

KINETIC INTERPRETATION OF THE IGNITION TEMPERATURE FOR COALS

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Abstract. The aim of this study is to determine the activation energy for the coal combustion process and compare it with its physico-chemical characteristics, such as volatile content and gross calorific value. These physico-chemical parameters are also compared with the ignition temperatures for two coals (EC4500 and EC5500) under two different experimental conditions: thermogravimetric analyzer (TGA) and bench-scale fluidized bed combustor (FBC). The determination of the activation energy was made employing thermogravimetric (TG) test and Model-Free Kinetics in five different heating rates between ambient temperature and 900 °C. In TG technique, the ignition temperature was taken as the temperature at which the TG curves in the oxidation (oxidant atmosphere) and pyrolysis (inert atmosphere) experiments diverge. To determine the coal ignition temperature under FBC conditions, the criterion adopted was changes in concentrations of the gases O₂, CO₂ and SO₂ during the coal combustion process. The average values of activation energy of the coal combustion were 223 kJ mol⁻¹ (EC4500) and 103 kJ mol⁻¹ (EC5500). In TG experiments, the coal ignition temperatures were 462 °C (EC4500) and 314 °C (EC5500) and under conditions of FBC they were 402 °C (EC4500) and 362 °C (EC5500). The results indicated that the coal with lower activation energy of the combustion process (EC5500) also presents lower ignition temperature, highest volatile content and higher gross calorific value. This fact indicates that the presence of volatiles favor the combustion process, since these matters involve the core of the particle.

Keywords: activation energy; ignition temperature; combustion; coal.

1. INTRODUCTION

The knowledge of the chemical kinetics in coal combustion process is important for both burning rate of the materials involved and project of reactors. There are several studies in the literature that focus on the determination of kinetic parameters, such as kinetic energy and constant of reaction in coal combustion processes. Kinetic studies employing thermal analysis can be achieved by isothermal or non-isothermal methods, but this issue is controversial. Non-isothermal methods have been extensively applied to complex heterogeneous reactions (Smith et al., 1981; Cumming, 1984; Ozawa, 1957; Morgan, 1986; Williams and Besler, 1993; Williams and S. Besler, 1995; Tanaka, 1995; Wu et al. 1997; Živkovic et al., 1998; Conesa et al., 1998; Senneca et al., 1999).

Some authors have observed that kinetic studies of coal combustion under non-isothermal conditions are hindered by the presence of several complex substances of the coal, and due to the large number of successive and parallel chemical reactions that occur (Kök et al., 1997; Solomon et al., 1993). On the other hand, Prasad et al. (1992) observed that in the isothermal assay, the samples change physically during the reaction, suggesting that there is not a single set of kinetic parameters that can be derived from the process as a whole.

Smith et al. (1981) studied the combustion kinetics of coal of different ranks, from lignite at low volatile bituminous coal, obtaining different values of activation energy, to four regions of combustion related to different temperature ranges. Cumming (1984) confirmed the findings of Smith et al. (1981) and proposed a procedure for determining the mean activation energy from the different values found at different ranges of temperature.

According to Laurendeau (1978), pore size distribution and the internal surface area of pores determine intrinsic reaction rates of coals. Dutta and Wen (1977) determined the reactivity of various coals in atmospheres of CO₂ and O₂-N₂. They observed that the reactive process in CO₂ atmosphere occurs in two different stages, i.e. pyrolysis and reaction to CO₂. The reactivity during pyrolysis is mainly a function of volatile fraction and heating rate and the reactivity during reaction to CO₂ is mainly a function of the coal type. Otherwise, the reactivity of coals in O₂-N₂ atmosphere is mainly a function of devolatilization extent. Fu et al. (1997) reported activation energies and Arrhenius pre-exponential factors for the combustion of a great variety of coals, including high ash coals. They found that the activation energy does not depend on the type and properties of coals, varying only with temperature. Otherwise, they observed that pre-exponential factors depend on both coal properties and combustion controlling mechanism.

The ignition behavior of coal particles is also an important feature in boilers projects and in the stability of the combustion process control (Crelling et al., 1992; Faúndez, et al., 2005). The study of ignition phenomena is mainly based on the measurement of the minimum gas temperatures required for the ignition of the coal particles. The knowledge of the coal ignition temperature is an important parameter for designing the startup burner and choosing the control parameter during the startup process (Yang, 2005). To Essenhigh et al. (1989), although the coal particle ignition has been a problem of interest for nearly 150 years, only recently has significant progress been made in understanding the ignition mechanism. There are several studies of ignition temperature in the literature and in general there is an agreement that the ignition of coal particles can be a multistage process (Crelling et al., 1992; Essenhigh, et

al., 1989, Zhang and Wall, 1994, Davini, et al., 1996; Chen, et al., 1996). However, the classification of the coal ignition mechanism differs somewhat from author to author.

Thermogravimetric methods have been widely used in the determination of coal ignition temperature (Tognotti et al., 1985; Crelling et al., 1992; Chen et al., 1996). However, the mostly accepted methodology was that proposed by Tognotti et al. (1985). In this method the ignition temperature is taken as the temperature at which the TG curves in the oxidation (oxidant atmosphere) and pyrolysis (inert atmosphere) experiments diverge.

Bubbling fluidized bed combustion of coals is characterized by a set of complex physico-chemical phenomena. Two well defined hydrodynamic patterns in bubbling bed regime may be considered: a particulate or emulsion phase characterized by gas dispersed particles, and a bubble phase characterized by gas voids with very few particles. Therefore, almost all heterogeneous reactions, such as coal combustion and sulfur sorption by limestone occur in the particulate phase. The effective rates of the heterogeneous chemical reactions are controlled by mass transport and chemical kinetics. The relevant mass transfer occurs between the bubble and the particulate phases, through the particulate phase and intra-particle (Carmargo et al., 2003).

Laboratory scale fluidized beds are often used to measure the coal ignition temperature, based on criteria, such as flame as spark characteristics, bed temperature response and oxygen response (Liu et al., 1995). In these systems, the coal ignition temperature is not only a function of the physico-chemical properties of the fuel, but also influenced by the heating rate, the fluidization velocity and the particle size, as well (Yang et al., 2005).

According to Yang et al. (2005) the coal ignition temperature is traditionally estimated from experience with little theoretical basis and relatively large uncertainties in the estimates, resulting in operating difficulties and economic losses. The authors affirm that 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 even more. Once the fuel concentration and temperature in the furnace have reached the critical conditions, the mixture flashes and the furnace temperature suddenly increases, leading to control problems.

Jia et al. (2006) investigated the coal ignition of petroleum cokes, a high volatile bituminous coal and the blends of the coal and the cokes in both bench and pilot-scale fluidized bed combustors. In addition, for the fluidized bed ignition tests, thermogravimetric analysis measurements were taken in all fuels and their chars. In the reactor in bench scale the authors evaluated the variation of CO-CO₂ concentrations with time and temperature of the bed. In the pilot-scale plant the increased levels of SO₂ were used as an indicator of the fuel ignition temperature. The results showed that different test methods and ignition criteria demonstrated significantly different ignition temperatures, with the largest variation arising between bench and pilot-scale equipment.

The aim of this study is to determine the activation energy of the coal combustion process for two coals and compare it with their physico-chemical characteristics, such as volatile content and gross calorific value. These parameters will also compare with the ignition temperatures for two energetic coals under two different experimental conditions: thermogravimetric analyzer and bench-scale fluidized bed combustor.

2. MATERIALS AND METHODS

2.1. Experimental Systems

The experimental systems utilized in this study were a thermogravimetric analyzer (TGA) and a bench-scale fluidized bed combustor (FBC) (Fig. 1).

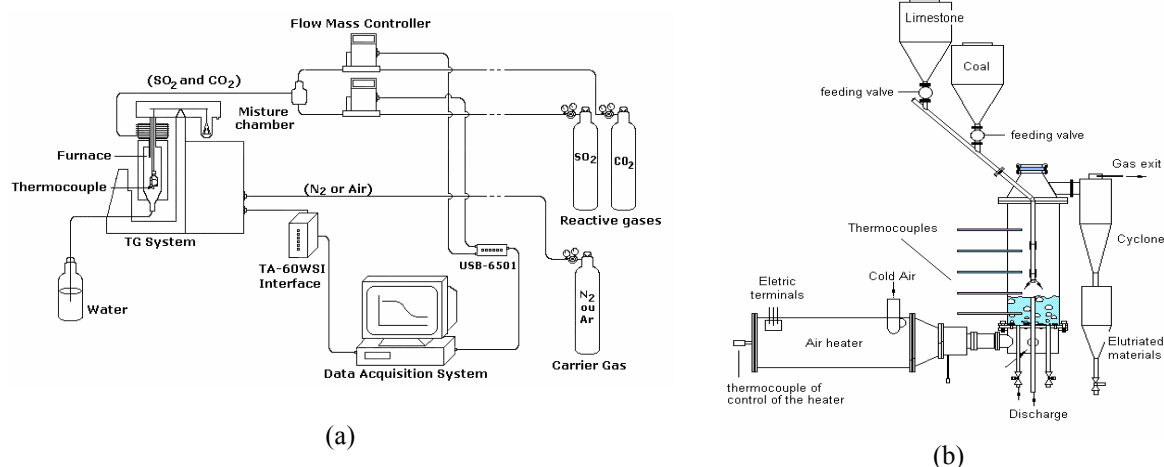


Figure 1. Experimental systems: (a) Sketch system TG (SHIMADZU – TGA-51) and (b) Sketch of the bench scale fluidized bed plant used in the experiments.

Figure 1(a) presents a sketch of TGA, data acquisition system and trajectory of the gas until the TGA furnace. Through the balance mechanism flows only the carrier gas (N₂ or Air), which is controlled by an internal flowmeter.

When the use of reactive gases (CO₂ and SO₂) is required, these gases do not come into contact with the balance mechanism, and are injected directly into the furnace by a mass flow control (Aalborg). The control of the mass flow of the gas reagents is accomplished by the programmed system control USB-6501 and *Lab View*, both from *National Instruments Corp.*

Figure 1(b) shows a sketch of the bench scale fluidized bed plant used in the experiments. The reactor is an atmospheric bubbling fluidized bed with 160 mm of internal diameter. The gaseous emissions are collected in the discharge of the cyclone, while the consequent variations of the exit concentrations of SO₂, CO₂, and O₂ are continuously measured in Horiba Enda 1400 gas analyzers. Two rotating valves are employed for the feeding systems of coal and limestone (to study the process of desulphurization). The mass flow rates of particle matters are given by the calibration curves of their rotary valves.

This reactor was designed and built at Group of Thermal and Fluids Engineering (EESC/USP). Paludo et al. (2006) presented this experimental system, including the main details of construction and project of the plant, stages of tests performed, problems and solutions obtained.

2.2. Experimental Procedure

Two coals were used in the experiments: a particular southern Brazilian bituminous coal with high ash and high sulfur content called EC4500 (e.g., energetic coal with higher calorific value of 4500 kcal kg⁻¹) and another from near the northern region of Brazil, called CE550 (e.g., energetic coal with higher calorific value of 5500 kcal kg⁻¹). Thus, two coals extracted from distant regions, with different geological and physico-chemical characteristics were evaluated.

The coal ignition temperature (T_{ig}^C) was established applying non-isothermal thermogravimetric (TG) experiments and coal samples of 5.0 ± 0.5 mg and 230 μ m mean size were used. The mean size particle 230 μ m resulted from its passing through a sieve with 260 μ m aperture and retention in a sieve with 200 μ m aperture. In the TG experiments, a heating rate of 30 °C min⁻¹ was applied in synthetic air atmosphere (combustion process) and nitrogen atmosphere (pyrolysis process) until 950 °C. The detailed methodology and curves obtained can be seen in Ávila et al. (2007).

Non-isothermal TG tests were applied to the kinetic study of coal combustion. Coal samples of $10 \pm$ mg and 230 μ m mean size were used in the experiments. Five heating rates, between 10 and 50 °C/min, from room temperature up to 900 °C were used. The reacting atmosphere was synthetic air, which was continuously blown over the samples through the TGA furnace at a volumetric rate of 100 mL min⁻¹.

In FBC, average diameters of coal equal to 383 μ m (EC4500) and 498 (EC5500) were used, following the method described by Howard (1989). The basic fluidized bed experiment consists in fluidizing a bed with 3 kg of silica sand particles (412 μ m) with pre-heated air at controlled temperatures. Heated air was used for a temperature lower than T_{ig}^C , which had been previously obtained in TG tests. The temperature was controlled in two points of the reactor: bed and freeboard. During the heating the correction of the fluidization velocity must be performed, as it varies with the temperature. The heater is turned off and then the coal is fed with mass flow of approximately 0.265 g s⁻¹ for 1 min, while are monitoring both the temperature and gases concentrations. Every 100 s, the process is repeated until the temperature of the bed has come close to 600 °C (in this case already in the combustion process). With the data obtained in the acquisition, the T_{ig}^C is then determined under FBC conditions. The height of bed is 180 mm and the velocity/minimum fluidization velocity (U/U_{mf}) of 3.0 was used.

2.3. Kinetic Methods

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

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

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

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

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

where α is the conversion, $f(\alpha)$ represents the reaction model and k is the Arrhenius rate constant.

From Eq. (2) it has

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

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

From Eq. (3) one obtains

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

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

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

Since $E/2RT \gg 1$, the temperature integral can be approximated by

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

Substituting the temperature integral, rearranging and logarithming, one has

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

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

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

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

3. RESULTS

To determine the activation energy for both coals, Model-free Kinetics was applied at five heating rates. Two combustion regions (first and second), as well as the whole combustion process as a single step were considered. For each heating rate, the temperature range between the beginning and the end of the process is different. The end of the event ($\alpha = 1$) was considered the burn-out temperature, as shown in Tab. 1.

Table 1. Initial temperature and burn-out temperatures at five heating rates for the first and second steps of the EC4500 and EC5500 coals.

Coals	Process Temperature (°C)	β (°C min ⁻¹)				
		10	20	30	40	50
EC4500	Initial temperature of the first step	388	365	377	396	395
	Burn-out temperature of the first step/initial temperature of the second step	494	508	532	546	545
	Burn-out temperature of the second step	640	692	721	757	769
EC5500	Initial temperature of the first step	291	300	300	320	320
	Burn-out temperature of the first step/initial temperature of the second step	487	487	500	500	509
	Burn-out temperature of the second step	608	666	724	752	783

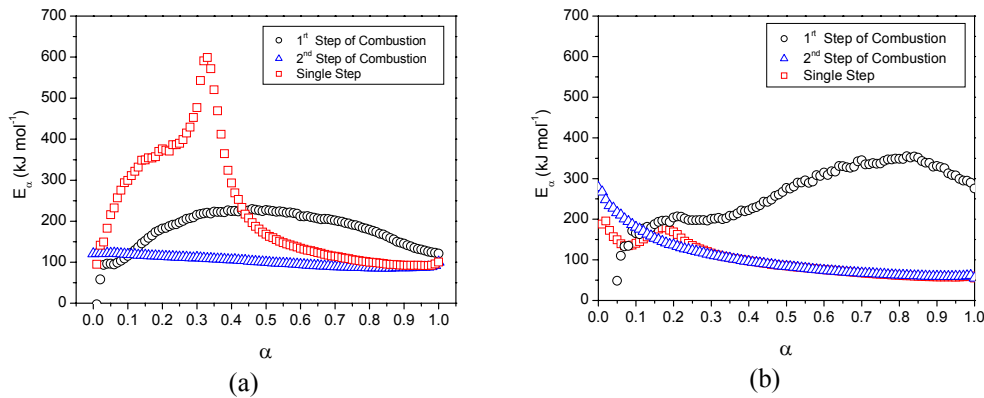


Figure 2. E_α versus α values (between 0 and 1) for two combustion steps (first and second) and the whole combustion process as a single step- (a) EC4500 and (b) EC5500.

$\ln\beta/T_\alpha^2$ versus $1/T_\alpha$ was plotted providing a series of straight lines with $-E_a/R$ slope. Therefore, the activation energy was obtained as a function of conversion. The results are showed in Fig. 2, in which the curves represent the activation energy versus conversion (α) for the first and second steps and the whole process as a single step.

The TG curves, presented in Fig. 3(a) and 3(b), were used to determine the T_{ig}^C for both coals. For each coal, there are two curves, one related to oxidation and the other, to pyrolysis. T_{ig}^C is taken in the point in which the curves diverge (Tognotti, 2006) and the ignition temperatures are 462 °C for EC4500 and 314 °C for EC5500.

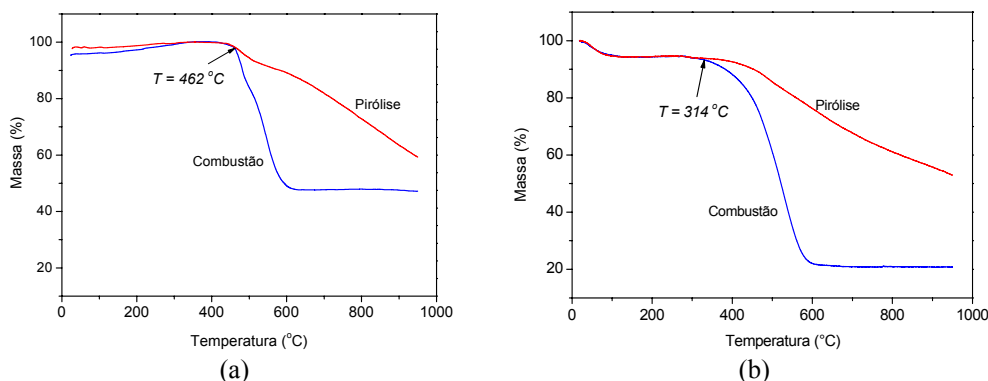


Figure 3. TG curves obtained in the combustion and pyrolysis process for coals (a) CE-4500 and (b) CE-5500.

Figures 4(a) and 4(b) present the variations of CO_2 and O_2 concentrations and temperature in both fluidized bed and freeboard. At the beginning of the run, combustion gases are under a steady condition, where the CO_2 concentration is around zero and O_2 is around 20 %. After feeding the bed with coal, the CO_2 curve increased and O_2 curve decreased. The tangency points of lines for both CO_2 and O_2 concentrations were a criterion used to determine the T_{ig}^C under fluidized bed condition. In this point the concentration of these gases changes because the combustion starts, and the values were 408 and 319 °C for EC4500 and 372 and 318 °C for EC5500, considering the temperatures of bed and freeboard, respectively.

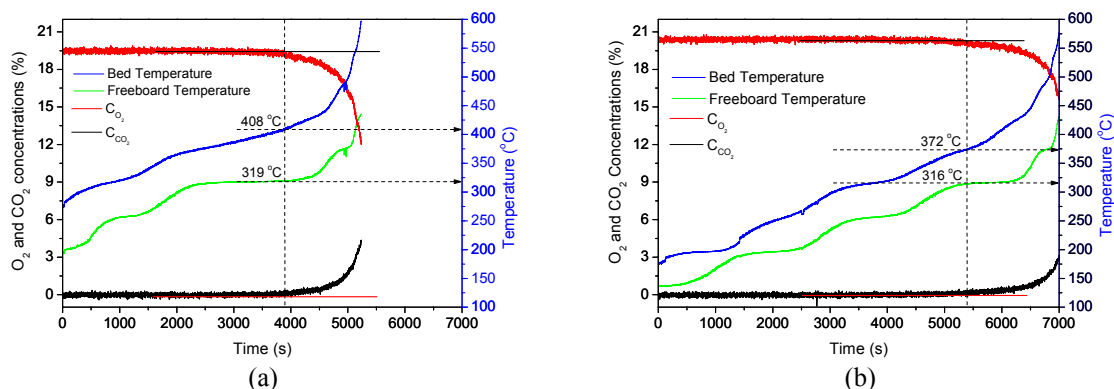


Figure 4. Concentration curves of CO_2 and O_2 and temperatures (fluidized bed and freeboard) versus time for (a) EC4500 and (b) EC5500.

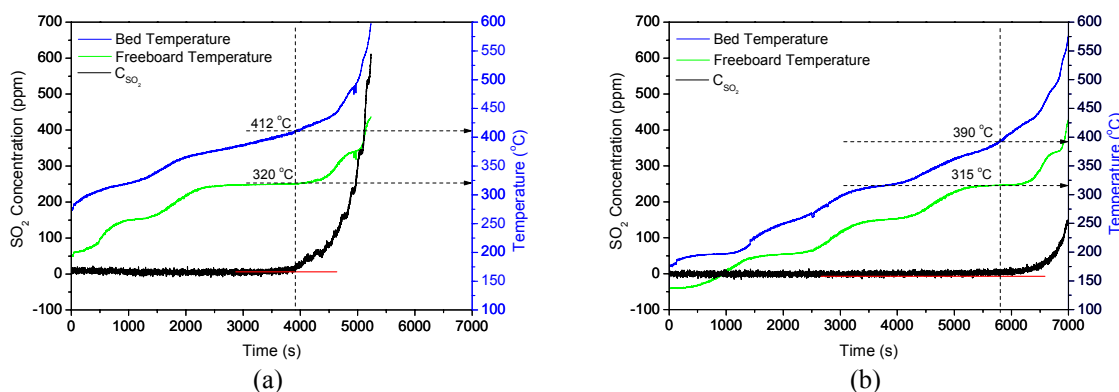


Figure 5. Concentration curves of SO_2 and temperatures (fluidized bed and freeboard) versus time temperature in fluidized bed for (a) EC4500 and (b) EC5500.

In addition, since coal contains high sulfur contents, the sudden increase in SO₂ emission is also indicative of the fuel's ignition start (Jia et al., 2006). Figures 5(a) and 5(b) show the concentration curves of SO₂ and temperatures (fluidized bed and freeboard) versus time, in which the tangency points of lines for SO₂ concentration were also another criterion used to determine the T_{ig}^C under fluidized bed condition. In this point the SO₂ concentration changes because the combustion starts, and the values determined were 412°C and 320 °C for EC4500 and 390°C and 315 °C for EC5500, considering the temperatures of bed and freeboard, respectively.

Table 2 presents all numerical results obtained in this study. Other parameters, such as proximate analysis and higher calorific value, or gross calorific value (GCV) of the coals are also showed. This set of physico-chemical characteristics is used to evaluate their effects on the coal's kinetic parameters and T_{ig}^C .

Table 2. Summary of results.

Analysis	Description	Coals	
		EC4500	CE5550
Coal Combustion Process E_a (kJ mol ⁻¹)	First Step (Primary)	183.5± 39.9	263.8± 69.1
	Second Step (Secondary)	101.3± 12.3	103.2± 51.8
	Single Step (whole range)	222.9± 139.5	98.2± 39.5
Ignition Temperature (°C)	TG Experiments	462	314
	Bed temperature (CO ₂ and O ₂ concentrations)	408	372
	FBC Bed temperature (SO ₂ concentration)	412	390
	Freeboard temperature (CO ₂ and O ₂ concentrations)	319	318
	Freeboard temperature (SO ₂ concentration)	320	315
Proximate analysis (%)	Moisture	1.2	10.8
	Volatile	24.5	42
	Fixed carbon	23.1	29
	Ash	51.2	18.2
Gross calorific value (J g ⁻¹)		19.527	24.624

4. DISCUSSION

Concerning proximate analysis, it can be noted that the coals' carbon percentage values are quite close and the values of moisture, volatile compounds, fixed carbon and ash are different.

Regarding the ignition temperatures, both criteria (concentration of CO₂ and O₂ and concentration of SO₂) utilized for the determination of T_{ig}^C under FBC conditions were very close, showing that the evaluation of the release of SO₂ from the coals was as efficient as the evaluation of the combustion gases.

The T_{ig}^C obtained for EC4500 coal were higher than those for EC5500 coal in both fluidized bed and thermogravimetric analysis. These differences could be attributed to the different volatiles content. These values are presented in Tab. 2, where it is possible to observe that the volatile matter content of EC5500 is about 42 % higher than that of EC4500. The same behavior was observed by Yang et al (2005), who showed that the volatiles normally ignite before the char, facilitating the combustion (homogeneous ignition mechanism). Therefore, the high volatile coal was expected to ignite in a lower temperature than low volatile coal.

It is observed that there is not temperature variation during 1350 and 750 seconds for EC4500 and EC5500 coals, respectively, in freeboard temperature curves (Fig.4 and 5). In these curves there is a change after the coals have been fed. The change for EC5500 was quicker than for EC4500, indicating that 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.

It is worth stressing the ignition temperature (T_{ig}^C) for EC4500 obtained under TG condition (462°C) was quite close to the T_{ig}^C obtained in the bed (408 and 412°C), and for EC 5500, the T_{ig}^C obtained in TG (314°C) was quite close to the T_{ig}^C obtained in the freeboard (318 and 315°C).

Activation energies for coals were determined for two different steps (primary and secondary combustion) and for the whole range. For the first step, the activation energy was higher for both coals, which can be explained by the transient behavior of the non-isothermal test. During the burning process, the coal's physical structure is continuously changed and when higher temperatures are reached (secondary combustion), the reaction has a tendency to be more controlled by intra-particle diffusion. With the continuous removal of carbon from the particles during combustion, an increase in porosity occurs and, consequently, the diffusion resistance decreases.

For both coals, the activation energy of the first step is different from the activation energy of the second step. This difference can be explained by the way in which the volatiles are released from the coal matrix. According to Hakvoort et al, 1989, the combustion of high volatile bituminous coal occurs in two main events: (1) volatiles combustion and (2)

char combustion.

As previously described, Fig. 2 presents three curves of activation energy versus conversion α related to single (the whole range), first and second steps of the combustion. In the single step curve of the EC4500 coal, at about $\alpha = 0,3$ there is a peak and in this region the value of E_a is very high, compared with the values obtained separately in the two steps. This behavior is attributed to the transition in the change of the reaction mechanism and from this assumption, for this coal, the model is better fitted considering the two steps separately.

On the other hand, concerning EC5500 coal, the highest values of E_a were obtained for the first step. Considering the process as a single step, the values of E_a were closer than those obtained for the second step. Since this coal presents higher quantities of volatiles than the other coal, the volatiles released from the coal matrix may make the physical conditions of the particles become similar to those of the fixed carbon's particles. Therefore, for EC5500 coal, the model is better described when a single step is considered.

As presented in this study, the physico-chemical characteristics of the coals can be correlated with their activation energies, i.e., both high volatiles and GCV (Gross calorific value), imply low T_{ig}^C and low activation energy

5. CONCLUSIONS

Two criteria were used to determine the ignition temperature of high sulfur coals. The first was a thermogravimetric analyser (TGA) and the second was the bench fluidized bed combustor (FBC).

For each coal, the values obtained in both TGA and FBC were close and presented a homogeneous ignition mechanism. The ignition temperature of EC4500 coal was higher than that of EC5500 coal, which is attributed to the low volatile compounds and low GCV of the EC4500 coal. It indicates that the presence of a high volatile content facilitates the combustion and, consequently, the fuel ignites more easily than the volatile free coal particles.

To evaluate the combustion reaction of the coals, a non-isothermal kinetic study was conducted. The activation energies were determined through thermogravimetry and Model –Free kinetics. It was observed that for EC4500 coal, the model was well fitted considering the two steps (first and second) separately, as this coal presents a transition in the reaction mechanism. On the other hand, for EC5500 coal, the model is better fitted when the combustion is considered a single step.

It was possible to conclude that the physico-chemical characteristics, such as volatiles and GCV influence the coal ignition temperatures and activation energy values of the combustion.

6. ACKNOWLEDGEMENTS

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