DETERMINATION OF THE KINETICS PARAMETERS OF OXY-FUEL COMBUSTION OF COAL WITH A HIGH-ASH CONTENT

[REV E1] Comentário: The title is imprecise. The authors should refer to Kinetics and not Kinetic. The correct is High-ash and not High Ash.

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ABSTRACT: The aim of this study is to determine the kinetic parameters of the oxy-fuel combustion of *char* from a bituminous coal with a high-ash content. The *char*, with a particle diameter of 715 µm, was prepared in an N_2 atmosphere at 1173 K. The oxy-fuel combustion assays were performed using a thermobalance at different temperatures with O_2/CO_2 gas mixtures of different concentrations. According to the unreacted core model, the process is controlled by chemical reaction at low temperatures, with an activation energy of 56.7 $kJ.mol^{-1}$, a reaction order of 0.5 at 973 K and a reaction order of 0.7 at all. The use of the continuous reaction model did not provide a good fit to the experimental data because the consumption of the particle during the reaction was not constant as predicted by the model. According to the Langmuir-Hinshelwood model, the value obtained for the activation energy for the first step was 37.3 $kJ.mol^{-1}$.

Key-words*: char, oxy-fuel combustion, thermobalance, kinetic*

1. INTRODUCTION

Among the energy sources available worldwide, the most widely used is fossil fuel, especially oil, natural gas and coal, the latter of which represents 27 % of the total fossil fuel supply (WCI, 2005). Although 80 % of Brazil´s domestic energy supply derives from combustion, and mineral coal is responsible for 5.2 % of the fuels used in combustion, the generation of electrical energy in Brazil is essentially hydroelectric (BEN, 2012). The coal is manly used in thermoelectric plants (85 %), the cement industry (6 %), cellulose (4 %) and chemical industries (5 %) (SOARES, *et al*., 2008).

[REV D2] Comentário: The Brazilian energy segment is based on hydraulic power, with coal being responsible for 30 % of the supply of non-renewable energy sources." is unclear. Note that the "electrical generation sector" is intensive in hydraulic energy, but "energy" in Brazil (including all primary energy sources) is about 80% generated by thermal means, mostly, oil, ethanol and wood. Check BEN 2011 and correct the statement.

[REV G3] Comentário: The first paragraph of the Introduction contains outdated data; as data for year 2005 is 9 years old, and many things have changed since for coal, with the advent of low priced shale/tight gas.

The abundance of mineral coal´s reserves and its geographical distributions, as well as its low cost and stable prices in relation to other fuels, are among the advantages of using this fuel. The greatest disadvantage of the use of this source of fossil energy is the resulting high rate of emission of greenhouse gases. Among these is CO_2, representing 80 % of greenhouse gas emissions (EIA, 2011). Due to great concerns over the levels of this gas in the atmosphere, technologies have been developed for its capture and storage (BACHU *et al*., 2007, BUHRE *et al*., 2005, CAILLY *et al*., 2005, MIDDLETON *et al*., 2011, QANBARI *et al*., 2011, TOFTEGAARD *et al*., 2010, STANGER and WALL, 2011, WALL *et al*., 2009).

One of the ways to CO_2 is oxy-fuel, which consists in burning a carbon source in an O_2 enriched atmosphere, using CO_2 and water as the main combustion gases (BUHRE *et al*., 2005, IRFAN *et al*., 2011, MIDDLETON *et al*., 2011, QANBARI *et al*., 2011, STANGER and WALL, 2011, TOFTEGAARD *et al*., 2010, WALL *et al*., 2009). Combustion with pure O_2 would lead to a high-temperatures flame, so CO_2 is recirculated in the burners to control the temperature of the system. The oxy-fuel process comprises simultaneous reactions of combustion and gasification, and the main reactions are as follows:

$$C_{(S)} + O_2 \rightarrow CO_{2(g)}$$

$$C_{(S)} + CO_{2\,(g)} \rightarrow 2\ CO_{(g)}$$

In both processes, coal pyrolysis occurs first, which leads to *char* production. The term ‘pyrolysis’ describes the devolatilisation of carbonaceous material under a controlled atmosphere and temperature. The volatilised material consists of water vapour, methane and tar, and the solid residue is known as *char*.

Oxy-fuel combustion differs from air combustion in several respects, including flame temperature, delay in flame ignition and the reduction of NO_X and SO_X emissions, effects that can be explained by the different properties of CO_2 and N_2 gases

[REV G4] Comentário: The first sentence of the second paragraph of Introduction (please insert page numbers!) makes no logical sense whatsoever “Despite being a highly polluting fuel, coal deposits are widely distributed throughout the word” There is no cause and effect relation in this sentence. Coal deposits can be widespread in the word, regardless of the pollution propensity of this fuel. There are many more sentences like this in the manuscript.

[REV D5] Comentário: The statemanet "However, investments in clean technologies are required to minimize or eliminate the emission of gas pollutants such as CO2, NOx, SOx as well as particulate matter." is incorrect. CO2 is not really a gas pollutant in the same sense as NOx, CO, and SOx. It is a GHG. It is related to plant efficiency and not to the completeness of the combustion or to the efficacy of the gas cleaning system.

[REV D6] Comentário: The statement "Despite being a highly polluting fuel,..." is not precise. It is possible to use a clean coal combustion system. Better would be to mention something related to the emission of CO2, or global atmospherif CO2 inventary, or something related to GHG.

(KHATAMI *et al.*, 2012).

Understanding the behaviour of mineral coal in this new combustion environment is important for the adaptation and/or sizing of equipment to yield a clean form of energy production.

Thermogravimetric analysis is widely used as an investigative or comparative tool in the study of thermal events such as combustion and coal pyrolysis.

Several studies conducted in the 1980s have addressed the kinetics of coal gasification in Brazil (SCHMAL *et al.*, 1982 e JOSÉ, H. J., 1989). For instance, Schmal *et al*. (1982) studied the kinetics of coal gasification of southern Brazil with a high-ash coal between the temperatures of 1073 K and 1273 K. The authors determined that the unreacted core model fit the results up a temperature of 1123 K, and above that temperature, the continuous reaction model was optimal.

HECHT *et al.* (2011) studied a volatile bituminous coal with a high-ash content under different concentrations of O_2 (12, 24 and 36 %) at a temperature of 1724 K and observed that the consumption of *char* reached an optimum point in an environment of 24 % of O_2, where oxidation and gasification accelerate the loss of mass of the particle.

LI *et al.* (2009) pyrolysed a sample of bituminous coal at 1273 K in atmospheres of 100 % N_2 and 21 %N_2/79 %CO_2 using 3 heating rates: 10, 20 and 30 K.min^{-1}. They observed that the faster the coal was heated, the less time was required for pyrolysis, which reduced the loss of mass during devolatilisation and, consequently, increased the proportion of carbonaceous matter. However, little influence was observed during combustion. For oxy-fuel combustion, concentrations of 21, 30, 40 and 80 % O_2 in CO_2 were used, and it was found that increasing the concentration of O_2 in the gaseous mixture reduced the need for high temperatures. The amount of released CO was greater in oxy-fuel combustion, despite the lower levels of SOx and NOx released.

[REV D7] Comentário: The statement: " ...effects that can be explained by the different properties of the CO2 and N2 gases (INCROPERA and DeWITT, 2003). " is not clear. Better improve or remove it. There is no point in citing this reference in this context.

[REV G8] Comentário: The second paragraph on page 3 (I paginated the manuscript) give no reference on ignition delay and reduction of NOx and SOx, as the reference to Incopera and DeWitt only refers to the different properties of gases. Suggested references are: R. Khatami, C. Stivers and Y. A. Levendis. “Ignition Characteristics of Single Coal Particles from three Different Ranks in O2/N2 and O2/CO2 Atmospheres.” Combustion and Flame, 159, 3554-3568, 2012.

[REV D9] Comentário: Literatture review: It would be kind to cite (and recognize) the pioneering work in the kinetics of gasification of Brazilian coals: Martin Schmal , Jose Luiz Fontes Monteiro , Jorge Luiz Castellan, Kinetics of coal gasification, Ind. Eng. Chem. Process Des. Dev., 1982, 21 (2), pp 256–266. Humberto Jorge José, Zur Reaktivität von Koksen aus Santa Catarina-Steinkohle, Brasilien, bei der Vergasung mit Wasserdampf und Kohlendioxid. Thesis, RWTH Aachen, Germany, 1989.

[REV G10] Comentário: Other discrepancies. On page 3, last paragraph: … and it was found that there is the need for a temperature increase with the increase in the concentration of O2….” Again, it makes no logical sense. The temperature increases with O2 by default. It is not because there is a need for that. An English language review may help here

GIL *et al.* (2011) studied four types of *char*: a semi-anthracite, a medium-volatile bituminous and two highly-volatile bituminous *chars*, pyrolysed at 1273 K in atmospheres of 100 % N_2 and 100 % CO_2. The authors concluded that there was a greater loss of mass during devolatilisation using 100 % CO_2 and that the *char* produced had as lower reactivity due to its more stable structure.

CAROTENUTO *et al.* (2011) studied 3 types of coal under oxy-fuel combustion, including a south Brazilian coal from Mina do Leão II, the same as that used in the present study. The temperatures studied were 1073, 1173 and 1273 K in atmospheres of 21 % O_2 in CO_2 and 21 % O_2 in N_2 (air). The authors reported a greater consumption of O_2 under conditions of oxy-fuel combustion compared to conventional combustion. They also observed that increasing the reaction temperature increased the consumption of O_2.

Based on the results of the research described above, experimental parameters were established for this work, including the atmosphere used for pyrolysis, the temperature of the oxy-fuel and the concentration of O_2 in CO_2 to evaluate the kinetic parameters of oxy-fuel combustion. The motivation for this study is based on the need to obtain a permanent set of data to understand the conversion of mineral coal *char* in oxy-fuel combustion conditions. Therefore, the present manuscript was aimed to study the oxy-fuel combustion of *char* produced in an atmosphere of N_2 from a Brazilian bituminous coal with a high ash content, using a thermobalance. The oxy-fuel combustion reaction was studied with concentration of 10 to 30 % O_2 in CO_2 and at temperatures ranging from 973 to 1273 K.

The experimental parameters used to evaluate the kinetics of the oxy-fuel combustion of a Brazilian sub-bituminous coal were selected for the purpose of gathering useful data for the sizing and modelling of fluidised-bed reactors.

[REV G11] Comentário: The last paragraph of Introduction should explain the need and the motivation for this work.

[REV G12] Comentário: Starting with the Abstract and the Introduction, the authors never say how their data and deduced activation energies at the moderate temperature of TGA will help advance the technology of high temperature pulverized fuel combustion, or are they targeting moderate temperature fluidized fuel combustion? They need to elaborate and explain what is the need for their work and what are the contributions to applications.

2. MATERIALS AND METHODS

2.1 Sample

A sample of *ROM* (Run of Mine) coal, which had been crushed and sieved to yield an average particle diameter of 715 µm was used for the production of *char* in an atmosphere of N_2. The results for immediate analysis, elemental analysis and surface area are shown in Table 1:

[REV D13] Comentário: in diameter between 590 and 840 µm". Do you mean the range of coal particle sizes in the sample? Clarify

(TABLE 1)

2.2. C*har* preparation

For the production of *char*, 100 g sample of coal was placed in a stainless steel reactor (14 cm high and 6 cm in diameter), and heated in a muffle furnace, as shown in Figure 1. The unit had an inert gas inlet and an outlet for the gases produced during pyrolysis, as well as a temperature controller and a thermocouple to measure the axial temperature of the reactor. During *char* production, an N_2 atmosphere, a granulometric range of 590 to 840 µm and a temperature of 1173 K were used. The heating rate of the sample was 20 $K.min^{-1}$ from room temperature to the final temperature. It was observed that after 100 minutes of heating, the sample mass remained unchanged, but all volatile matter had been eliminated. Due to the heterogeneity of the raw material being worked on, a residence time in the reactor of 105 minutes was established.

[REV D14] Comentário: Specify the amount of sample used (in grams) and the aspect ratio of the sample: diameter and height of the coal sample (e.g., the diameter and height of the sample bed within the crucible).

[REV D15] Comentário: After pyrolysis, how much of the volatile contents was removed? How the mass after pyrolysis compare to the proximate analysis?

(FIGURE 1)

2.3. Oxy-fuel combustion

The oxy-fuel combustion of *char* was analysed with the use of a thermobalance (Netzsch 409) under atmospheric pressure. Approximately 30 mg of *char* was placed in a dish crucible whose base was formed by a platinum screen, allowing the passage of reagent gases through the sample. A thermocouple located below the dish monitored the temperature, which ranged from 973 to 1273 K. The gases used in the experiments were introduced in the thermobalance at a rate of 120 mL.min^{-1}, with O_2 concentrations in CO_2 varying from 11 to 30 %. The X conversion of *char* was calculated according to equation (1):

$$X = \frac{M_i - M}{M_i - M_C} \qquad (1)$$

Where M_i represents the initial mass of the *char* (mg), M is the instantaneous mass (mg), and M_C is the final mass after oxy-fuel combustion (mg) (LEVENSPIEL, 1976).

2.4. Kinetic model

Models for the interpretation of kinetic data from gas-solid reactions may be found in the literature. Three of these models were used to model the experimental results obtained and to determine the kinetic parameters of the oxy-fuel combustion reaction of the studied *char*:

- Unreacted Core Model: the reaction starts at the outside surface and moves to the centre of the solid, leaving a layer of inert solid, i.e., ashes. The model considers the occurrence of five sequential steps: 1st: diffusion of reagent gas through the stagnant film of gas at the surface of the solid particle; 2nd: diffusion of reagent gas through the ash layer; 3rd: reaction of gas with the solid on its surface 4th: diffusion of the gas product generated by chemical reaction through the ash layer; 5th: diffusion of the gas product through the layer of stagnant film of gas around the particle.

Each of the steps is modelled by a mathematical equation depending on conversion over time (BARRANCO *et al.*, 2009, LEVENSPIEL, 1976).

Whenever the diffusion of the reagent gas A through the stagnant film of gas on the surface of the solid particle controls the reaction, the reaction may be modelled by equation (2), where the expression for τ is shown in equation (3):

$$\frac{t}{\tau} = X \tag{2}$$

$$\tau = \frac{\rho\, R}{3k_g P_{O_2}} \tag{3}$$

Where τ is the time for the full conversion (s), R is the radius of the *char* particles (cm), ρ is the specific mass of the *char* sample (g.cm^{-3}), P_{O_2} is the partial pressure of oxygen (atm) and k_g is the coefficient of mass transfer between the fluid and solid (g.cm^{-2}.s^{-1}.atm^{-1}).

If the ash layer acts as a barrier controlling the process, then the results can be modelled according to equation (4), where the expression for τ is shown in equation (5):

$$\frac{t}{\tau} = 1 - 3(1 - X)^{2/3} + 2(1 - X) \tag{4}$$

$$\tau = \frac{\rho\, R^2}{6\mathcal{D}_e P_{O_2}} \tag{5}$$

Where τ is the time for the full conversion (s), R is the radius of the *char* particles (cm), ρ is the specific mass of the *char* sample (g.cm^{-3}), $\mathcal{D}_e$ is the coefficient of effective diffusivity (cm².s^{-1}) and P_{O_2} is the partial pressure of oxygen (atm).

[REV D16] Comentário: Eq. (10) relates a volumetric concentration of C to a surface reaction rate. Considering the particle as spherical, the ratio of V/As results in R/3. Therefore, a number constant 3 is missing in the denominator of Eq. (10). Eq. (12) and the reported values of pre-exponential factors should be corrected appropriately.

[REV E17] Comentário: Equations 3 to 5 are too simplistic to express the series of mass-transfer resistances. The authors would find much more complete treatments in the literature.

[REV G18] Comentário: What is r in equation 2 ? It is not explained. Is it R, the radius of the particle

[REV D19] Comentário: It is not clear to me why in Eqs (3) to (5) the authors use "Tau" and in Eq. (6) they use "k". This distinction seems unnecessary to me and could use either one or the other, but should use a uniform notation.

If case the chemical reaction is the limiting step of the reaction, such gas-solid surface reaction can be modelled according to equation (6), where the expression for τ is shown in equation (7):

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3} \tag{6}$$

$$\tau = \frac{\rho\, R}{k\, P_{O_2}} \tag{7}$$

[REV D20] Comentário: Identify the symbol "r" in equation 2.

Where τ is the time for the full conversion (s), R is the radius of the char particles (cm), ρ is the specific mass of the *char* sample (g.cm^{-3}), k is the superficial first-order reaction rate constant (g.cm^{-2}.s^{-1}.atm^{-1}) and P_{O_2} is the partial pressure of oxygen (atm).

- Continuous Reaction Model: the reaction occurs simultaneously across the entire particle as the reagent gas is consumed. This model was developed for those cases where the diffusion of the reagent gas is much faster than the chemical reaction involved. Equation (8) represents this model:

$$-\ln(1 - X) = kt \tag{8}$$

- Langmuir-Hinshelwood Model: this model establishes a formula for the rate of heterogeneous chemical reaction that combines the behaviours of the steps of adsorption, desorption and chemical reaction. The reaction occurs via two elementary steps (9) and (10):

$$C + O_2 \overset{k_1}{\rightarrow} C(O) \tag{9}$$

$$C(O) \overset{k_2}{\rightarrow} CO \tag{10}$$

Where C(O) represents the species adsorbed on the particle surface. According to the model, the order of the reaction varies with the oxygen concentration and with temperature, and the model itself should be used for high temperatures. In this case, the reaction rate can be expressed by equation (11):

$$(-r_A) = \frac{k_1 k_2 P_{O_2}}{k_1 P_{O_2} + k_2} \qquad (11)$$

Where $(-r_A)$ is rate of reaction, k_1 (gmol.cm^{-2}.min^{-1}) and k_2 (gmol.atm.cm^{-2}.min^{-1}) represent the specific speeds of reactions (9) and (10), respectively, and P_{O_2} represents the partial pressure of oxygen (atm).

[REV D21] Comentário: After Eq. 9: k1 and k2 are not specific speeds. They are effective rate constants. Note that an equilibrium constant for O adsorption is lumped in k1 as well as a measure of the active surface areas (ash is not reactive, but may influence reaction)

Note that in the Langmuir-Hinshelwood model, two parallel reaction step in the gaseous phase of oxidation of CO (equation 12) are not considered.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad (12)$$

[REV D22] Comentário: In the presence of excess oxygen, a third reaction may come into play: CO + 1/2 O2 = CO2, i.e., the gas phase CO oxidation reaction. Why is this not listed as a possible reaction in parallel with the LH mechanism (reactions (7) and (8)

3. RESULTS AND DISCUSSION

3.1. Effect of temperature

To evaluate the effect of temperature on the reaction rate of oxy-fuel combustion of *char*, the temperatures 973 K, 1073 K, 1173 K and 1273 K were used, and the other variables were fixed. These temperatures were selected considering the preliminary results obtained in the thermogravimetric tests shown in Figure 2, which were carried out at Brandenburg University of Technology in Cottbus – Germany using a sample of coal from Mina Leão II in the granulometric range 0.125 – 0.500 mm (CAROTENUTO *et al.*, 2012).

(FIGURE 2)

As shown in Figure 2, the loss of normalised carbon demonstrates consistent behaviour up to 1073 K, both under N_2 and CO_2 atmospheres. Above this temperature, the Boudouard reaction occurs, and consequently, the carbon is consumed.

Figure 3, below, shows the curves of *char* conversion relative to time for the temperatures 973 K, 1073 K, 1173 K and 1273 K, using a mixture of 20 %O_2/80 %CO_2 as the reagent gas.

(FIGURE 3)

It can be seen that increasing the temperature increases the rate of consumption of *char*, i.e., increases the reaction rate. For the temperatures of 973 and 1073 K, the behaviour of *char* conversion in relation to time is very similar, but for the temperatures of 1173 and 1273 K, there is a significant increase in the reaction rate in relation to temperature. Most likely, the increase in temperature causes an increase in the surface area of the *char*, facilitating the access of reagent gases to the sample surface. This behaviour shows that the kinetic regime controls the process.

[REV D23] Comentário: After presenting Figure 3: The statement "This occurs because the activation energy of the reaction decreases with increasing temperature. " is not correct. In a purelly chemical kinetics determined regime, the activation energy is a constant, i.e., not affected by the temperature. But, the reaction speed depends exponentialy on the temperature and increases as the temperture increases. Figure 3 shows that a reaction mechanism peaks up at a temperature above 1073 K

[REV G24] Comentário: Now there is an issue that is confusing: On the first page of the Section Results and Discussion (page 9 on my count), last two lines “This occurs because the activation energy of the reaction increases with increasing temperature.” This statement merits further discussion, why is that the case ? Where is this shown ? If this is indeed the case, then please include an expression for the activation energy as a function of temperature. And how come the authors reported in the Abstract and Conclusions Sections one value of the activation energy (per model) and not different values at different temperatures ?

3.2. Influence of O_2 concentration in the gas mixture

Due to differences in the physicochemical properties of N_2 and CO_2, it is known that the ignition of coal is delayed in an oxy-fuel combustion atmosphere when a given concentration of O_2 is added to either N_2 or CO_2. To obtain the same temperature profile as in atmospheric air, which normally contains 21 % O_2 in N_2, a reagent mixture must contain 30 % O_2 in CO_2 (LIU *et al.*, 2005, KATHAMI *et al.*, 2012).

[REV G25] Comentário: On page 10, section 3.2: “To obtain the same adiabatic flame temperature..” Better yet compare with the same actual temperature using the reference: R. Khatami, C. Stivers, K. Joshi, Y. A. Levendis and A. F. Sarofim. “Combustion Behavior of Single Particles from Three Different Coal Ranks and from Sugar Cane Bagasse in O2/N2 and O2/CO2 Atmospheres.” Combustion and Flame, 159, 1253-1271, 2012.

Therefore, based on this information, the present study analyzed O_2/CO_2 gas mixtures in the proportions 10 % O_2/90 % CO_2, 20 % O_2/80 % CO_2 and 30 % O_2/ 70 % CO_2 at the temperatures 973 K, 1073 K, 1173 K and 1273 K, shown in Figure 4 and 5, as follows.

(FIGURE 4 AND 5)

For the four temperatures, it was observed that the increase in the O_2 concentration in the gas mixture increases the rate of conversion of *char*. This phenomenon indicates that the process is controlled by chemical reaction, although the overlap of the curves of 20 % and 30 % of O_2 in the mixture at a temperature of 1273 K point to a change in the controlling reaction states.

3.3. Kinetic Models

3.3.1. Unreacted core model

Figure 6 presents the fit of the unreacted core model to the experimental data at the temperature of 973 K for the steps controlled by the diffusion of the reagent gas through the stagnant film of gas on the surface of the solid particle and by the diffusion of the reagent gas in the layer of ash, respectively.

(FIGURE 6)

As seen in Figure 6, the proposed models do not provide a good fit to the experimental data because a continuous change occurs in the inclination of the straight lines, indicating an exchange of reactive control.

In Figure 7, the fit of the experimental data to the unreacted core model at the temperature of 973 K was calculated considering step 3 of the reaction process as the controlling step. It can be seen, in this case, that there is a good fit of the experimental data to the model, indicating that the chemical reaction is indeed the controlling step of the reaction process.

(FIGURE 7)

It can also be observed that at low concentrations of oxygen in the gaseous mixture, reaction is slower and the determining character of the chemical kinetics becomes more evident.

[REV D26] Comentário: The statement "the process occurs more slowly, thus facilitating the control " could be replaced by "reaction is slower and the determining character of the chemical kinetics becomes more evident.".

When the chemical reaction controls the reaction process, the time τ for the full conversion of the particle is given by equation (13):

$$\tau = \frac{\rho\, R}{k\, P_{O_2}} \qquad (13)$$

Where τ is the time for the full conversion (s), R is the radius of the *char* particles (cm), ρ is the specific mass of the *char* sample ($g.cm^{-3}$), k is the superficial first-order reaction rate constant ($g.cm^{-2}.s^{-1}.atm^{-1}$) and P_{O_2} is the partial pressure of oxygen (atm).

[REV E27] Comentário: Equation 2 should be corrected. “r” is not specified. On the other hand, the authors indicate “R” as particle radius, which does not appear on Equations 1 or 2.

Assuming that the rate of reaction $(-r_A)$ obeys equation (14):

[REV E28] Comentário: What are the units of “rA”? Further in the text, one finds Equation 12, which seems the correct one. However, and still, that should also be better supported with arguments and assumptions clearly listed.

$$(-r_A) = k\, P_{O_2}^{n} \qquad (14)$$

The rate of reaction $(-r_A)$ can therefore be calculated using equation (15):

$$(-r_A) = \frac{R.\rho}{\tau} \qquad (15)$$

Where $(-r_A)$ is the rate of reaction ($g.cm^{-2}.s^{-1}$), $R = 0.363$ mm, $\rho = 1.96\ g.cm^{-3}$ e τ

= the experimental values obtained from **Figures 4 and 5**.

By linearizising equation (14), it´s possible to determine the values of *k* and *n*, the order of the reaction. Using the Arrhenius equation, the pre-exponential factor, *A* (gmol.min^{-1}.cm^{-2}), and the activation energy of the reaction, *Ea* (kJ.mol^{-1}), may also be calculated. The Arrhenius equation is represented in equation (16):

[REV D29] Comentário: After Eq. (13) the authors should emphasize that the variation with T is used to determine k (in an Arrhenius plot) while the variation with pO2 is used to evaluate n

$$k = A\ exp\left(\frac{E_a}{\mathcal{R}T}\right) \tag{16}$$

Figure 8 presents the graph of the linearised Arrhenius equation. Analysing the behaviour of the results, it can be observed that there is a change in the dominant reaction mechanism, from chemically controlled at low temperatures to diffusion-controlled at high temperatures.

[REV D30] Comentário: Arrhenius plots of ln k versus 1/T are used to evaluate the activation energies. Therefore it is important to assure the reader that even at the higher temperatures the reaction regime remains determined by surface chemical kinetics

(FIGURE 8)

Thus, for the unreacted core model, values of 56.7 kJ.mol^{-1} for the energy of activation and 0.78 gmol.min^{-1}.cm^{-2} for the pre-exponential factor were obtained for temperatures between 973 K and 1073 K. For temperatures between 1073 K and 1273 K, the activation energy was 23.4 kJ.mol^{-1} and the pre-exponential factor was 0.56 gmol·min^{-1}·cm^{-2}. The order of reaction was 0.5 for 973 K and 0.7 for the other temperatures.

[REV D31] Comentário: The unit for Ea after Eq. 13 should not be "cal", but "J"

For the calculation of the kinetic parameters, the partial concentration of O_2 was considered as being proportional to the concentration of the reagent gas, a situation that occurs only at temperatures lower than 1073 K. For temperatures above 1073 K, it is also necessary to consider Boudouard’s reaction because in this case, reactions (17) and (18) occur simultaneously:

$$C + O_2 \rightarrow CO_2 \tag{17}$$

$$C + CO_2 \rightarrow 2CO \tag{18}$$

Figure 9 shows a sample of 30 mg of *char* on the platinum screen before being added to the thermobalance and the *char* obtained after oxy-fuel combustion. Due to the high-ash content of the samples, the particles did not suffer from size reduction after the oxy-fuel combustion process, which reinforces the hypothesis of the unreacted core model.

(FIGURE 9)

3.3.2. Continuous Reaction Model

The experimental data were not fitted to the continuous reaction model.

[REV D32] Comentário: The homogenoeus model does not provide a good fit, as shown in Figure 8. Therefore, what is the point in calculating kinetic parameters for this model ? I believe this is misleading and should be removed. I think the application of the homogeneous model should be presented up front and then disregarded as being inadequate to reproduced the measurements.

The *char* particles used contained 59.7 % ash scattered throughout their volume, making the consumption of carbon heterogeneous as the reaction proceeded to the interior of the particle. Therefore, the assumptions of the continuous reaction model were not satisfied in this case.

3.3.3. Langmuir-Hinshelwood Model

Because the rate of reaction $(-r_A)$ can be expressed according to equation (19), the specific rates k_1 and k_2 of reactions (9) and (10) can be evaluated through the determination of the angular and linear coefficients of the referred line:

$$\frac{1}{(-r_A)} = \frac{1}{k_2} + \frac{1}{P_{O_2}} \cdot \frac{1}{k_1} \tag{19}$$

Figure 10 shows the lines obtained at the temperatures of 973 K, 1073 K, 1173 K and 1273 K, using the Langmuir-Hinshelwood model to fit the experimental data of the oxy-fuel combustion of *char*.

(FIGURE 10)

Based on the equations of the lines shown in Figure 10, one can determine the specific rates for each step of elementary reactions (9) and (10), according to equations (20) and (21):

$$k_1 = A_1 exp\left(\frac{(E_a)_1}{RT}\right) \tag{20}$$

$$k_2 = A_2 exp\left(\frac{(E_a)_2}{RT}\right) \tag{21}$$

Table 2 shows the results obtained from k_1 and k_2 for the temperatures of 973 K, 1073 K, 1173 K and 1273 K.

(TABLE 2)

In Table 2, it can be seen that an increase in temperature causes the values of k_2 to increase more significantly than the values of k_1. This phenomenon indicates that increased temperature favours oxygen adsorption in the active sites of the carbon than the desorption of carbon monoxide from active sites, and, therefore, the reaction is a zeroth-order (HURT and CALO, 2001).

To determine the frequency and activation energy for each elementary step of the reaction, the Arrhenius equations (20) and (21) were used in linearised form, as shown in Figure 11.

(FIGURE 11)

The activation energy found for step 1 of the reaction process was 19.8 kJ.mol^{-1} (reaction 9) and 37.3 kJ.mol^{-1} for step 2 (reaction 10). The pre-exponential factor for step 1 was 0,995 gmol.cm^{-2}.min^{-1} and 2 gmol.atm.cm^{-2}.min^{-1} for step 2 of the reaction.

4. CONCLUSIONS

A high-ash mineral coal from Mina Leão II, previously pyrolysed with N_2 at 1173 K, was used in a study of oxy-fuel kinetics (using mixtures of O_2/CO_2 in concentrations of 10, 20 e 30 % O_2 in CO_2) at temperatures of 973, 1073, 1173 e 1273 K. The main conclusions of this study were as follows:

According to the unreacted core model, it was possible to observe the exchange of reactive control within the range of temperatures used. Below 1073 K, kinetic control predominates the reactions, with an activation energy of 23.4 kJ.mol^{-1} and a pre-exponential factor of 0.56 gmol.min^{-1}.cm^{-2}. Above this temperature, the control mechanism shifts and diffusion predominates, with an activation energy of 56.7 kJ.mol^{-1} and a pre-exponential factor of 23.5 gmol.min^{-1}.cm^{-2}. For the calculation of kinetic parameters, only the partial concentration of O_2 was considered as being proportional to the concentration of the reagent gas, a situation that occurs only at temperatures lower than 1073 K. For temperatures above 1073 K, it is also necessary to consider that the Boudouard reaction occurs simultaneously. This would explain why the order of the reaction is 0.5 for the temperature of 973 K and 0.7 for other temperatures.

Using the continuous reaction model did not yield a good to the experimental data because the model assumes a uniform consumption of carbon during the reaction, which does not occur experimentally due to the large amount of ash distributed throughout the *char* particles.

The activation energy found for the C-O_2 reaction using the Langmuir-Hinshelwood model was 19.8 kJ.mol^{-1} for the adsorption of oxygen atoms in the active sites of the carbon and 37.3 kJ.mol^{-1} for the desorption of carbon monoxide from active sites. The reaction and desorption steps of the Langmuir-Hinshelwood model not give us an exact value for the order of reaction.

Based on the experimental results obtained in this study, it is recommended that the unreacted core model be used to interpret data in the kinetic regime, for the scaling and modelling of fluidised bed oxy-fuel reactors using mineral coal.

NOMENCLATURE

A pre-exponential factor, gmol.min^{-1}.cm^{-2}

$\mathcal{D}_e$ the coefficient of effective diffusivity, cm^2.s^{-1}

E_a activation energy, kJ.mol^{-1}

k the superficial first-order reaction rate constant, g.cm^{-2}.s^{-1}.atm^{-1}

k_g the coefficient of mass transfer between the fluid and solid, g.cm^{-2}.s^{-1}.atm^{-1}

k_1 specific rates, gmol.cm^{-2}.min^{-1}

k_2 specific rates, gmol.atm.cm^{-2}.min^{-1}

M_i the initial mass of the *char*, mg

M the instantaneous mass, mg

M_c the final mass after oxy-fuel combustion, mg

n order of the reaction

P_{O_2} is the partial pressure of oxygen, atm

R the radius of the *char* particles, cm

$\mathcal{R}$ gas constant, 8.314 J.mol^{-1}.K^{-1}

$(-r_A)$ rate of reaction, g.cm^{-2}.s^{-1}

[REV G33] Comentário: Finally, on the second paragraph: The statement: “The particle can be considered homogeneous due to the amount of ash” make no sense. Why high ash induces particle homogeneity ?

[REV G34] Comentário: Also the three models had some discrepancies in their results. Which model is recommended ?

[REV G35] Comentário: In the Conclusions Section: Please reconcile your work with the requested statements of Introduction on the need and the motivation for this work. Did you succeed and why? What are your contributions ?

[REV E36] Comentário: The authors should provide a List of Symbols or Nomenclature.

T Temperature, K

t time, s

GREEK SYMBOLS

τ the time to complete the reaction, s

ρ the specific mass of the *char* sample, g.cm^{-3}

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Table 1 Composition of the coal and the *char* produced

Analyses	Levels (%)
Proximate analysis	
Volatile analysis[1]	18.4
Ashes[1]	48.7
Fixed carbon[1]	32.9
Elemental analysis[2]	
C	63.4
H	6.4
N	1.6
S	2.1
O	26.5
Surface area[3] - BET ($m^2.g^{-1}$)	29.7

[1] dry basis

[2] ash free dry basis

[3] analysis in the char produced.

[REV D37] Comentário: Table 1: Surface area = BET surface area ? Clarify.

Table 2 Values of the rate constants for each elementary step of the equation

Temperature (K)	k_1 (gmol.cm^{-2}.min^{-1}).10^{-2}	k_2 (gmol.atm.cm^{-2}.min^{-1}).10^{-2}
973	8.80	1.81
1073	9.94	3.62
1173	14.40	3.91
1273	14.75	5.83

[REV D38] Comentário: What does the uncertainty in k1 and k2 listed in Table 2 mean? Reduce the significant figures in the results listed in Table 2. For example, if the uncertainty in k2 for 1273 K is 7, why list k2 as 19.45? It is not possible to believe in an uncertainty listed as 9.25e-5 (??) (k1 for 1173 K).

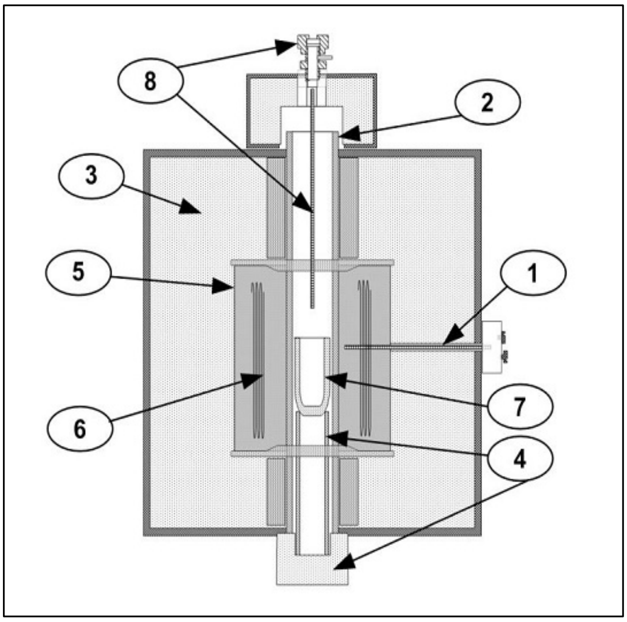


Figure 1: Schematic diagram of the furnace used in the experimental study. 1- thermocouple; 2- alumina tube; 3- refractory lining; 4- ceramic support to the crucible; 5- heating chamber; 6- resistances ($MoSi_2$); 7- reactor; 8- inert gas inlet

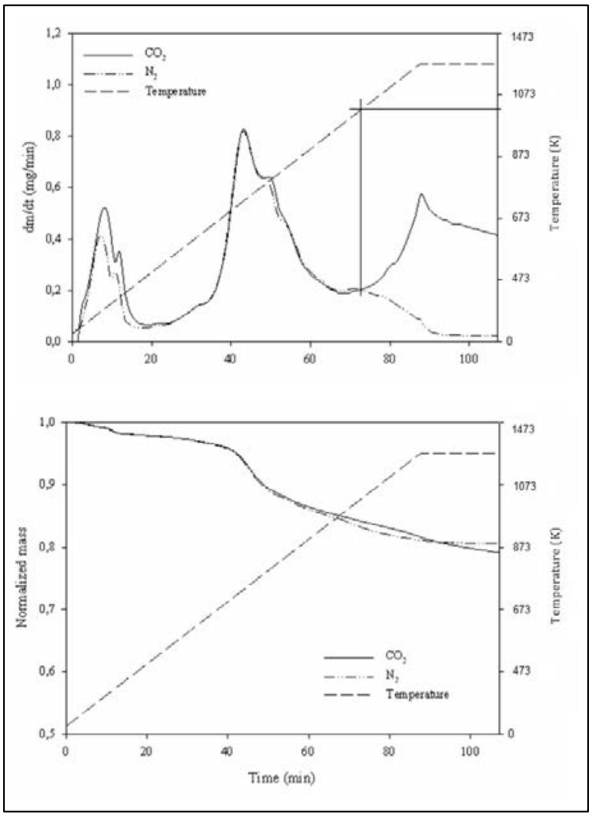


Figure 2: Normalized mass loss and Curve of the reaction rate of coal from Mina do Leão II in relation to time (granulometry between 0.125 – 0.500 mm).

Font: CAROTENUTO *et al*., 2012.

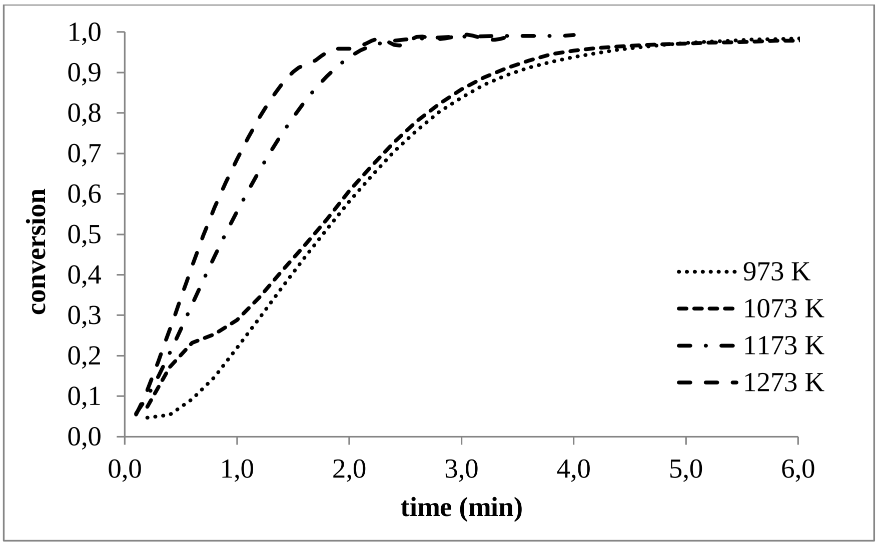


Figure 3 Reaction rate versus temperature for the mixture 20 % O_2/80 %CO_2.

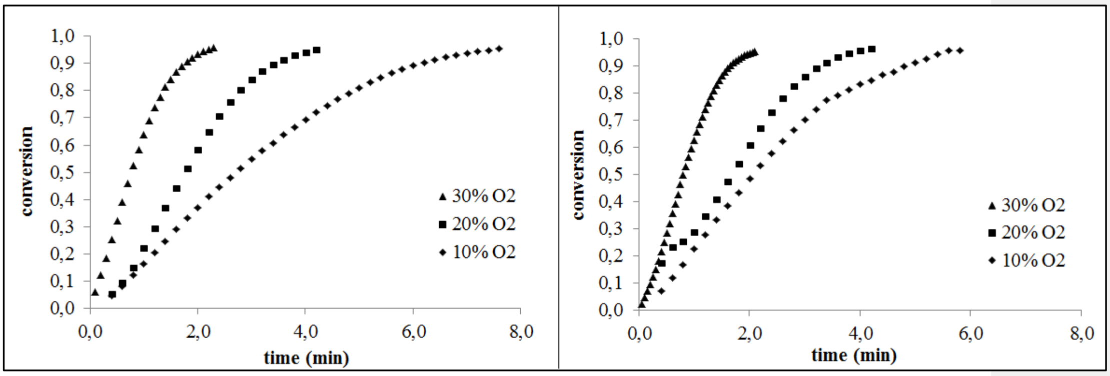


Figure 4 Conversion of *char* versus the time for different concentrations of the O_2/CO_2mixture at 973 K and 1073 K.

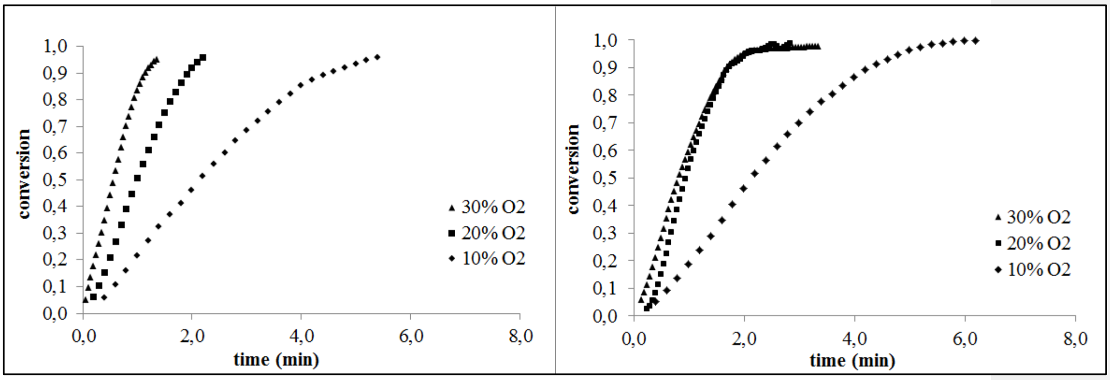


Figure 5 Conversion of *char* versus the time for different concentrations of the O_2/CO_2 mixture at 1173 K and 1273 K.

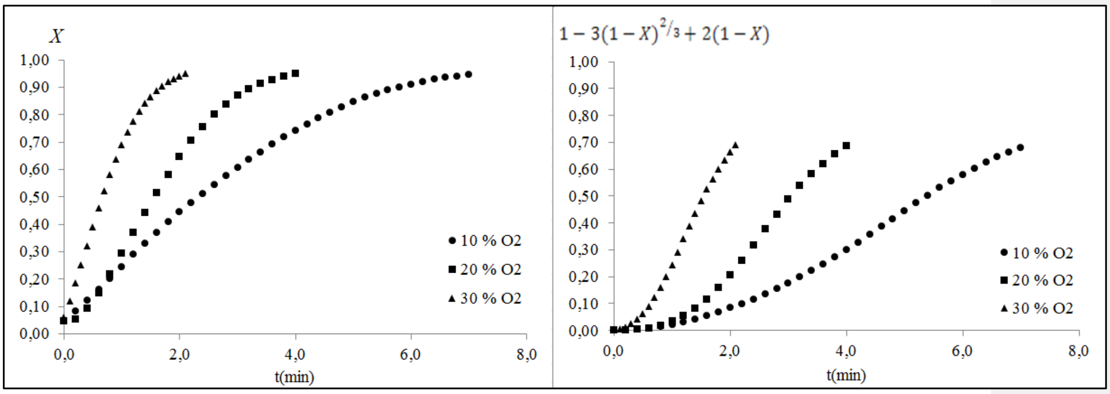


Figure 6 Adjustment of experimental results to the unreacted core model when diffusion in the gas layer outside the particle controls the reaction process, and when diffusion of reagent gas in the ash layer controls the process, for temperature of 973 K

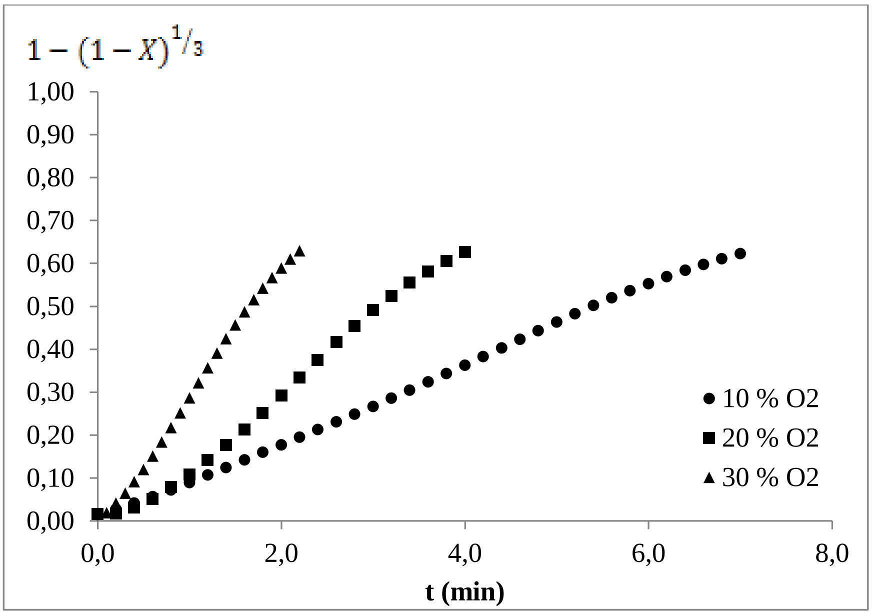


Figure 7 Adjustment of experimental data to the unreacted core model when the chemical reaction controls the process, for a temperature of 973 K

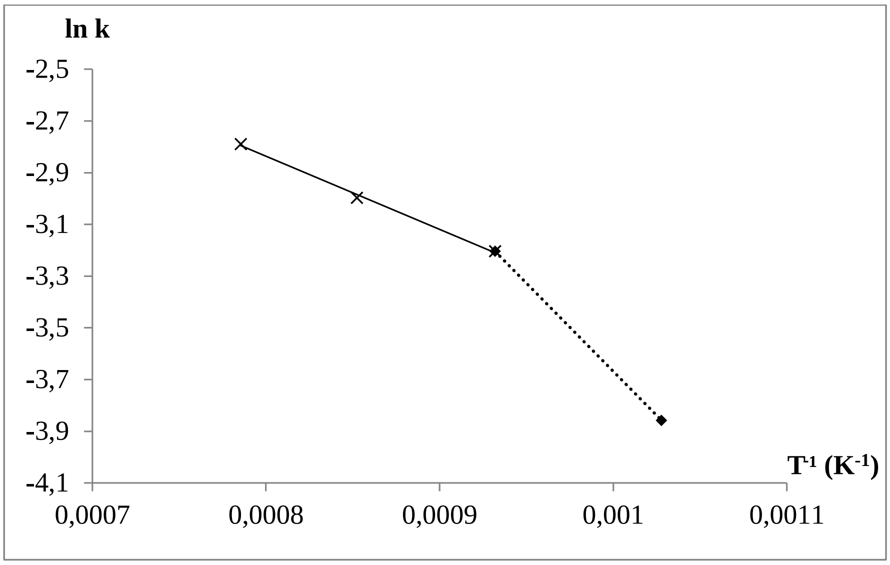


Figure 8 Effect of temperature on the reaction C + O_2 → 2CO.

Figure 9 *Char* before and after oxy-fuel combustion.

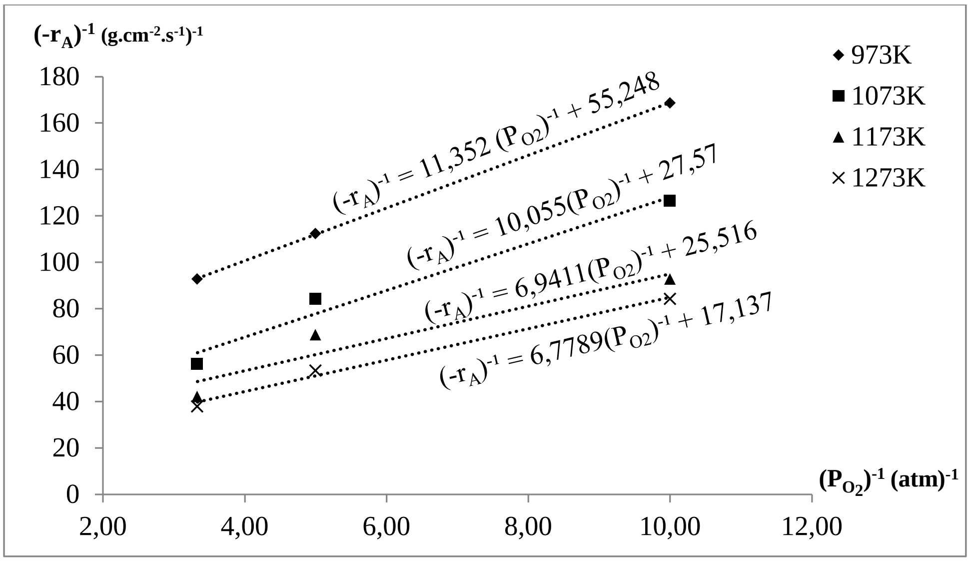
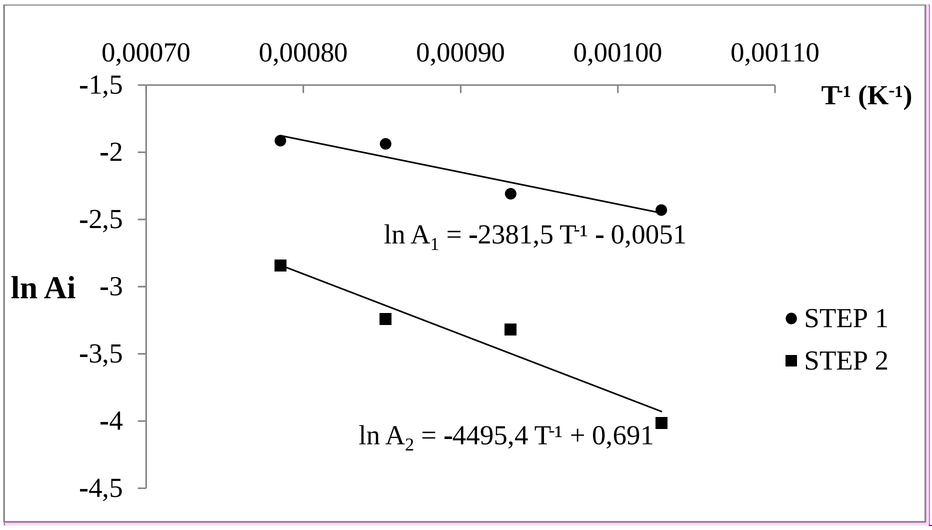


Figure 10 Graph obtained from the linearization of the equation 17 for determination of specific speeds of reaction of each step elementary.

[REV D39] Comentário: Improve the legend for Fig. 9



[REV D40] Comentário: Translate the insert in Fig. 10 to English

Figure 11 Chart for determining the activation energy and the frequency factor of the reactions.