FISEVIER

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng



Research Paper

Use of a fluidized bed combustor and thermogravimetric analyzer for the study of coal ignition temperature



Ivonete Ávila a,b,*, Paula M. Crnkovic b, Carlos M.R. Luna a, Fernando E. Milioli b

- ^a São Paulo State University (Unesp), School of Engineering, Guaratinguetá, Department of Energy, Laboratory of Combustion and Carbon Capture (LC₃), CEP 12.516-410 Guaratinguetá, SP, Brazil
- b USP University of São Paulo, School of Engineering of São Carlos, Group of Thermal and Fluids Engineering, CEP 13566-590 São Carlos, Brazil

HIGHLIGHTS

- Coal ignition tests were conducted in a fluidized bed and thermogravimetric conditions.
- The use of two different ignition criteria showed a similar coal ignition temperature.
- Coal ignition temperature was obtained by the changes of gas concentrations in FBC.
- Ignition temperatures were associated with the activation energy of coal combustion.

ARTICLE INFO

Article history: Received 13 April 2016 Revised 26 October 2016 Accepted 23 November 2016 Available online 24 November 2016

Keywords: Ignition temperature Fluidized bed combustor Thermogravimetric analyzer Coal Activation energy

ABSTRACT

Ignition experiments with two bituminous coals were carried out in an atmospheric bubbling fluidized bed combustor (FBC) and a thermogravimetric analyzer (TGA). In the FBC tests, the rapid increase in O_2 , CO_2 , and SO_2 concentrations is an indication of the coal ignition. In the TGA technique, the ignition temperature was determined by the evaluation of the TGA curves in both combustion and pyrolysis processes. Model-Free Kinetics was applied and the coal ignition temperatures were associated with changes in the activation energy values during the combustion process. The results show the coal with the lowest activation energy also showed the lowest ignition temperature, highest values of volatile content and a higher heating value. The application of two different ignition criteria (TGA and FBC) resulted in similar ignition temperatures. The FBC curves indicated the high volatile coal ignites in the freeboard, i.e. during the feeding in the reactor, whereas the low volatile coal ignites in the bed. Finally, the physicochemical characteristics of the investigated coal types were correlated with their reactivities for the prediction of the ignition temperatures behaviors under different operating conditions as those in FBC.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The knowledge on coal reactivity is fundamental for the development of tools that optimize the combustion process. The physicochemical properties of solid fuels have been extensively studied, so that combustion phenomena can be understood. Parameters, such as ignition temperature and kinetic data are very important features for the combustion design, operation and simulation [1], and control of combustion instability [2–4].

E-mail address: iavila@feg.unesp.br (I. Ávila).

Coal ignition temperature is a relevant information for design of burners and choice of the control parameter during the star-up process [5]. The study of ignition phenomena is based mainly on the measurement of the minimum gas temperatures required for the ignition of coal particles [6]. The coal ignition temperature is traditionally estimated from experience with a some theoretical basis and relatively large uncertainties, which results in operational difficulties and economic losses [5]. If the coal is fed into a furnace at a temperature lower than the ignition temperature, it will not burn and the furnace temperature will decrease [5,6].

Although the classification of coal ignition mechanisms differs somewhat from author to author, there is a consensus that the ignition of coal particles depends on the quality of coal, particle sizes, volatile matter content, and test methods [2,4,6–10], and

^{*} Corresponding author at: São Paulo State University (Unesp), School of Engineering, Guaratinguetá, Department of Energy, Laboratory of Combustion and Carbon Capture (LC₃), CEP 12.516-410 Guaratinguetá, SP, Brazil.

can be a multistage process, i.e. either homogeneous or heterogeneous involving two or up to three stages [8,10,11].

The determination of the ignition and burnout temperatures of a fuel may also be influenced by the operating conditions [12]. Fluidized beds in laboratory scales are often used in measurements of the coal ignition temperature, based on criteria, as spark characteristics, bed temperature response and oxygen response [5]. In such systems, the coal ignition temperature has a dependence of several factors, for instance, physicochemical properties of the fuel, heating rate, fluidization velocity, and particle size [5]. The variation in the CO-CO₂ profiles as a function of time and bed temperature and the rapid increase in the SO₂ level can be also used as indicators of the fuel ignition temperature [6].

Thermogravimetric analysis (TGA) has also been widely used for the determination of ignition temperature [2,10,13–15] and combustion characteristics of the coal [16–18]. An important methodology for the obtaining of the ignition temperature employing TGA was proposed by Tognotti et al. [13] and has been largely used [6,10,16,17]. In such method, the ignition temperature is taken as the temperature at which the TGA curves in combustion (oxidant atmosphere) and pyrolysis (inert atmosphere) experiments diverge.

Although the relationship between ignition temperature and the reactivity of coals has been explored for over 150 years [8], this issue still plays a meaningful role in the optimization of the combustion process. The ignition temperature of a fuel is related to the difficult in induction of a combustion reaction, i.e. a lower ignition temperature indicates a favorable reaction activity of the fuel [18]. Moreover, kinetic data, such as activation energy and pre-exponential factors can be used in the estimation of the difficulty and intensity of a combustion reaction.

Kinetic studies that employ thermal analysis can be developed applying either isothermal or non-isothermal methods. Non-isothermal methods have been extensively applied to complex heterogeneous reactions [19–29]. Some authors have observed kinetic studies under non-isothermal conditions have been hindered by the presence of several complex substances of the coal, and the a large number of successive and parallel chemical reactions that occur during the combustion process [30,31]. On the other hand, in isothermal essays, the samples change physically during the reaction, which suggests no single set of kinetic parameters can be derived from the process as a whole [32].

TGA results should be carefully evaluated prior to their application in combustion processes, e.g. as in fluidized bed combustors, because different experimental conditions can result in different values of ignition temperature. Jia et al. [6] observed different test methods and ignition criteria led to significantly different values of ignition temperatures. Therefore, it is emphasized the importance of accurate measurements of ignition temperature on a laboratory scale that represent the real feed temperatures at which coal is used [5,6].

According to the above-mentioned investigations, the ignition experiments were carried out under different conditions. However, few studies have correlated the ignition temperatures obtained in thermogravimetric essays with the conditions in which the coal are burned as those in FBC.

The present paper addresses the determination and comparison of the fuel ignition temperature of two coals and evaluation of their reactivity through their physicochemical characteristics, such as activation energy of combustion process, volatile content, higher heating value and surface area. Tests were carried out in a bench-scale fluidized bed combustor and techniques of thermogravimetry and porosimetry were applied. Activation energy of the combustion was determined by Model-Free Kinetics.

2. Experimental procedure and methods

2.1. Preparation and characterization of the coal samples

Two bituminous coals were used in this study: a Brazilian coal called CE4500 (energetic coal with higher heating value up to 4500 kcal/kg) provided by Carbonífera Metropolitana S.A. and a Colombian coal called CE5500 (energetic coal with higher heating value up to 5500 kcal/kg) provided by Alunorte (Alumina do Norte do Brasil S.A.). They were extracted from different regions, with different geological and their physicochemical characteristics were evaluated.

In thermogravimetric analysis (TGA) tests, smaller particles were adopted for minimizing the heat and mass transfers, and reducing temperature gradients within the sample. Coal samples of 230 μ m average size were used for tests in both thermogravimetric analyzer (TGA) and calorimetric bomb. Such particles were selected by means of two subsequent ASTM sieves (210 μ m and 250 μ m).

Due to the amount of coal required for the tests in the fluidized bed combustor (FBC), the particle size distributions were selected among seven ASTM sieves that range from $1000~\mu m$ to $250~\mu m$. The determination of the average size of the particles followed the method described by Howard [33]. The average diameters of the coals used in FBC tests were 383 μm for CE4500 and 498 μm for CE5500, and were also used in porosimetry experiments.

Tests were conducted for the obtaining of the ultimate and proximate analyses, higher heating values and surface area of the coal samples. The ultimate analysis of the coal samples was conducted in laboratories of the University of São Paulo (IQ/USP – São Paulo) in accordance with the ASTM methodologies (ASTM D5373 and ASTM D3176). The higher heating values (HHV) were determined in an IKA calorimetric bomb (C200) and porosimetry experiments by Nitrogen Gas Adsorption were performed in a Micromeritics porosimeter (ASAP – 2020). Three replicate experiments were conducted for each coal with sample weights of 1.0 ± 0.1 g for the obtaining of HHV and S_{BET} .

2.2. Thermogravimetric tests

Thermogravimetric tests were performed in a Shimadzu TGA-51H for the determination of the ignition temperature, proximate analysis, and activation energy of the coals. The data were recorded and analyzed by TGA data acquisition software in which weight loss (TGA curve) and differential weight loss (DTG curve) were obtained. Table 1 shows a summary of the experimental conditions adopted in the TGA tests.

Atmospheres of synthetic air (combustion process) and nitrogen (pyrolysis process) were used for the determination of ignition temperature and ultimate analysis of the samples. The ignition temperature was established by the application of non-isothermal tests, according to the methodology proposed by Tognotti et al. [13], and approach developed by Karatepe and Küçükbayrak [34] was adopted in the proximate analysis of the coals.

TGA tests were conducted under a non-isothermal condition for five different heating rates (10, 20, 30, 40 and $50\,^{\circ}\text{C/min}$) for the determination of the activation energy of the combustion. The temperature ranged from room temperature up to $900\,^{\circ}\text{C}$ under air atmosphere.

2.3. Tests in fluidized a bed combustor

Fig. 1 shows the schematic of the bench-scale atmospheric bubbling fluidized bed combustor (FBC) used in the experiments. The

Table 1 Experimental conditions adopted in TGA tests.

Analysis	Mass (mg)	β (°C/min)	Set point (°C)	Hold (min)	Atmosphere
Ignition temperature	5 ± 0.5	10 10	950 950	-	Air Nitrogen
Proximate analysis	10 ± 0.5	20 40 -20	110 950 750	30 10 60	Nitrogen Nitrogen Air
Kinetic study	10 ± 0.5	10, 20, 30, 40 and 50	900	-	Air

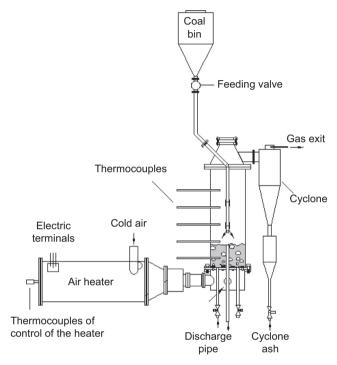


Fig. 1. Schematic of the bench-scale bubbling fluidized bed combustor (FBC).

reactor is a cylindrical stainless steel body (AISI 304) of 160 mm internal diameter, 450 mm total height - 180 mm and 270 mm bed and freeboard heights, respectively, which supports tests at temperatures up to 950 °C. The bed temperature is basically uniform, with lateral differences lower than 5 °C. A rotating valve was employed for the feeding system of the coals and heated air was used for the temperature control. Prior to the test, the feeding rates of the coal in the reactor were provided by the calibration curves of the rotating valve through the application of different tensions (V) for each coal.

The fluidized bed tests were started with the fluidization of a bed with 3 kg of 412 μm silica sand particles and air heating at controlled temperatures (lower than 200 °C). A 3.0 value was used for the ratio of velocity and minimum fluidization velocity (U/U_{mf}). U_{mf} is the minimum fluidization velocity at which the gravitational force balances the drag force, and U is the operational velocity, that carries away the fuel particle from the bed.

Gaseous emissions were collected in the discharge of the cyclone, while variations in the exit concentrations of SO_2 , CO_2 , and O_2 were continuously measured by gas analyzers. The concentrations of the gases were measured by gas analyzers (Horiba ENDA 1400) and the data were acquired by a system from the National Instruments Corporation.

The temperature was controlled in two regions of the reactor, namely bed and freeboard. During heating, of the fluidization velocity must be corrected as it varies in function of the tempera-

ture. When the temperature reached 200 °C, the heater was turned off and the coal was fed with a mass flow of approximately 0.265 g/s for 1 min. Both temperatures and gas concentrations were monitored for the assessment of the burning process. If the coal was not burned, the heater was turned on again and the temperature was increased for 1 min. The process was repeated until the ignition temperature, i.e. 600 °C was reached (in this case, the coal had already started burning). Temperatures and gas concentrations curves were plotted according to the data acquired in the tests and the ignition temperature was established under FBC conditions.

2.4. Kinetic method

The Model-Free Kinetics method was applied to determine the activation energy as a function of conversion of the chemical reaction [35,36]. The model is based on isoconversional techniques and different values of activation energy are obtained for each conversion value normalized between 0 and 1, i.e. its value is obtained for each physical and chemical processing that occurs during the reaction [37]. The conversion (α) of a chemical reaction is given by:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}, \tag{1}$$

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

Under nonisothermal conditions, the temperature varies at a constant heating rate (β = dT/dt) and Eq. (2) is described an isoconversional linear integral method [35–39].

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

where T is the temperature, R is the universal gas constant, A is the pre-exponential factor, E is the activation energy, and g (α) is the integral form of the reaction model. A and E are called Arrhenius parameters.

Subscript α in Eq. (2) represents the value of a given conversion (α). Therefore, the activation energy (E_{α}) is obtained as a function of the conversion [35–38]. $\ln\left(\beta/T_{\alpha}^{2}\right)$ is plotted against $1/T_{\alpha}$ for each α value and the least-squares method (linear regression) is applied for the establishment of the straight lines whose slopes ($-E_{\alpha}/R$) provide the activation energy values [37]. At least three different heating rates (β) and the respective conversion curves evaluated from the TGA curves measured must be obtained for the application of the Model-Free Kinetics method [38].

3. Results

3.1. Characterization of the coals

The ultimate analyses of both coals are given in Table 2. HHV tests were carried out according to the ASTM D-2015 standard test

Table 2 Ultimate analysis (wt%) of coals.

Analysis (wt%)	CE4500	CE5500
Carbon	54.96	64.93
Hydrogen	3.59	4.57
Nitrogen	1.07	1.18
Sulfur	1.18	0.61
Chlorine	0.17	0.03
Oxygen	7.92	8.27

method and the average values were 19,527 J/g and 24,624 J/g for CE4500 and CE5500, respectively.

 S_{BET} was calculated by Brunauer, Emmett, and Teller equation (BET equation), and values of $2.54 \, \text{m}^2/\text{g}$ and $13.08 \, \text{m}^2/\text{g}$ were obtained for CE4500 and CE5500, respectively.

The proximate analyses were determined by TGA and the percentage values (wt%) of moisture, volatile, fixed carbon, and ash were, respectively, 1.2, 23.1, 24.5, and 51.2 for CE4500, and 11.1, 43.6, 30.7 and 14.6 for the CE5500.

3.2. Activation energy by Model-Free Kinetics

Model-Free Kinetics was applied and TGA tests were conducted at five different heating rates (β = 10, 20, 30, 40 and 50 °C/min). Figs. 2 and 3 show the TGA and DTG curves for both CE4500 and CE5500, respectively.

The combustion of high volatile bituminous coal occurs in two main events. The DTG curves of both coals clearly showed such reactive events, which are identified as primary and secondary combustion steps. In the primary combustion occurs devolatilization and simultaneous fixed carbon combustion whereas in the secondary combustion only the char combustion occurs whereas in the secondary combustion only the char combustion occurs [2,40]. The DTG peaks are more pronounced in both primary and secondary combustion steps for higher values of B. Moreover, for the CE4500 coal, such these regions shift to a higher temperature range, where the maximum rate of reaction occurs. For each β value adopted, the temperature range between the beginning and the end of the process is different, as shown in Table 3. The end of the event is the point at which the conversion value (α) is equal to a unit $(\alpha = 1)$, which is considered the burn-out temperature.

Fig. 4 shows conversion (Eq. (1)) as a function of temperature for both CE4500 (Fig. 4a) and CE5500 (Fig. 4b). For six conversion values (α = 0.1, 0.3, 0.5, 0.7 and 0.9), as depicted in Fig. 5, a given conversion is reached at a different temperature, depending on the heating rate. The Model-Free Kinetics was applied for the α values indicated in Fig. 4, the data of $\ln \left(\beta/T_{\alpha}^2 \right)$ were plotted against $1/T_{\alpha}$ and the straight lines were obtained (Fig. 5).

A linear regression enabled the calculation of the activation energy for all conversions desired. The E_{α} values were obtained

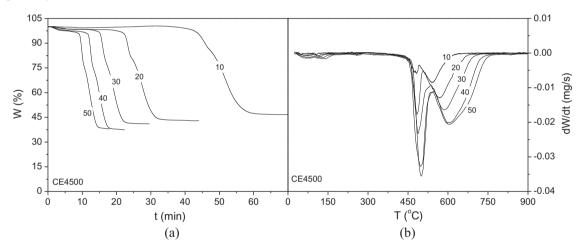


Fig. 2. (a) TGA curves, weight loss (W) versus time (t), and (b) DTA curves, dW/dt versus temperature (T) for CE4500. The numbers in the curves indicate the heating rates used in the experiments, i.e. 10–20–30–40 and 50 °C/min.

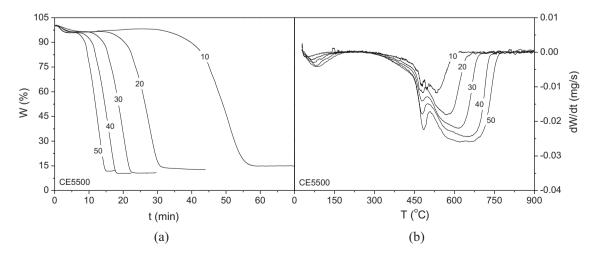


Fig. 3. (a) TGA curves, weight loss (W) versus time (t), and (b) DTA curves, dW/dt versus temperature (T), for CE5500. The numbers in the curves indicate the heating rates used in the experiments, i.e. 10-20-30-40 and 50 °C/min.

Table 3Initial temperature and burn-out temperatures at five heating rates for the first and second steps of the CE4500 and CE5500 coals.

Coals	Process temperature (°C)	β (°C/min)				
		10	20	30	40	50
CE4500	Initial temperature of the first step	388	365	377	396	395
	Burn-out temperature of the first step or Initial temperature of the second step	494	508	532	546	545
	Burn-out temperature of the second step	640	692	721	757	769
CE5500	Initial temperature of the first step	291	300	300	320	320
	Burn-out temperature of the first step or Initial temperature of the second step	487	487	500	500	509
	Burn-out temperature of the second step	608	666	724	752	783

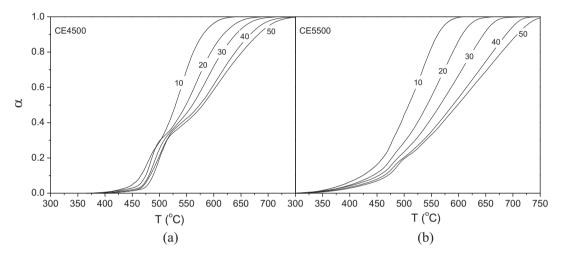


Fig. 4. Conversion (α) *versus* temperature (T) for (a) CE4500 and (c) CE5500. The numbers in the curves indicate the heating rates used in the experiments, i.e. 10–20–30–40 and 50 °C/min.

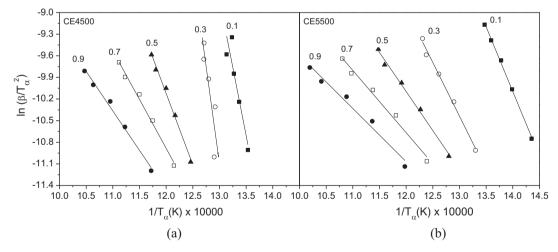


Fig. 5. In $\left(\beta/T_{\alpha}^{2}\right)$ versus $1/T_{\alpha} \times 10,000$ obtained for both (a) CE4500 and (b) CE5500 in dynamic synthetic air atmosphere. The numbers above the straight line, indicate the values obtained for five different levels of α (α = 0.1, 0.3, 0.5, 0.7 and 0.9).

for α between 0 and 1 with a 0.01 step and the results of the activation energy are presented in Fig. 6 for CE4500 and CE5500 coals. The values of α were split into two ranges for both primary and secondary combustion. The values of average activation energy (E_{α}) , standard deviation, and minimum and maximum values were determined for each range of α for both coals (Table 4).

3.3. Ignition temperature by TGA

The TGA curves depicted in Fig. 7 were used for the determination of the coal ignition temperature ($T_{\rm ig,C}$) for both CE4500

(Fig. 7a) and CE5500 (Fig. 7b). For each coal, two curves can be observed: one related to oxidation (synthetic air atmosphere) and the other to pyrolysis (nitrogen atmosphere). In the TGA tests, the $T_{\rm ig,C}$ values were 409 °C and 320 °C for CE4500 and CE5500 coals, respectively.

3.4. Ignition temperature by FBC

Fig. 8 shows the curves of CO_2 (C_{CO_2}) and O_2 (C_{O_2}) concentrations and temperature as a function of time for both coals, CE4500 (Fig. 8a) and CE5500 (Fig. 8b); the temperature were monitored

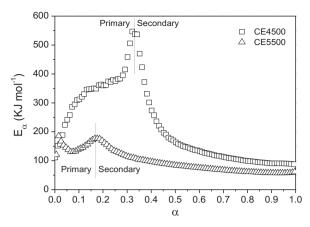


Fig. 6. Activation energy (E_{α}) as a function of conversion (α) for both coals: (a) CE4500 and (b) CE5500 $(\alpha$ between 0 and 1 with a step of 0.01). The values of α were split into two ranges, considering the primary and secondary combustion processes.

at two points of the reactor (bed and freeboard). Previously to the experiments, concentration of the gases remained under a steady condition, i.e. C_{CO_2} with 0% and C_{O_2} with 20%. After the raising of the temperature and feeding of the coal into the bed, the C_{CO_2} curve increased and the C_{O_2} curve decreased. The tangency points of lines for both C_{CO_2} and C_{O_2} were a criterion used for the determining of the coal ignition temperatures ($T_{ig,C}$) under fluidized bed condition. At this point, the concentration of the gases changed, because the combustion started and the values were 412 °C and 319 °C for CE4500 and 384 °C and 316 °C for CE5500, for both bed and free-board temperatures, respectively.

Since coal contains high sulfur contents, the sudden increase in the SO_2 emission is also indicative of the fuel's ignition start [6]. Fig. 9 shows the curves of SO_2 concentration (C_{SO_2}) and tempera-

ture (fluidized bed and freeboard) *versus* time for both coals CE4550 (Fig. 9a) and CE5500 (Fig. 9b). The tangency points of the line where C_{SO_2} increased suddenly were 403 °C and 317 °C for CE4500 and 409 °C and 315 °C for CE5500, for both bed and freeboard temperatures, respectively.

4. Discussion

Table 5 shows a summary of the results. The set of physical-chemical characteristics is used in the evaluating of the behavior of both studied coals related to the ignition temperature and activation energy.

Notable differences regarding ultimate and proximate analyses are observed between the two coals (Table 5). The percentage values of fixed carbon are quite close, however, the values of moisture, volatile compounds, and ash are different. The results for CE4500 are reasonable, because the high sulfur (Table 2) and ash contents (Table 5) are typical of southern Brazilian coals [41]. The values of S_{BET} and HHV were, respectively, 5.1 and 1.2 times higher for CE5500. Such results show physical-chemical characteristic can explain the different activation energies and ignition temperatures determined for both coals and enable the inference that CE5500 is more reactive than CE4500.

Porosity affects the reactivity of coal, as observed by Rubak et al. [42], who recognized the importance of Knudsen diffusion in the determination of the effective diffusivity of oxygen within the coal particle. Karcz et al. [43] also concluded the oxidation rate is controlled by diffusion of oxygen into pores. They obtained the values of activation energies for various carbonaceous samples and the results were approximately half of those expected when the internal mass transfer resistances in the theory were negligible.

Table 5 shows only the average values of E_{α} obtained in primary and secondary combustion steps. For both coals, the E_{α} values in the primary combustion were higher than those in the secondary combustion, and the lowest values were obtained for CE5500. Such

Table 4

Mean, standard deviation, minimum and maximum values of the activation energy (kl/mol) determined for both coals.

Events of combustion	Range of α	Mean	Standard deviation	Minimum	Maximum
Primary	0-0.328	337.13	90.22	110.88	564.83
Secondary	0.329-1.0	158.67	102.82	80.12	561.88
Whole range	0–1	217.08	129.57	80.12	564.82
Primary	0-0.177	152.65	16.11	120.70	185.43
Secondary	0.177-1	85.46	29.47	53.85	177.67
Whole range	0–1	97.07	37.54	53.85	185.43
	Primary Secondary Whole range Primary Secondary	Primary 0-0.328 Secondary 0.329-1.0 Whole range 0-1 Primary 0-0.177 Secondary 0.177-1	Primary 0-0.328 337.13 Secondary 0.329-1.0 158.67 Whole range 0-1 217.08 Primary 0-0.177 152.65 Secondary 0.177-1 85.46	Primary 0-0.328 337.13 90.22 Secondary 0.329-1.0 158.67 102.82 Whole range 0-1 217.08 129.57 Primary 0-0.177 152.65 16.11 Secondary 0.177-1 85.46 29.47	Primary 0-0.328 337.13 90.22 110.88 Secondary 0.329-1.0 158.67 102.82 80.12 Whole range 0-1 217.08 129.57 80.12 Primary 0-0.177 152.65 16.11 120.70 Secondary 0.177-1 85.46 29.47 53.85

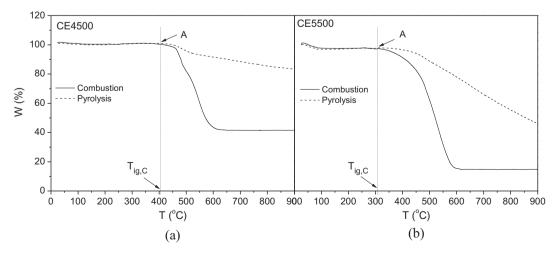


Fig. 7. TGA curves, weight loss (W) versus temperature (T), obtained in the combustion and pyrolysis process for both coals: (a) CE4500 and (b) CE5500.

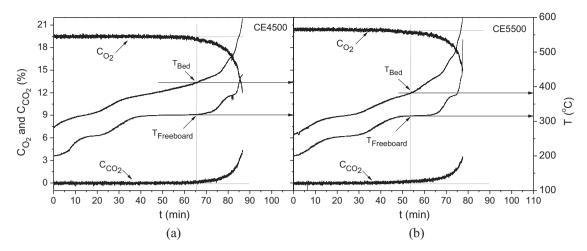


Fig. 8. Concentration curves of CO₂ (C_{CO2}) and O₂ (C_{O2}) and temperatures in the bed (T_{Bed}) and freeboard (T_{Freeboard}) versus time (t) for both coals: (a) CE4500 and (b) CE5500.

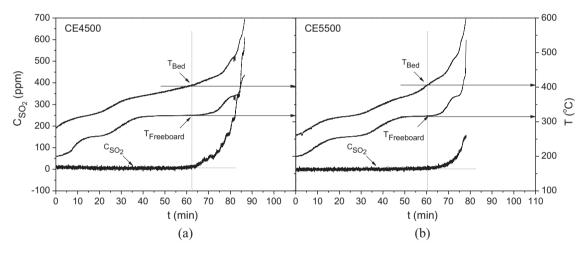


Fig. 9. Concentration curves of SO₂ (C_{SO₂}) and temperatures in the bed (T_{Bed}) and freeboard (T_{Freeboard}) versus time (t) for both coals: (a) CE4500 and (b) CE5500.

Table 5Summary of results.

Analysis/description		Coals	
		CE4500	CE5500
Proximate analysis by TGA (wt%)	Moisture Volatile Fixed carbon Ash	1.2 23.1 24.5 51.2	11.1 43.6 30.7 14.6
S_{BET} (m^2/g)		2.54	13.08
HHV (J/g)		19,527	24,624
Average values of $E\alpha$ (kJ/mol)	Primary combustion Secondary combustion	337.13 158.67	152.65 85.46
Ignition temperature by TGA (°C)		409	320
Ignition temperature by FBC (°C)	Bed temperature (CO ₂ and O ₂ concentrations)	412	384
	Freeboard temperature (CO ₂ and O ₂ concentrations)	319	316
	Bed temperature (SO ₂ concentration)	403	409
	Freeboard temperature (SO ₂ concentration)	317	315

results are consistent with the physicochemical characteristics of the coals, i.e. lower E_{α} values were observed for CE5500 in both combustion steps, which has a higher volatile content and higher S_{BET} than CE4500.

The results can also be explained by the transient behavior of the non-isothermal test and the way volatiles are released from the coal matrix [16]. During the burning process, the coal's physical structure is continuously changed and when higher temperatures are reached (secondary combustion), the reaction tends to be more controlled by intra-particle diffusion. Porosity increases with the continuous removal of carbon from the particles during combustion, consequently, the diffusion resistance decreases [16].

Hakvoort et al. [40] studied several coal whose with volatile contents ranged between 9.9 and 41.5%. In contrast to the present study, the authors concluded that the primary combustion is characterized by lower activation energies than those of the secondary combustion. However, in a sample of high volatile coal, a similar behavior was observed. The authors concluded that the volatiles content was strongly linked with a higher activation energy in the primary step. Moreover, the average values of the activation energy obtained in this study can be comparable to those obtained for coals and char (between 100 and 155 kJ/mol) described in the literature [16,44–48].

The evaluation of the two techniques that determine $T_{ig,C}$, i.e. TGA and FBC, revealed differences in experimental conditions resulted in different ignition temperatures for both TGA and FBC conditions, as also observed by Jia et al. [6]. Regarding the particles motion of coals, the particles were static in TGA test, whereas under FBC condition, they were kept in turbulent motion due to fluidization. Moreover, the test conditions are also different in both techniques, i.e. in the TGA were non-isothermal and FBC were isothermal. Smaller particles were adopted in TGA tests for the minimization of the heat and mass transfer and reduction in the temperature gradients within the sample. Consequently, lower ignition temperatures were obtained under TGA conditions, but similar behaviors were observed between two techniques applied to determine $T_{ig,C}$. The $T_{ig,C}$ values obtained for CE4500 were higher than those for CE5500 under both conditions applied. Such differences can be attributed to the different volatiles content. According to the results in Table 5, the volatile matter content in CE5500 is approximately 88% higher than that in the CE4500 coal. The same behavior was observed by Yang et al. [5], who showed volatiles normally ignite earlier the char, which facilitates combustion (homogeneous ignition mechanism). Therefore, the high volatile coal was expected to ignite at a lower temperature than the low volatile coal.

Regarding both criteria adopted for the ignition temperature determination under FBC conditions, i.e. C_{CO_2} and C_{O_2} curves (Fig. 8) and C_{SO_2} curve (Fig. 9), the results for $T_{ig,C}$ values were similar, which shows the evaluation of the SO_2 release from the coals is as efficient as the evaluation of the combustion gases.

According to Fig. 8, the temperature in the freeboard temperature curves does not vary in the ranges of 44–67 min for CE4500 and 51–61 min for CE5500. The change for CE5500 was faster than that for CE4500, which indicates the high volatile coal ignites in the freeboard, i.e. during the feeding in the reactor. On the other hand, the low volatile coal ignites within the bed material, from the first particle layer to the bulk of the bed. Fig. 9 shows the SO_2 release for CE4500 was faster than that for CE5500 due to the higher sulfur content in the CE4500 coal (Table 1).

According to results in Table 5, $T_{ig,C}$ for CE4500 obtained under TGA condition (409 °C) was quite close to the $T_{ig,C}$ values obtained in the bed (412 °C and 403 °C), whereas for CE5500, the $T_{ig,C}$ obtained in TGA (320 °C) was quite close to the $T_{ig,C}$ obtained in the freeboard (316 °C and 315 °C). Therefore, the application of the TGA technique for the obtaining of the proximate analysis [34] and ignition temperature [13] enable the prediction of the behavior of the ignition of coal particles under FBC condition. Moreover, CE4500 showed a higher value of $T_{ig,C}$ than CE5500, which means that CE4500 is thermally stable and this behavior is due to the high level of ash, which influences on the difficulty in the coal ignition.

The FBC results were quite similar to those of the ignition temperature obtained by Jia et al. [6] for a high volatile bituminous coal (33.1 wt%), i.e. 410 ± 5 °C. However, they were lower than those obtained by Yang et al. [5] under similar conditions in an FBC bench-scale. However, the coal used by these authors [5,6] had very different features compared those used in this work, containing 52.3 and 6.9 wt% of fixed carbon and volatile, respectively, with ignition temperature between 631 and 664 °C, and the particle sizes applied ranged from 180 to 6000 μ m.

The physicochemical characteristics of the coals can be correlated with their ignition temperatures, i.e. both higher volatiles and HHV imply lower $T_{ig,C}$ and activation energy. Furthermore, the knowledge about such parameters and additional data, as S_{BET} and sulfur content in the fuels, enable the prediction of the coals behavior in the combustion process and its influence on the reactivity parameters.

5. Conclusions

This paper has addressed the determining of the fuel ignition temperature of two types of coal, a Brazilian coal (CE4500) and a Colombian coal (CE5500). The results were correlated with some of their physicochemical characteristics, such as BET surface area, chemical composition, higher heating value and activation energy.

A non-isothermal kinetic study was conducted for the evaluation of the combustion reaction of the coals. The average values of the activation energy of the coal combustion were 337.14 and 152.65 kJ/mol (CE4500) and 158.67 and 85.46 kJ/mol (CE5500) for primary and secondary combustions, respectively. The lower values of the secondary combustion may be due to the coal's physical structure, which is continuously changed, and at higher temperatures (secondary combustion), the reaction was more controlled by intra-particle diffusion.

The ignition temperatures of the coals $(T_{ig,C})$ were determined under two different experimental conditions, i.e. in a thermogravimetric analyzer (TGA) and in a bench fluidized bed combustor (FBC). The application of different ignition criteria resulted in similar ignition temperatures and a homogeneous ignition mechanism. The $T_{ig,C}$ values were 409 °C for CE4500 and 320 °C for CE5500 in the TGA experiment, and 317–412 °C for CE4500 and 315–409 °C for CE5500 under FBC conditions. The highest values of $T_{ig,C}$ obtained for CE4500 were attributed to the low volatile compounds of the coal. The results showed that the presence of a high volatile content facilitates the combustion and, consequently, the fuel ignites more easily than the volatile free coal particles. Furthermore, the FBC curves indicated the high volatile coal ignites in the freeboard, i.e. during the feeding in the reactor; on the other hand, the low volatile coal ignites in the bulk of the bed.

According to the results, the coal with highest volatile content (CE5500) showed lower ignition temperature and lower activation energy in the combustion process, whereas the coal with lower activation energy in the combustion process (CE5500) showed lower ignition temperature and highest volatile content. As expected, physicochemical characteristics, as volatiles and HHV influenced the coal ignition temperatures. Therefore, the physicochemical characteristics of coals could be correlated with their reactivity for the prediction of the ignition temperatures under FBC conditions.

Acknowledgements

The authors are indebted to the National Council of Technological and Scientific Development (CNPq - Processes 150894/2014-7 and 301819/2015-7) and Research Foundation of São Paulo State (FAPESP - Project 2008/54062-9) for the financial support given to this research. The English language review provided by Professor Angela Pregnolato Giampedro is also acknowledged.

References

- [1] B. Liu, Z. Zhang, H. Zhang, H. Yang, D. Zhang, An experimental investigation on the effect of convection on the ignition behaviour of single coal particles under various O₂ concentrations, Fuel 116 (2014) 77–83, http://dx.doi.org/10.1016/ j.fuel.2013.07.112.
- [2] J.C. Crelling, E.J. Hippo, B.A. Woerner, D.P. West, Combustion characteristics of selected whole coals and macerals, Fuel 71 (1992) 151–158, http://dx.doi.org/ 10.1016/0016-2361(92)90003-7.
- [3] J. Faúndez, A. Arenillas, F. Rubiera, X. García, A.L. Gordon, J.J. Pis, Ignition behaviour of different rank coals in an entrained flow reactor, Fuel 84 (2005) 2172–2177, http://dx.doi.org/10.1016/j.fuel.2005.03.028.
- [4] R. Jovanovic, A. Milewska, B. Swiatkowski, A. Goanta, H. Spliethoff, Numerical investigation of influence of homogeneous/heterogeneous ignition/combustion mechanisms on ignition point position during pulverized coal combustion in oxygen enriched and recycled flue gases atmosphere, Int. J. Heat Mass Transf. 54 (2011) 921–931, http://dx.doi.org/10.1016/j.ijheatmasstransfer.2010.10.011.

- [5] H. Yang, J. Lu, H. Zhang, G. Yue, Y. Guo, Coal ignition characteristics in CFB boiler, Fuel 84 (2005) 1849–1853, http://dx.doi.org/10.1016/j.fuel.2005.03.029.
- [6] L. Jia, E.J. Anthony, I. Lau, J. Wang, Study of coal and coke ignition in fluidized beds, Fuel 85 (2006) 635–642, http://dx.doi.org/10.1016/ i.fuel.2005.09.012.
- [7] D. Zhang, T.F. Wall, Ignition of coal particles: the influence of experimental technique, Fuel 73 (1994) 1114–1119, http://dx.doi.org/10.1016/0016-2361 (94)90247-x.
- [8] R.H. Essenhigh, M.K. Misra, D.W. Shaw, Ignition of coal particles: a review, Combust. Flame 77 (1989) 3–30, http://dx.doi.org/10.1016/0010-2180(89) 90101-6.
- [9] P. Davini, P. Ghetti, D. Michele, Investigation of coal of the combustion of particles, Fuel 75 (1996) 1083–1088.
- [10] Y. Chen, S. Mori, W. Pan, Studying the mechanisms of ignition of coal particles by TG-DTA, Thermochim. Acta 275 (1996) 149–158, http://dx.doi.org/10.1016/ 0040-6031(95)02727-0.
- [11] A. Ponzio, S. Senthoorselvan, W. Yang, W. Blasiak, O. Eriksson, Ignition of single coal particles in high-temperature oxidizers with various oxygen concentrations, Fuel 87 (2008) 974–987, http://dx.doi.org/10.1016/ j.fuel.2007.06.027.
- [12] J.-J. Lu, W.-H. Chen, Investigation on the ignition and burnout temperatures of bamboo and sugarcane bagasse by thermogravimetric analysis, Appl. Energy 160 (2015) 49–57, http://dx.doi.org/10.1016/j.apenergy.2015.09.026.
- [13] L. Tognotti, A. Malotti, L. Petarca, S. Zanelli, Measurement of ignition temperature of coal particles using a thermogravimetric technique, Combust. Sci. Technol. 44 (1985) 15–28, http://dx.doi.org/10.1080/ 00102208508960290.
- [14] B.G. Ma, X.G. Li, L. Xu, K. Wang, X.G. Wang, Investigation on catalyzed combustion of high ash coal by thermogravimetric analysis, Thermochim. Acta 445 (2006) 19–22, http://dx.doi.org/10.1016/j.tca.2006.03.021.
- [15] X. Huang, X. Jiang, X. Han, H. Wang, Combustion characteristics of fine- and micro-pulverized coal in the mixture of O₂/CO₂, Energy Fuels 22 (2008) 3756– 3762, http://dx.doi.org/10.1021/ef800444c.
- [16] C.G. da Silva Filho, F.E. Milioli, A thermogravimetric analysis of the combustion of a Brazilian mineral coal, Quim. Nova 31 (2008) 98–103, http://dx.doi.org/ 10.1590/S0100-40422008000100021.
- [17] C. Shen, W. Lin, S. Wu, X. Tong, W. Song, Experimental study of combustion characteristics of bituminous char derived under mild pyrolysis conditions, Energy Fuels 23 (2009) 5322–5330, http://dx.doi.org/10.1021/ ef900306w.
- [18] Z. Yang, S. Zhang, L. Liu, X. Li, H. Chen, H. Yang, et al., Combustion behaviours of tobacco stem in a thermogravimetric analyser and a pilot-scale fluidized bed reactor, Bioresour. Technol. 110 (2012) 595–602, http://dx.doi.org/10.1016/j. biortech.2011.12.119.
- [19] T. Ozawa, Kinetic analysis of derivative curves in thermal analysis, J. Therm. Anal. 2 (1970) 301–324, http://dx.doi.org/10.1007/BF01911411.
- [20] S.E. Smith, R.C. Neavel, E.J. Hippo, R.N. Miller, DTGA combustion of coals in the Exxon coal library, Fuel 60 (1981) 458–462, http://dx.doi.org/10.1016/0016-2361(81)90103-4.
- [21] J.W. Cumming, Reactivity assessment of coals via a weighted mean activation energy, Fuel 63 (1984) 1436–1440.
- [22] P.A. Morgan, S.D. Robertson, J.F. Unsworth, Combustion studies by thermogravimetric analysis: 1. Coal oxidation, Fuel 65 (1986) 1546–1551.
- [23] P.T. Williams, S. Besler, The pyrolysis of rice husks in a thermogravimetric analyser and static batch reactor, Fuel 72 (1993) 151–159, http://dx.doi.org/ 10.1016/0016-2361(93)90391-E.
- [24] P.T. Williams, S. Besler, Pyrolysis-thermogravimetric analysis of tyres and tyre components, Fuel 74 (1995) 1277–1283, http://dx.doi.org/10.1016/0016-2361 (95)00083-H.
- [25] H. Tanaka, Thermal analysis and kinetics of solid state reactions, Thermochim. Acta 267 (1995) 29–44, http://dx.doi.org/10.1016/0040-6031(95)02464-6.

- [26] C.-H. Wu, C.-Y. Chang, J.-P. Lin, J.-Y. Hwang, Thermal treatment of coated printing and writing paper in MSW: pyrolysis kinetics, Fuel 76 (1997) 1151– 1157, http://dx.doi.org/10.1016/S0016-2361(97)00113-0.
- [27] Ž. Živković, D. Živković, D. Grujičić, V. Savović, Kinetics of the oxidation process in the system Zn-Fe-S-O, Thermochim. Acta 315 (1998) 33–37, http://dx.doi. org/10.1016/S0040-6031(98)00274-3.
- [28] J.A. Conesa, R. Font, A. Fullana, J.A. Caballero, Kinetic model for the combustion of tyre wastes, Fuel 77 (1998) 1469–1475, http://dx.doi.org/10.1016/S0016-2361(98)00068-4.
- [29] O. Senneca, P. Salatino, R. Chirone, A fast heating-rate thermogravimetric study of the pyrolysis of scrap tyres, Fuel 78 (1999) 1575–1581, http://dx.doi. org/10.1016/S0016-2361(99)00087-3.
- [30] P.R. Solomon, T.H. Fletcher, R.J. Pugmire, Progress in coal pyrolysis, Fuel 72 (1993) 587–597, http://dx.doi.org/10.1016/0016-2361(93)90570-R.
- [31] M.V. Kök, E. Özbas, C. Hicyilmaz, Ö. Karacan, Effect of particle size on the thermal and combustion properties of coal, Thermochim. Acta 302 (1997) 125–130, http://dx.doi.org/10.1016/S0040-6031(97)00205-0.
- [32] T.P. Prasad, S.B. Kanungo, H.S. Ray, Non-isothermal kinetics: some merits and limitations, Thermochim. Acta 203 (1992) 503–514, http://dx.doi.org/10.1016/ 0040-6031(92)85220-P.
- [33] J.R. Howard, Fluidized Bed Technology: Principles and Applications, CRC Press, New York, 1989.
- [34] N. Karatepe, S. Küçükbayrak, Proximate analysis of some Turkish lignites by thermogravimetry, Thermochim. Acta 213 (1993) 147–150, http://dx.doi.org/ 10.1016/0040-6031(93)80012-Y.
- [35] S. Vyazovkin, D. Dollimore, Linear and nonlinear procedures in isoconversional computations of the activation energy of nonisothermal reactions in solids, J. Chem. Inform. Model. 36 (1996) 42–45, http://dx.doi.org/10.1021/ci950062m.
- [36] S. Vyazovkin, N. Sbirrazzuoli, Confidence intervals for the activation energy estimated by few experiments, Anal. Chim. Acta 355 (1997) 175–180, http:// dx.doi.org/10.1016/S0003-2670(97)00505-9.
- [37] I. Ávila, P.M. Crnkovic, F.E. Milioli, K.H. Luo, Thermal decomposition kinetics of Brazilian limestones: effect of CO₂ partial pressure, Environ. Technol. (UK) 33 (2012) 1175–1182, http://dx.doi.org/10.1080/09593330.2011.618930.
- [38] S. Vyazovkin, C.A. Wight, Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data, Thermochim. Acta 340–341 (1999) 53–68, http://dx.doi.org/10.1016/S0040-6031(99)00253-1.
- [39] I. Majchrzak-Kuceba, W. Nowak, Application of model-free kinetics to the study of dehydration of fly ash-based zeolite, Thermochim. Acta 413 (2004) 23–29, http://dx.doi.org/10.1016/j.tca.2003.10.021.
- [40] G. Hakvoort, J. Schouten, P. Valkenburg, The determination of coal combustion kinetics with thermogravimetry, J. Therm. Anal. 35 (1989) 335–346.
- [41] T. Süffert, L. Fernando, F. De Albuquerque, CARVÃO NOS ESTADOS DO RIO GRANDE DO SUL, 1997.
- [42] W. Rubak, H. Karcz, M. Zembrzuski, Evaluation of intrinsic kinetic parameters of coal combustion, Fuel 63 (1984) 488–493, http://dx.doi.org/10.1016/0016-2361(84)90284-9.
- [43] H. Karcz, W. Kordylewski, W. Rybak, Evaluation ignition of kinetic parameters of coal, Fuel 59 (1980) 799–802.
- [44] S. Dutta, C.Y. Wen, Reactivity of coal and char. 2. In oxygen-nitrogen atmosphere, Ind. Eng. Chem. Process Des. Dev. 16 (1977) 31–37, http://dx. doi.org/10.1021/i260061a005.
- [45] I.W. Smith, The intrinsic reactivity of carbons to oxygen, Fuel 57 (1978) 409–414, http://dx.doi.org/10.1016/0016-2361(78)90055-8.
- [46] N.M. Laurendeau, Heterogeneous kinetics of coal char gasification and combustion, Prog. Energy Combust. Sci. 4 (1978) 221–270.
- [47] N.V. Russell, T.J. Beeley, C.-K. Man, J.R. Gibbins, J. Williamson, Development of TG measurements of intrinsic char combustion reactivity for industrial and research purposes, Fuel Process. Technol. 57 (1998) 113–130, http://dx.doi. org/10.1016/S0378-3820/98)00077-0.
- [48] A. Williams, M. Pourkashanian, J.M. Jones, The combustion of coal and some other solid fuels, Proc. Combust. Inst. 28 (2000) 2141–2162, http://dx.doi.org/ 10.1016/S0082-0784(00)80624-4.