their mixtures, the ignition temperature range was defined as the burnout temperature for the 3 heating rates. The range between ignition and burnout temperatures is the same as that of the burning process of all components, both in combustion and oxyfuel combustion environments. For the mineral coal sample, the activation energy value was determined for a single event between the initial chemisorption temperatures described by Crelling et al. (1992) [56] and the burnout temperature in both environments.

The activation energy variation (E<sub>α</sub>) profiles as a function of conversion (α) of coal, SB, and BSB are presented in Fig. 9.

In both environments, the activation energy values of coal decrease as the degree of conversion increases, in which the smallest values were obtained in an oxy-fuel combustion environment. It is observed that, in a combustion environment, E<sub>α</sub> values remain practically constant until 65% of conversion is reached and until 70% in an oxy-fuel combustion environment, in which an E<sub>α</sub> reduction can be observed. This event occurs at temperatures ranging between 350 and 425 °C in combustion environment and between 325 and 370 °C in an oxy-fuel combustion environment. These temperatures indicate the end of cellulose decomposition and the beginning of residual lignin decomposition. The variation profile of E<sub>α</sub> as a function of conversion (α) in an oxy-fuel combustion environment presents lower values than those obtained in a combustion environment.



**Fig. 8.** Characteristics of combustion (combustion index) for (a) SB/Coal and (b) BSB/Coal blends, both in the proportion of 10/90, 25/75, 50/50 and 75/25 (%wt), under atmospheres of conventional combustion (20%  $O_2$  – 80%  $N_2$ ) and oxy-fuel combustion (20%  $O_2$  – 80%  $CO_2$ ).



**Fig. 9.** Activation energy ( $E_\alpha$ ) versus conversion ( $\alpha$ ) of the thermal decomposition of the coal, SB and BSB in an atmosphere of (a) combustion and (b) oxy-fuel combustion for three heating rates ( $\beta = 10$  °C/min, 15 °C/min, and 20 °C/min).

In a combustion environment,  $E_\alpha$  value of BSB increases as the degree of conversion does. In an oxy-combustion environment,  $E_\alpha$  shows a slight reduction as the degree of conversion increases. It is possible to observe a reduction in activation energy values when 70–80% conversion is reached, which occurs at temperatures ranging between 331 and 367 °C in both environments. This event is similar to that observed for sugarcane bagasse and also corresponds to the end of cellulose decomposition and the beginning of residual lignin decomposition.

The values of activation energy ( $E_\alpha$ ) for conversion rates of coal, sugarcane bagasse (SB) and biomass sorghum bagasse (BSB) in combustion and oxyfuel combustion environments obtained from the KAS method are presented in Tables 6 and 7. It is noted that in an oxy-fuel combustion environment, the materials activation energy values are lower than the one obtained in a combustion environment and in both environments the SB has a lower average activation energy value than the one obtained for BSB. López et al. (2014b) [39] described a

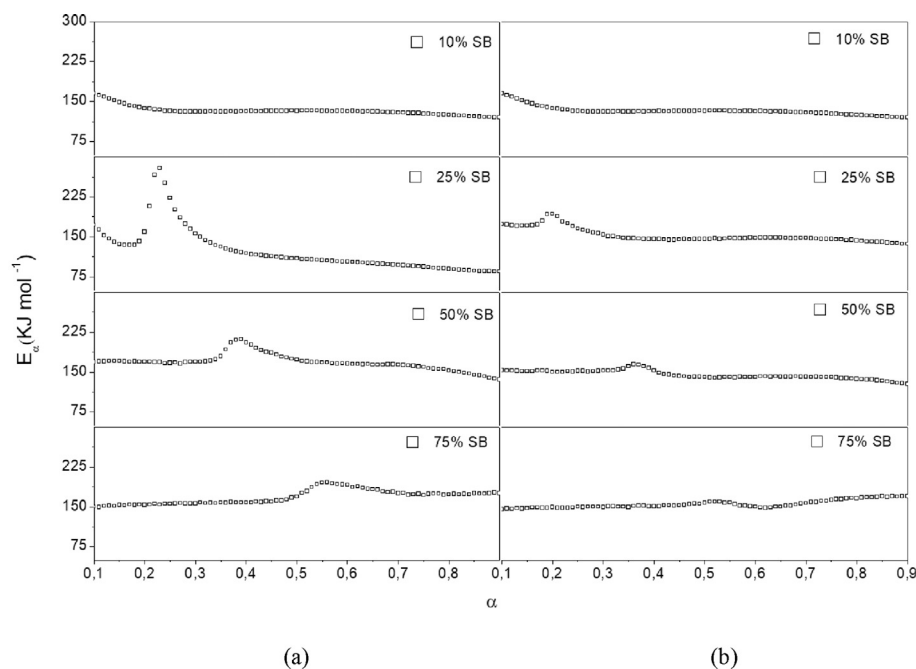
**Table 6**

Activation energy values of pure materials and blends in conventional combustion.

Conversion ( $\leq \alpha <$ )	Coal	SB	BSB	SB				BSB			
				10%	25%	50%	75%	10%	25%	50%	75%
0.1–0.2	136.04	152.21	146.94	110.74	144.56	169.37	152.55	144.19	127.42	155.93	144.97
0.2–0.3	132.20	154.80	154.39	113.52	211.95	168.11	155.91	127.23	104.80	155.85	141.98
0.3–0.4	130.47	157.00	160.18	120.26	132.85	187.16	157.39	125.63	108.20	146.95	139.16
0.4–0.5	127.29	158.71	169.92	124.48	113.26	186.59	161.17	125.92	113.12	141.03	135.79
0.5–0.6	122.68	161.45	188.67	125.44	105.94	168.24	188.40	124.18	121.71	142.57	134.78
0.6–0.7	117.61	149.70	199.78	123.15	100.08	164.55	182.58	120.64	124.08	133.91	142.45
0.7–0.8	114.63	114.20	178.63	117.68	93.52	158.93	173.84	115.40	121.48	145.29	155.66
0.8–0.9	117.70	133.04	183.80	111.90	86.55	144.80	174.81	109.46	115.61	135.43	192.83
average	124.83	147.64	172.79	118.40	123.59	168.47	168.33	124.08	117.05	144.62	148.45

**Table 7**  
Activation energy values of pure materials and blends in Oxy-fuel combustion.

Conversion ( $\leq \alpha <$ )	Coal	SB	BSB	SB				BSB			
				10%	25%	50%	75%	10%	25%	50%	75%
0.1–0.2	117.31	105.98	127.77	150.31	175.40	151.93	147.18	120.38	140.04	144.00	167.92
0.2–0.3	116.47	107.92	123.99	133.35	169.35	151.15	149.21	116.15	110.49	140.02	182.19
0.3–0.4	116.40	105.48	120.87	131.46	148.10	157.69	150.74	118.81	109.38	130.99	197.82
0.4–0.5	114.96	102.32	117.51	132.50	145.27	143.55	153.45	122.46	110.55	122.08	205.87
0.5–0.6	112.65	98.45	117.70	132.68	146.96	140.41	156.23	123.85	115.14	126.00	185.26
0.6–0.7	110.27	93.57	114.34	131.02	147.94	141.47	151.22	122.37	118.80	119.62	167.57
0.7–0.8	108.77	74.30	101.43	127.37	145.46	139.70	162.66	118.72	117.43	126.55	182.79
0.8–0.9	111.12	78.82	108.81	122.33	139.72	133.09	168.67	113.77	111.92	126.07	206.96
average	113.50	95.85	116.55	132.63	152.27	144.87	154.92	119.56	116.72	129.42	187.05



**Fig. 10.** Activation energy ( $E_{\alpha}$ ) versus conversion ( $\alpha$ ) of the thermal decomposition of the SB/Coal blends in an atmosphere of (a) combustion and (b) oxy-fuel combustion for three heating rates ( $\beta = 10$  °C/min,  $15$  °C/min, and  $20$  °C/min).

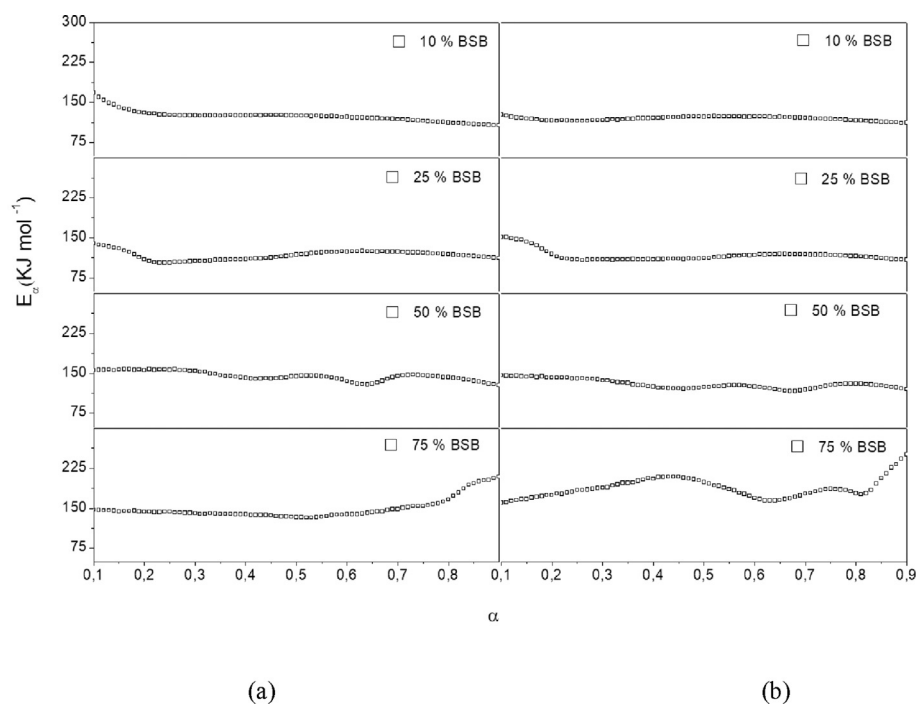
reduction in activation energy value in an oxy-fuel combustion environment, but this is not similar for all materials being tested. Cruz and Crnkovic (2016) [59] investigated the environment influence on activation energy values of five types of biomass (pine sawdust, sugarcane bagasse, coffee husk, rice husk and tucumã seed). The results showed that the activation energy values of sugarcane bagasse, pine sawdust, coffee husk and tucumã seed are lower in a  $\text{CO}_2$  environment. However, the authors concluded that the variation in activation energy values is more dependent on the type of biomass than on the environment in which combustion occurs.

### 3.2.2. Coal-biomass blends

The activation energy variation ( $E_{\alpha}$ ) profiles as a function of conversion ( $\alpha$ ) of coal-SB and coal-BSB mixtures are shown in Figs. 10 and 11, respectively. In both environments, up to 50% of biomass in coal-SB and coal-BSB mixtures, activation energy values decrease with as the degree of conversion increases. This behavior is in accordance with that presented by Aboyade et al. (2011) and Leroy et al. (2010) [69,70]. For 75% of biomass in the mixture, in both environments, an increase of activation energy is observed as the degree of conversion increases. By comparing the degree of synergism (Table 5) values with the behavior of  $E_{\alpha}$  versus  $\alpha$  curves, it can be assumed that for 75% of biomass in the mixture, the synergism between mixture components increases the complexity of the combustion reaction, thus raising activation energy values.

In coal-SB mixtures in both environments, it is possible to observe an increase in  $E_{\alpha}$  between 20 and 30% conversion with 25% of biomass, between 35 and 45% conversion with 50% of biomass and between 50 and 60% conversion with 75% of biomass. This event is the same as the one observed for the variation profiles of  $E_{\alpha}$  as a function of  $\alpha$  of pure SB, which corresponds to the end of the cellulose decomposition event and the beginning of residual lignin decomposition. However, it is observed a reduction in the value of  $E_{\alpha}$  for the pure material and an increase in the value of  $E_{\alpha}$  for the mixtures. This behavior observed in the mixtures can be attributed to an interaction between the beginning of residual lignin decomposition and the beginning of coal combustion.

Average values of activation energy ( $E_{\alpha}$ ) of coal-SB and coal-BSB mixtures in combustion and oxyfuel combustion environments obtained from the KAS method are presented in Tables 6 and 7. It is noted that in an oxy-fuel combustion environment, the average value of activation



**Fig. 11.** Activation energy ( $E_a$ ) versus conversion ( $\alpha$ ) of the thermal decomposition of the BSB/Coal blends in an atmosphere of (a) combustion and (b) oxy-fuel combustion for three heating rates ( $\beta = 10$  °C/min, 15 °C/min, and 20 °C/min).

energy obtained for 50 and 75% of biomass for the coal-SB mixture and 10, 25 and 50% of biomass for the coal-BSB mixture are lower than the one obtained in a combustion environment. In the combustion environment, for the coal-biomass mixture with 10 and 25% of SB and BSB, the activation energy value is lower than that of pure coal ( $124.83 \text{ kJ mol}^{-1}$ ). In an oxy-fuel combustion environment, both mixtures have an activation energy value which is higher than  $113.50 \text{ kJ mol}^{-1}$ , which is the same as that of pure mineral coal in an oxy-fuel combustion environment.

The activation energy of coal and biomass mixtures has an increasing tendency as there is a larger amount of biomass in the mixture [36]. Kocabas-Atakli; Okyay-oner; Yurum (2015) [71] affirm that a co-combustion of coal and biomass improves coal combustion and lower activation energy values can be found with up to 20% of biomass in the mixture. The results presented by Gil et al. (2010) [34] demonstrate that in quantities of over 50% of biomass in the mixture, the presence of coal does not significantly affect combustion and activation energy values do not vary significantly.

#### 4. Conclusions

This study approaches the combustion reactivity behavior of Brazilian coal, two biomasses and their respective mixtures. The experiments were carried out in conventional combustion (20%  $\text{O}_2$  and 80%  $\text{N}_2$ ) and typical oxy-fuel combustion (20%  $\text{O}_2$  and 80%  $\text{CO}_2$ ) environments.

It was concluded that there was a synergistic effect between coal and biomass for all mixtures studied in both environments, which was attributed to an interaction between the volatile material released by burning biomass and coal. An improvement in coal combustion performance was observed when it was mixed with biomass due to greater reactivity and lower combustion temperature of biomasses, given that the combustion index value increased as biomass percentage increased. Moreover, when  $\text{N}_2$  was replaced with  $\text{CO}_2$ , an improvement in combustion performance was also observed. For pure materials, when  $\text{N}_2$  was replaced with  $\text{CO}_2$ , a decrease in activation energy values was observed. For coal and biomass mixtures, the lowest activation energy values were obtained at 25% of biomass in the mixture in both environments.

In general, an improvement in combustion parameters was observed in the oxy-fuel condition which may be largely due to physical-chemical properties and structural characteristics of materials than to their combustion environment. By taking into account all evaluated parameters and comparing the tested types of biomass, it can be concluded that although sugarcane bagasse and its mixtures with coal presented a greater potential for application in thermochemical processes for clean energy generation, the results of evaluated parameters for coal and both biomasses mixtures were similar. Thus, biomass sorghum bagasse is a viable alternative to be used for energy generation during sugarcane off-season.

#### Acknowledgments

The authors are indebted to the National Council for Scientific and Technological Development (CNPq – processes 134366/2015-8, 301819/2015-7, 506317/2013-7, and 150868/2017-0) for the financial support given this research.

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