FACTORIAL DESIGN FOR THE EVALUATION OF THE INTERACTION EFFECT BETWEEN PARTICLE SIZE AND HEATING RATE IN THE KINETIC ENERGY OF COAL COMBUSTION

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Abstract. *This paper evaluates the behavior of kinetic energy for different heating rates (α) and particle sizes of the material in the study of the coal combustion process. It aims to obtain a response surface in a large range of particle size, using heating rates between the minimum and maximum values allowed by the equipment. Therefore it searches for a model to evaluate the interaction effect between particle size and the heating rate and to predict the activation energy of the process studied. The activation energy of the process was determined using the isoconversional model Model Free Kinetcs. In this model, the activation energy (E_α) is obtained as a function of the reaction extent (α). The subscript in E_α designates the values related to a given value of conversion (α). All experiments were conducted in thermogravimetric balance using samples of a Brazilian coal (EC4500) witch average particle size between 163 to 650 μm and heating rates between 10 and 40 $^oC\ min^{-1}$ in dynamic atmosphere of air. A Central Rotatable Composite Design was applied for the 2^2 factorial design including 4 tests under the axial conditions and 3 repetitions in the central point. As expected, the results show that both the particle size and the heating rate affected significantly the values of activation energy of the coal combustion process obtained by the model used.*

Keywords*: kinetics, combustion, Factorial Design, DCCR*

1. INTRODUCTION

The knowledge on chemical kinetics of coal combustion process is important for both burning rate of the involved materials 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 combustion processes of coals and chars (Dutta and Wen, 1977, Smith, 1978; Laurendeau, 1978; Cumming, 1984; Hakvoort et al., 1989).

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 for different ranks of coals, from lignite with low volatile to bituminous coal. They considered four combustion regions at different ranges of temperature and obtained different values of activation energy. Cumming (1984) confirmed the findings of Smith et al. (1981) and proposed a procedure for determining the mean activation energy for different values at different ranges of temperature.

According to Laurendeau (1978), pore size distribution and internal surface area of pores determine intrinsic reaction rates of coals. Dutta and Wen (1977) determined the reactivity of various coals in atmospheres of CO_2 and O_2-N_2. They observed that the reactive process in CO_2 atmosphere occurs in two different stages, i.e. pyrolysis and char-CO_2 reaction. The reactivity during pyrolysis is mainly a function of volatile fraction and heating rate and the reactivity during reaction to CO_2 is mainly a function of the coal type. Otherwise, the reactivity of coals in O_2-N_2 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, but only on temperature. Otherwise, they observed that pre-exponential factors depend on both coal properties and combustion controlling mechanism.

Isoconversional methods have been extensively used to calculate the activation energy from thermogravimetric experiments with a constant heating rate. The main advantage of these methods is the obtaining of energy activation regardless of kinetic model. However, depending on the heating rates used, different values of activation energy are

obtained for the same process studied. However, different activation energy is also observed for other variables of the process

Factorial Experimental Designs is a tool that can be used to evaluate the effects of independent variables or factors in the process (Rodrigues and Iemma, 2005). For determination of activation energy of combustion process using TGA and isoconversional method, two variables have influence on determination of activation energy: heating rate and particle size

The aim of this study is to evaluate the behavior of activation energy for secondary combustion (char combustion) using different heating rates (β) and particle sizes of a Brazilian coal. A Central Rotatable Composite Design (DCCR) to obtain a response surface was applied.

2. EXPERIMENTAL

2.1. Experimental Procedure

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}) was used in the experiments.

Thermogravimetric (TG) experiments, coal samples with mean size of 163 to 650 μm and 5.0 ± 0.5 mg were used. For kinetic study of coal combustion, non-isothermal TG tests were applied. Different heating rates, between 10 and 40 ^{o}C/min, from room temperature up to 900 ^{o}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}.

2.2. Kinetic Methods

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

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

The approach considers conversions measured in multiple experiments, thereby avoiding the uncertainty that results from a single experiment (Crnkovic et al., 2007). The kinetics of heterogeneous reactions in solids is usually described in terms of a single step kinetic correlation, such as Eq. (1) (Vyazovkin and Dollimore, 1996).

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

where t is the time, T is the temperature, α is the extent of conversion, and f(α) is the reaction model.

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

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

The explicit temperature dependence of the rate constant is introduced by replacing k(T) with the well known Arrhenius equation, which gives

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

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the universal gas constant.

From Eq. (3) one obtains

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

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

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

Since E/2RT >> 1, the above temperature integral can be approximated by (Vyazovkin, S., Dollimore, D., 1996; Majchrzak-Kucęba and Nowak, 2004):

$$\int_0^{T} \exp\left(-\frac{E}{RT}\right) dT \approx \frac{R}{E} T^2 \exp\left(-\frac{E}{RT}\right) \tag{6}$$

Substituting Eq. (6) into Eq. (5), and applying the natural logarithm operator, one has

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

where subscript α represents the values related to a given conversion.

In the model-free kinetics method, the activation energy (E) as a function of the conversion (α) is found. The conversion is determined as shown in Eq. (8):

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

where *m* is the local sample mass that varies with the time, m_0 is the initial sample mass and m_∞ is the final sample mass.

The thermal degradation is carried out at least in three different heating rates (β) and the respective conversion curves are calculated from the measured TG data. For each conversion (α), $\ln(\beta/T^2)$ is plotted against $1/T_\alpha$ that results to a straight line with slope ($-E_\alpha/R$), thus providing the activation energy as a function of conversion.

2.3. Statistical Analysis - Experimental Designs

A Central Rotatable Composite Design (CRCD) was applied for the 2^2 factorial design including 4 tests under the axial conditions and 3 repetitions in the central point (0). Codes of -1.4142, -1, 0, +1, +1.414, for each factor were used (Tab. 1).

Table 1. 2^2 Factorial Design: Experimental Matrix.

Variables	Levels				
	-1.4142	-1	0	+1	+1.4142
ϕ_m (μm)	158.7	225	385	545	611.3
β ($^oC\ min^{-1}$)	10.9	15	25	35	39.1

Table 1 shows the variables used in this study: heating rate (β) and average particle size (ϕ_m). The second to fifth columns show the corresponding coded factor to the two levels (high and low, or +1 and −1), to the axial conditions ($(2^2)^{1/4}$, or +1.4141 and -1.4141) and to the central point (0) for each variables.

Table 2. 2^2 Factorial Design: Experimental Matrix to ϕ_m

Variables	Levels				
	-1.388	-0.969	0	+1	+1.656
ϕ_m (μm)	163	230	385	545	650
Variables	Levels				
	-1.5	-1	0	+1	+1.5
β ($^oC\ min^{-1}$)	10±5	15±5	25±5	35±5	40±5

The averages particles size values are limited to values obtained between two subsequent ASTM sieves. Thus, it was used values closest possible those values calculated considering the sieves available in the laboratory and the coded factor was recalculated (Tab.2). The values of heating rate were approximate to integer values and each set correspond to the heating rate value of β ± 5°C/min, for example: for β = 25°C/min, the set is β=25 ± 5°C/min, i.e., 20, 25 and 30 °C/min (Tab. 2).

In these conditions, the quadratic model is used for both variables that are fitted to the data, represented by Eq. (9):

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 \tag{9}$$

where b_0, b_1, b_2, b_{11}, b_{22} and b_{12} are the estimators of model parameters and x_1 and x_2 represent the factors encoded, that are obtained by the method of least squares. In its matrix form, we have:

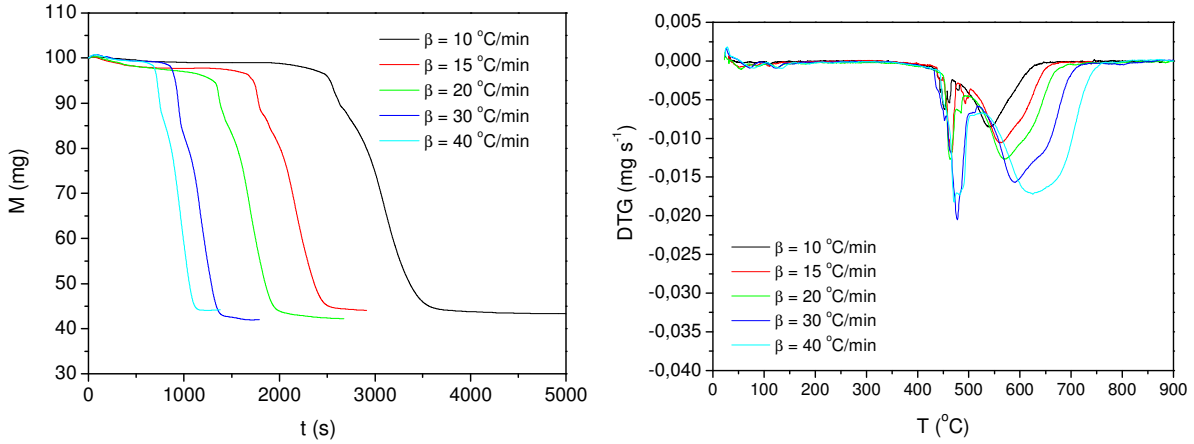
$$b = \left(X^t X\right)^{-1} X^t y \tag{10}$$

where y is the array with the values activation energy obtained by Model-Free Kinetics.

3. RESULTS

3.1. Effect of particle size and heating rate on the Thermal Decomposition of Coal

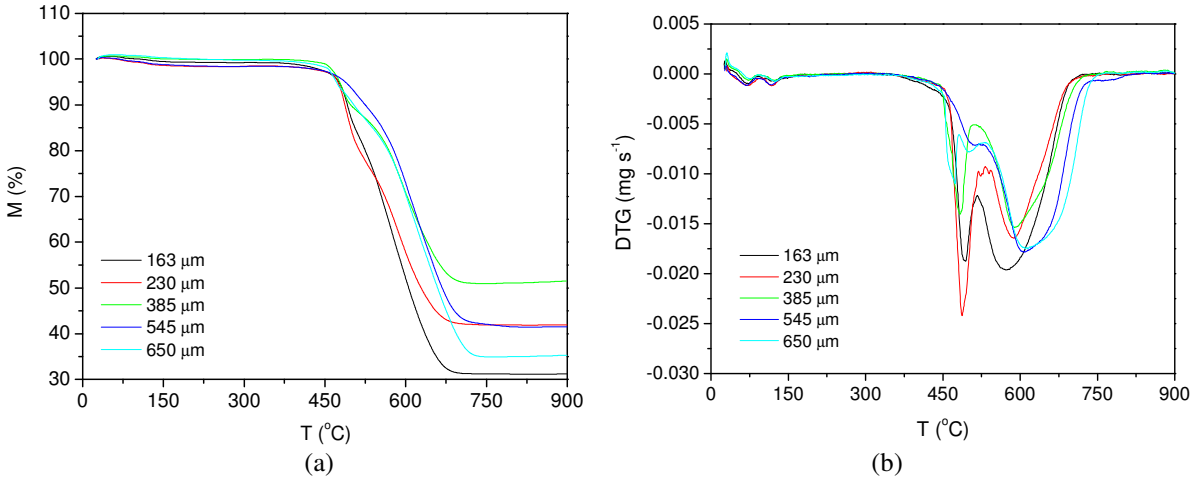
Figures 1a and 1b show the effect of heating rate (β) on the range of temperature for coal thermal decomposition.



(a) (b)

Figure 1. Effect of heating rate (β) in the decomposition of coal EC4500 with an average particle size of 385 μm: (a) TG curves and (b) DTG curves.

Figure 2 shows the effect of average particle size ($ø_m$) in TG curves (Fig. 2.a) and in their DTG curves (Fig. 2.b.).



(a) (b)

Figure 2. Effect of average particle size ($ø_m$) curves of coal combustion EC4500 with β = 30 °C/min: Profiles (a) TG and (b) DTG as a function of temperature.

Through DTG curves (Fig. 1b) it can be clearly observed the occurrence of two distinct events of mass loss at temperatures between 400 and 750 ° C. These events are identified as primary combustion (combustion of volatile) and secondary combustion (combustion of char) (Crelling et al., 1992). The results show that these events were more intense at higher heating rate.

It is noted in Fig. 2a that there are different decomposition behaviors for different particle size. DTG curves (Fig. 2b) shows that both primary and secondary combustion are more pronounced for smaller particles size (163 and 230 μm). It may be correlated with the releasing of the compounds from the bulk of the particles during combustion process, i.e., the smaller the particle size, more readily the compounds are released.

As can be seen in Figs. 1 and 2 both factors (β and ϕ_m) affect the behavior of the coal combustion process and, in this work, activation energies for the secondary combustion were evaluated for 9 different combinations of β and ϕ_m using factor design.

3.2. Application of Model Free in different particle sizes and ratios of heating

Model-free Kinetics was applied at three heating rates to determine the activation energy for EC4500 in one combustion region (secondary combustion – combustion of char).

The results are shown in Fig. 3, in which the curves represent the activation energy versus conversion (α) for the char combustion of coal EC4500.

It is noted in Fig. 3 that depending on the particle size and heating rate adopted, different values of E_α were obtained. For the case using particle size of 650 μm and heating rate of 25 ± 5 °C/min (20, 25 and 30 °C/min) the average of activation energy (0< α < 1) was 67.05 kJ/kmol and for the case using particle size of 545 μm and heating rate of 15 ± 5 °C/min (10, 15 and 20°C/min) the average of activation energy was 137.12 kJ/kmol

In addition, Fig. 3 shows that using other combinations of particle size and heating rate, other activation energy values are obtained. To obtain a response surface and evaluate the behavior of activation energy for different combinations between factors (heating rate and particle size), the Factorial Experimental Designs was used.

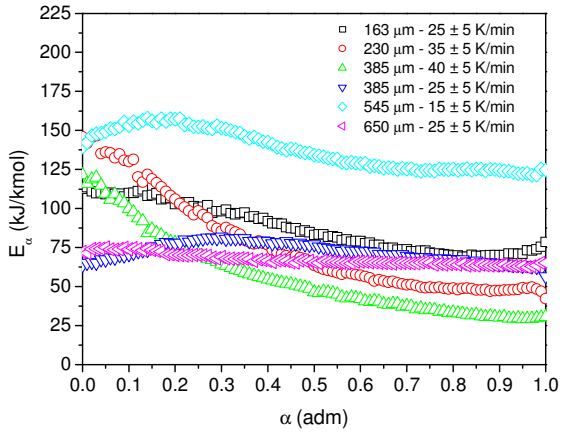


Figure 3. Activation energy (E_α) against conversion (α) along the second region of coal combustion (char combustion) to EC4500. E_α values considering three tests on β ± 5 °C/min were obtained.

3.3. Application of Factorial Design

Table 3 shows the experimental matrix and the results (activation energy of the secondary combustion of the CE 4500 coal) obtained for each combination of the CRCD 2^2 Factorial Design. It is observed that for application of Model Free Kinetics was necessary to obtain three TG curves, i.e. for each value of beta was required two more tests around its value, as previously described, in this work, β ± 5 °C/min, was adopted.

It is noted in Tab. 3 that lower value was obtained for high set of heating rate (40 ± 5 °C/min) and particle size of 385 μm.

Figure 4 shows the response surface and contour curves for activation energy of the char combustion obtained from experiments of factorial design.

The transient behavior of the non-isothermal tests, in which the coal's physical structure is continuously changed, and when higher temperatures are reached, 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 of porosity occurs and, consequently, the diffusion resistance decreases (Silva Filho, 2002). Another explanation for this behavior, can be given based on the interaction of the primary combustion on the secondary combustion, i.e., the start of the secondary combustion occurs after a complete combustion of the first step (primary combustion). Products from primary

combustion burn at the front of the particle contributing for its heating. From this statement and the results presented in Tab. 3, it may be said that higher heating rates favor the overlap of both stages and consequently leading to a decrease of the activation energy of the secondary combustion

Table 3. 2^2 Factorial Design: Experimental Matrix and Experimental Results.

No. of Tests	Value of Parameter in coded units		Value of Parameter in real units		[y] Average E_α (kJ/mol)
	x_1	x_2	$\phi_m \mu m$	$\beta \pm 5$ °C/min	
1	-0.969	-1	230	15	126.05
2	1	-1	545	15	137.11
3	-0.969	1	230	35	73.32
4	1	1	545	35	73.41
5	0	0	385	25	68.77
6	0	0	385	25	72.59
7	0	0	385	25	91.35
8	-1.388	0	163	25	86.45
9	0	-1.5	385	40	53.63
10	1.656	0	650	25	67.05
11	0	1.5	385	10	116.64

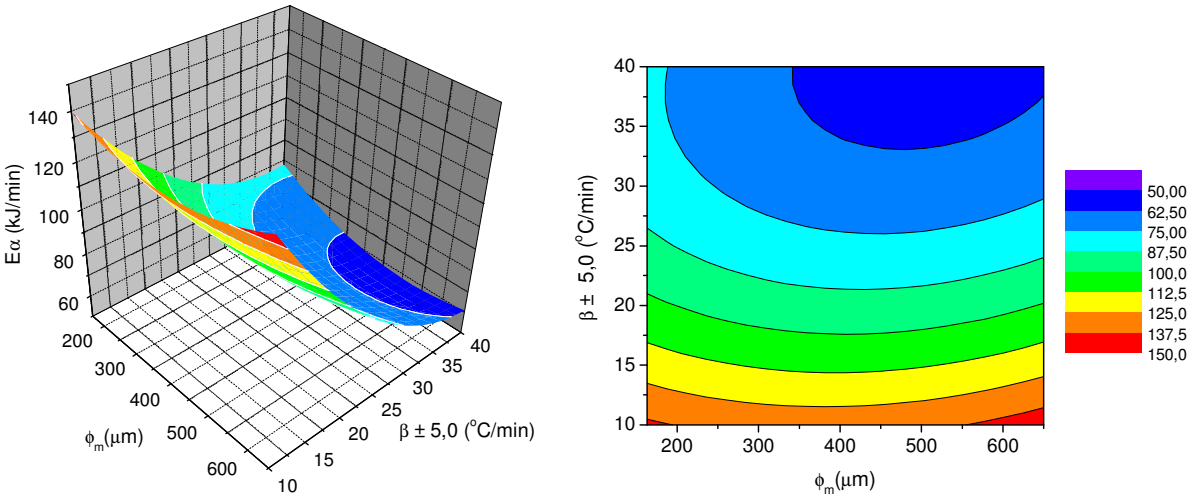


Figure 4. Response surface and contour curves for the char combustion to coal EC4500.

With respect to particle size, it was expected that particles sizes smaller than 545 μm could facilitate the coal thermal decomposition. But from results obtained in this work, different behavior was observed, the approaching to macroscopic gas-solid reactions given by the classic "*unreacted shrinking core*" model (Levenspiel, 1972; Wen and Wei, 1971), the reaction takes place along a symmetrical front that recedes towards the center of the particle. As the reaction front passes to any given point within the particle, total conversion of carbon occurs; moreover, an ash layer can form around about the central unreacted core (Laurendeau, 1978). In this case, the coal core is consumed by only chemical reaction and the combustion is controlled by a combined mechanism of oxygen diffusion in the direction of the particles of coal, oxygen diffusion through the ash and kinetics of chemical reaction in the core surface unreacted. Considering this hypothesis, possibly when the reaction progresses inwards, the internal temperature increases and,

consequently, favors the reaction kinetics of combustion thereby reducing the kinetic energy. With smaller particles sizes, possibly this increasing of internal temperature does not occur .

These results suggest that high heating rates favor the secondary combustion and consequently leading to a decrease of activation energy.

Table 4 presents some literature data of activation energy to both coal and char combustion. It is observed that the result obtained in this work is within the range of activation energies reported in the literature.

Table 4. Results to activation energy presents in literature to both coal and char combustion.

References	Type	E (kJ/mol)
Field et al. (1967)	Several coals and chars	149.5 (average)
Dutta and Wen (1977)	Several coals and chars	129.8 (average)
Smith (1981)	Several coals and chars	100-167
Cumming [17]	Lignite [(a)]; Bituminous [(b)]; Anthracite [(c)]	56-65[(a)]; 72-114[(b)]; 108-153[(c)]
Hakvoort et al. (1989)	Several coals	108-142

4. CONCLUSIONS

In this study the EC4500 coal was used and activation energies for the secondary combustion were determinate using thermogravimetry and Model-Free Kinetics. Depending on particle size and heating rate, values between 53.63 and 137.1 kJ/mol were obtained.

Two experimental factors affect the combustion process and the combinations of different ranges of them were used to use Central Rotatable Composite Design (DCCR) - 2^2 factorial design including 4 tests under the axial conditions and 3 repetitions in the central point.

For each combination of particle size and heating rate an activation energy value was calculated and the response surface and contour curves showed that the activation energy for the secondary combustion region were lower in conditions of high heating rate (40 ^{o}C/min) and particle size between 400 and 500 μm.

This result is an indicative that for this particle size, possibly when the reaction progress inwards, the internal temperature increases favoring the reaction kinetics of combustion This increasing of internal temperature does not occur for smaller particle size. Considering heating rate, as the testes are in a transient condition probably the primary combustion has an interaction on the secondary combustion for higher heating rate, i.e., products from primary combustion burn at the front of the particle, contributing for the heating of the particle and consequently supplying energy for the secondary combustion. From these statements, it can be concluded that the combination of the appropriate particle size and heating rate, less external energy is required, explaining lower activation energy

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