KINETIC PARAMETERS FOR THE REACTIONS OF LEATHER SHAVINGS WITH OXYGEN AND CARBON DIOXIDE

by

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ABSTRACT

This paper describes a kinetic study of the carbon reactions with oxygen and carbon dioxide ($C\text{-}O_2$ and $C\text{-}CO_2$ reaction). The tests were carried out in a thermobalance using carbon from leather shavings char, under isothermal conditions and atmospheric pressure. The experimental results showed a good fit with the Shrinking Unreacted-Core model controlled by chemical reaction, and the Progressive-Conversion model did not describe the process. According to Shrinking Unreacted-Core model, the reaction initially occurs on the external surface of the particle and the reaction zone moves toward the center of the particle, leaving behind a layer of inert solid (ash). On the other hand, in the Progressive-Conversion model reaction occurs simultaneously in the entire volume of the particle. The activation energies of the $C\text{-}O_2$ and $C\text{-}CO_2$ reactions were determinate, as well as their reaction orders.

ABSTRACTO

Este trabajo describe un estudio cinético de las reacciones del carbono con oxígeno y dióxido de carbono ($C\text{-}O_2$ y la reacción $C\text{-}CO_2$). Las pruebas fueron realizadas en una termobalanza usando carbón obtenido de virutas de cuero pirolizadas, bajo condiciones isotérmicas y a presión atmosférica. Los resultados experimentales demostraron un buen ajuste con el modelo de Encogimiento No Reactivo del Núcleo controlado por la reacción química, mientras el modelo de Conversión Progresiva no describió adecuadamente el proceso. Según el modelo de Encogimiento No Reactivo del Núcleo la reacción ocurre inicialmente en la superficie externa de la partícula y la zona de la reacción se mueve hacia el centro de la partícula, dejando detrás una capa sólida inerte (ceniza). Por otra parte, en el modelo de Conversión Progresiva la reacción ocurre simultáneamente en el volumen entero de la partícula. Las energías de activación de las reacciones de $C\text{-}O_2$ y $C\text{-}CO_2$ fueron determinadas, así como el orden de la reacción.

INTRODUCTION

A step in the hide tanning process is the stage in which the leather is shaved to result in a product with uniform thickness. This step generates a solid residue called leather shavings which sometimes contain chromium. The disposal of this residue has been a concern due to the possibility of causing environmental damage, being the thermal treatment (pyrolysis, gasification, combustion) one of the available alternatives to partially solve this problem. Besides reducing residue volume, this kind of treatment allows chromium recovery and, at the same time, generates energy that can be used in the tannery.

Gasification is a process that converts carbonaceous materials, such the coal, petroleum, petroleum coke or biomass into a combustible gas[1-3]. The knowledge of the kinetics of the $C\text{-}O_2$ and $C\text{-}CO_2$ reactions is important to improve the design of the gasifier.

There are, in literature, models for the kinetics of the reactions involving a solid particle containing carbon[4-10]. The Progressive-Conversion model assumes that the gas reacts with the solid simultaneously throughout its entire surface[11, 12]. This is a simple model, which is adequate for application in processes under atmospheric pressure, and is much used in simulations of combustion processes.

The Shrinking Unreacted-Core model considers five successive steps which occur during the reaction: (1) diffusion of the reacting gas towards the surface of the solid through the stagnant gaseous layer surrounding the particle; (2) penetration and diffusion of the reacting gas towards the surface of the unreacted core through the ash layer; (3) reaction of the gas with the solid at the reaction surface; (4) diffusion of the gaseous products through the ash layer; (5) diffusion of the gaseous products through the gaseous layer. One or more of these steps may be a rate determining step[13, 14]. Although the kinetics of the $C\text{-}O_2$ and $C\text{-}CO_2$ reactions for

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several fuels, especially coal, has been thoroughly studied through the last decades, no information on the kinetics of these reactions with char from leather shavings was found in literature. The objective of this paper is to determine the kinetic parameters of these reactions.

EXPERIMENTAL

The equipment used for the experiments was a NETZSCH-STA 409 thermobalance. It is a fixed-bed differential reactor that operates at atmospheric pressure and enables one to follow a gas-solid reaction through the mass variation of a sample as a function of time. It can be seen on Figure 1. The therobalance resolution is 0.1±0.05 mg and all tests were accomplished in duplicate.

During the experiments, the following procedure was employed:

i. the experiment was started by purging the reaction chamber, analytic balance and gas collector with nitrogen (N_2). After purging, the equipment was subjected to a vacuum followed by re-injection of nitrogen. Chromatographic analyses confirmed that under these circumstances the atmosphere inside the chamber was inert;

ii. once atmospheric pressure was reached inside the reaction chamber, heating was started at a rate of 40 K/min, still within the inert atmosphere;

iii. when the reaction chamber reached the desired temperature, the isothermal period began. The sample was kept in the inert atmosphere for 8 minutes at reaction temperature, a time necessary to stabilize the sample mass. Finally, the reacting gas (O_2 or CO_2) was introduced into the reaction chamber at a constant flow rate of 300 ml/min.

Fuel characterization

The samples used in this study were offered, as produced in the leather shaving stage of chromium tanned hides, by three companies located in the Vale do Rio dos Sinos - RS, Brazil. From the material received, strips with an average thickness of 0.8 mm and approximate length of 10 mm were selected. The elemental and proximate analyses are presented in Table I.

RESULTS AND DISCUSSION

Figure 2 presents a typical result of the experiments conducted in this work. At the beginning of the experiment (point 1), there was an apparent increase in the sample's mass. This happens because the gas flow inside the reaction chamber exerts a drag force on the crucibles. In the pyrolysis stage, the sample releases volatile matter in the inert atmosphere, while at point (2) there is the injection of the reacting gas. The reaction is considered finished when the sample reaches a constant mass. The mass loss of the sample during the pyrolysis stage reached the maximum rate (mg/min) around 623 K. It is important to point out that the sample is called char at point (2).

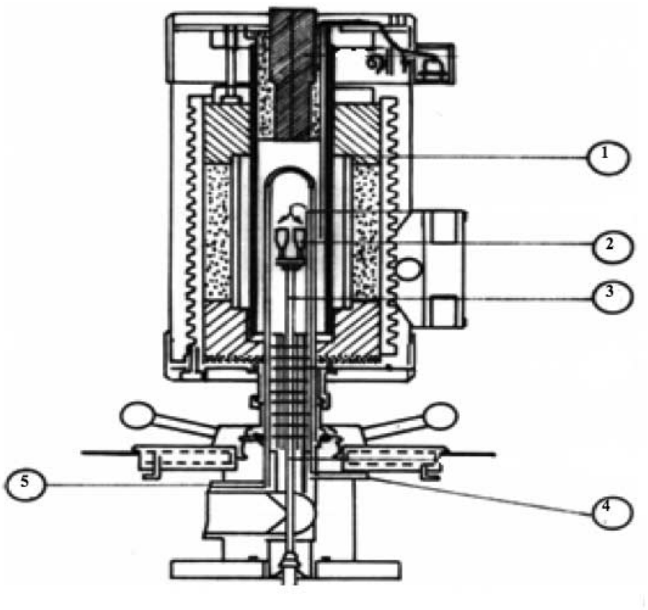

Figure 1: Thermobalance (1.electric heating; 2.crucibles; 3.thermocouple; 4.gas inlet; 5. gas outlet)

TABLE I
Leather Shaving Analysis

Elemental analysis (%weight, d.b.)	
Carbon[1]	44.9
Hydrogen[1]	5.6
Nitrogen[1]	16.4
Sulfur[2]	2.0
Proximate analysis (%weight; d.b.)	
Volatile matter[3]	73.5
Ash[4]	9.7
Carbon fixed[5]	16.8
bulk density (kg/m^3)[6]	400

[1] ASTM D-5373;
[2] ASTM D-4239;
[3] ISO 562;
[4] ASTM D-6716;
[5] by difference,
[6] ASTM D 2346;
d.b.: dry basis

Influence of the crucible geometry and of the reacting gas flow rate

The geometry of the crucible that contains the sample and the reacting gas flow rate inside the reaction chamber may induce the formation of a stagnant gaseous film around the sample. The formation of this film is undesired because it hampers the access of the reacting gas to the carbon, making the diffusion step contribute significantly to the global resistance.

The usual procedure to establish whether the formation of this limiting film is induced is to verify if the reaction rate changes

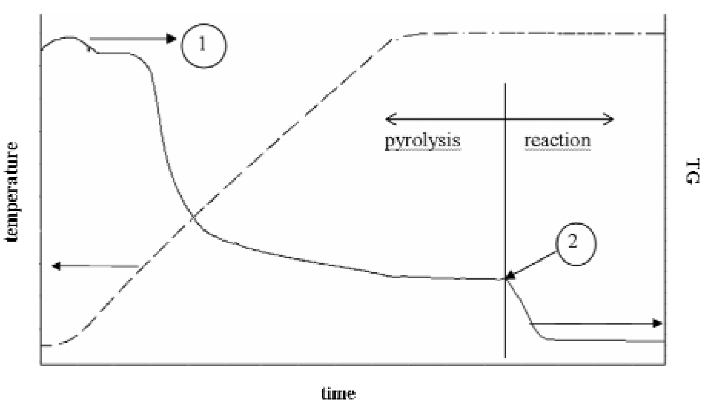

Figure 2: Typical result of an experiment.

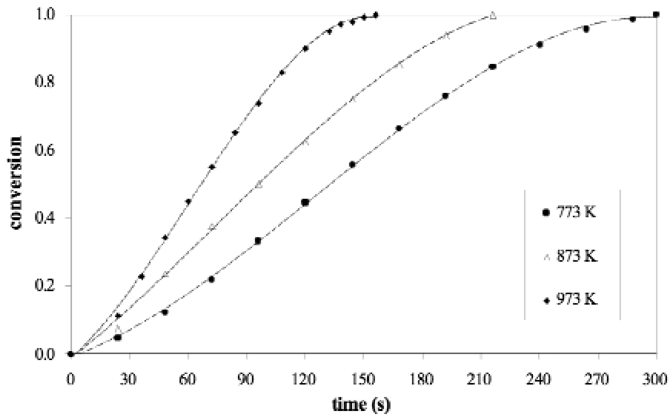

Figure 3: Conversion as a function of the temperature (PO2= 0.21 atm)

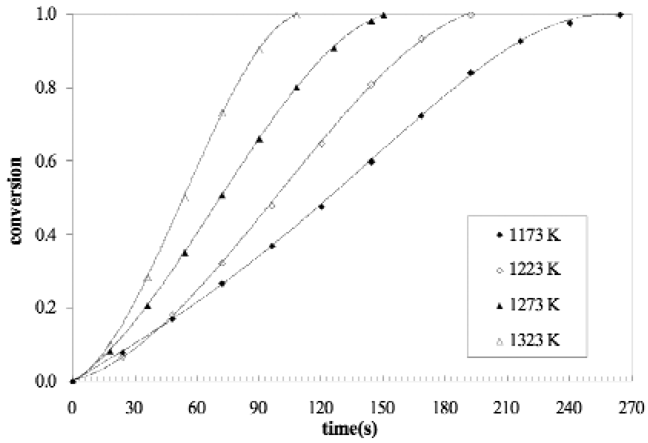

Figure 4: Conversion as a function of the temperature (PCO2=1 atm)

with the crucible geometry and/or the reacting gas flow rate. This work tested several types of crucibles and reacting gas flow rates. Under the applied experimental condition, the resistance, due to a stagnant gaseous film around the particle, becomes negligible in relation to the global resistance. Further details may be found elsewhere[15].

Influence of the temperature

Figures 3 and 4 present the behavior of the reaction rate as a function of the temperature, using the oxygen and carbon dioxide as reacting gases, respectively. The experiments for the C-O_2 reaction were conducted at temperatures ranging from 773 to 973 K and oxygen partial pressure of the 0.21 atm. The experiments for the C-CO_2 reaction were conducted at temperatures ranging from 1,173 to 1,323 K, and carbon dioxide partial pressure of the 1.00 atm. The conversion (X_c) is determined based on equation (1), where m_0 is the sample mass at the beginning of the reaction.

$$X_c = \frac{m_0 - m}{m_0} \tag{1}$$

These figures show that as the temperature increases there is an increment of the reaction rate. This behavior indicates the importance of the chemical reaction to the total resistance of the process. The behavior of the reaction rate as a function of the temperature, for the other partial pressures of the reacting gas, is similar to what is presented in these figures.

Influence of the reacting gas partial pressure

Experiments were conducted at O_2 partial pressures of 0.05; 0.10; 0.15 and 0.21 atm. For the CO_2 the partial pressures used were 0.40; 0.60; 0.80 and 1.00 atm. The variation of the conversion as a function of time for the different partial pressures of the reacting gas is shown in Figures 5 and 6.

An equation describing chemical reaction rate may be obtained using the existing kinetic models, already presented in this paper. Among those, the Shrinking Unreacted-Core model and the Progressive-Conversion model are the most commonly used.

The Shrinking Unreacted-Core model

In this model the reaction initially occurs on the external surface of the particle. The reaction zone moves toward the center of the particle, leaving behind a layer of inert solid (ash). Thus, in a partial conversion of the solid, there is a non-reacted core that decreases in size during the reaction. This model assumes five sequential steps, which occur during the process. Each one of these steps, when mathematically modeled, produces a specific equation relating conversion (X_c) and time (t). With the experimental conditions described elsewhere[15], the resistance related to the external diffusion stages, when compared to the total resistance of the process, was minimized. Therefore, the process is assumed to be controlled by the chemical reaction and/or by the diffusion in the ash layer. The appropriate way to establish which of these steps controls the process, is to verify which of the respective equations best reproduces the experimental results. When the diffusion of the reacting gas through the layer of ashes controls the process, in flat plate (strip) samples, equation (2) should closely reproduce the experimental results of conversion versus time. In this equation, "τ" is the time required for a complete particle conversion.

$$\frac{t}{\delta} = X_c^2 \tag{2}$$

Figure 7 compares the theoretical values of conversion as a function of the time obtained by equation (2) with the experimental results. The conversion of the sample is calculated using equation (1). The experiments were conducted

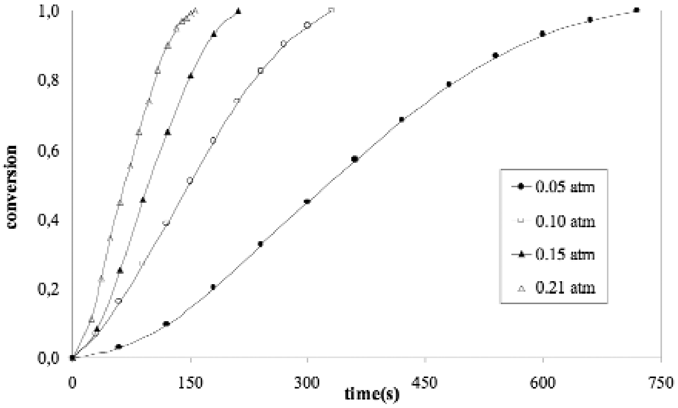

Figure 5: Conversion as a function of the oxygen partial pressure (T = 973 K).

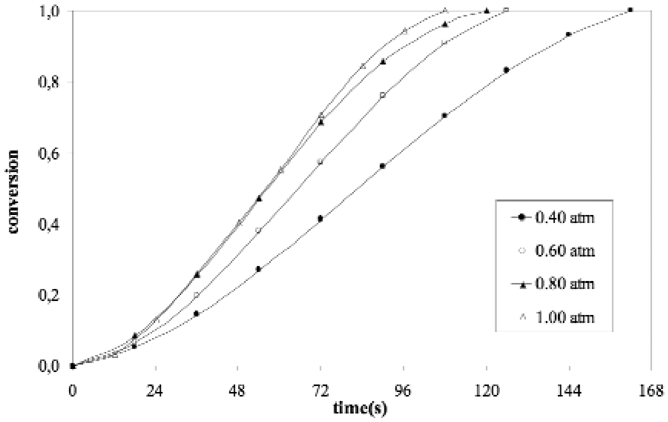

Figure 6: Conversion as a function of the carbon dioxide partial pressure (T = 1,323 K).

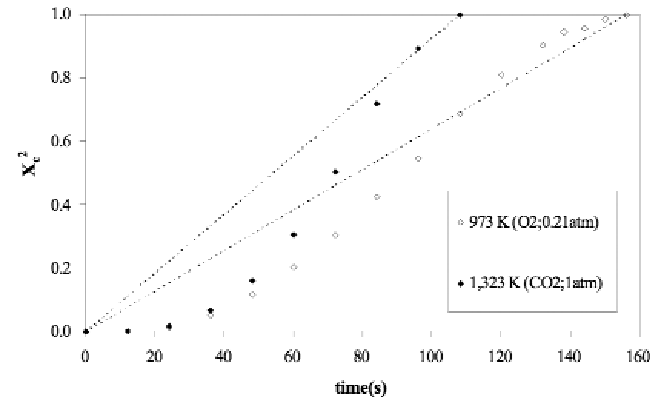

Figure 7: Theoretical (dashed line) and experimental values of conversion as a function of time.

with a reacting gas flow rate of 300 ml/min, and a CO_2 partial pressure of 1 atm at a temperature of 1,323 K, and a O_2 partial pressure of 0.21 atm at a temperature of 973 K.

As can be observed in Figure 7, there was no coincidence between the experimental results and equation (2). That indicates that the process is not being controlled by the gaseous diffusion through the ash layer, even at more elevated temperatures and concentrations of the reacting gas, when this step is expected to be more significant. It can be observed that at high conversions (above 90%), where the ash layer represents almost the totality of the sample, the data for O_2 and CO_2 present linear behavior, indicating a possible kinetic control by the gaseous diffusion through the ash layer.

TABLE II
Time for a Complete Particle Conversion

Partial Pressure O_2(atm)	0.05	0.10	0.15	0.21
T(K)		τ(s)		
773	1,260	600	360	300
823	1,200	570	330	264
873	1,020	480	300	216
923	780	360	258	168
973	720	330	210	156
Partial Pressure CO_2(atm)	0.40	0.60	0.80	1.00
T(K)		τ(s)		
1,173	336	288	276	264
1,223	300	240	216	192
1,273	240	180	162	150
1,323	162	120	126	108

In spite of the possibility of change in the kinetic control mechanism, this would only happen at high conversions, suggesting that almost the entire process is being controlled by the chemical reaction, for both reacting gases. In this case, for flat plate (strip) samples, the process is described by equation (3):

$$\tau = \frac{t}{X_c} \qquad (3)$$

Thus, equation (3) allows one to obtain the time required for a complete particle conversion (τ). Table II shows the time for a complete particle conversion calculated for all tests accomplished in this work.

The chemical reaction rate ($-r_A$) is obtained using equation (4):

$$(-r_A) = \frac{C_c L}{\tau} \qquad (4)$$

In equation (4), C_c represents the concentration of carbon in the solid (mol of carbon/volume of the solid), L represents half of the thickness of the strip and ($-r_A$) represents the chemical reaction rate [mol of carbon/(area of the sample.time)]. The concentration of carbon in the solid (C_c) is obtained using equation (5), where ρ_{ls} is the bulk density of the leather shavings (g/cm^3), C_f is the mass fraction of the carbon fixed and "12" is the atomic mass of carbon.

$$C_c = \frac{\rho_{ls} C_f}{12} \qquad (5)$$

Knowing the reaction rate, it is possible to determine the reaction order (n) and reaction rate constant (k) using equation (6). In this equation C_g represents the molar concentration of the reacting gas (mol/cm^3):

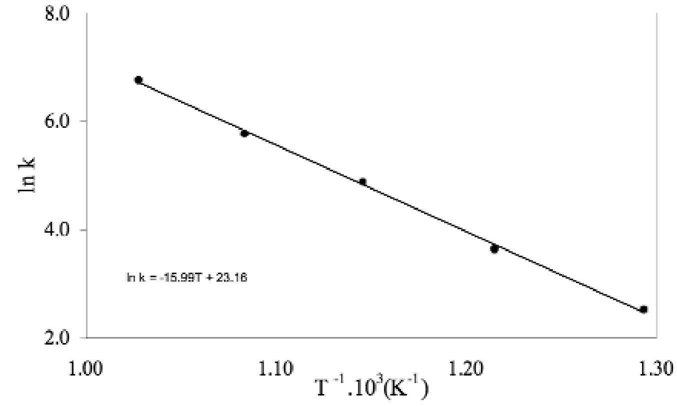

Figure 8: Arrhenius equation for the C-O_2 reaction

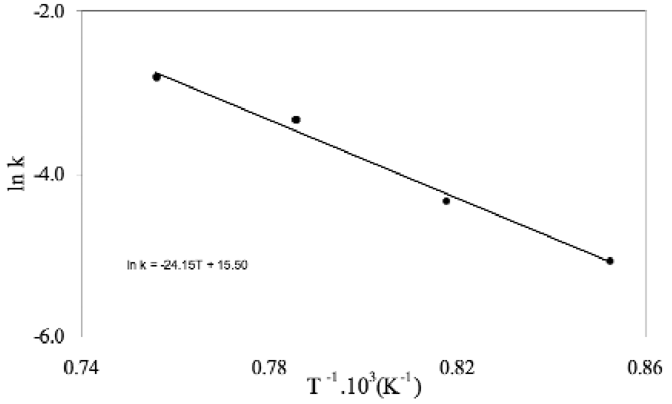

Figure 9: Arrhenius equation for the C-CO_2 reaction

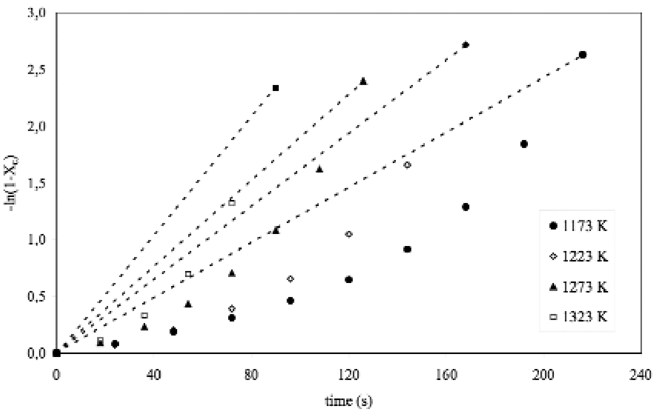

Figure 10: Progressive-conversion model for C-O_2 reaction.

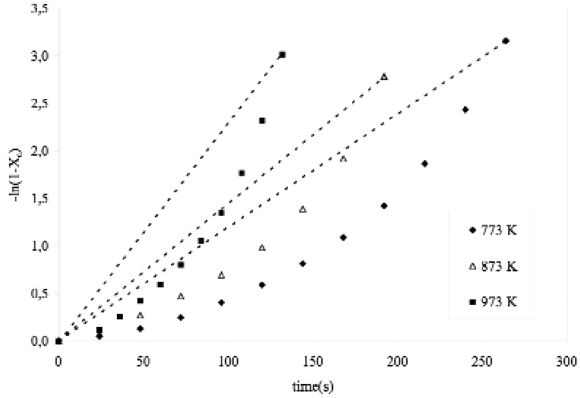

Figure 11: Progressive-conversion model for C-CO_2 reaction.

TABLE III
Reaction Rate Constants and Reaction Orders

C-O_2 reaction			C-CO_2 reaction		
T (K)	k $\left(\frac{cm^{3n-2}}{\min.mol^{n-1}}\right)$	n (reaction order)	T (K)	k $\left(\frac{cm^{3n-2}}{\min.mol^{n-1}}\right).10^{-2}$	n (reaction order)
773	12.4	0.99	1,173	0.63	0.41
823	38.0	1.06	1,223	1.31	0.47
873	131.2	1.14	1,273	3.56	0.52
923	321.9	1.16	1,323	5.99	0.54
973	864.6	1.24			

$$(-r_A) = k\,C_g^n \qquad 6)$$

Using the Arrhenius equation, the pre-exponential factor (k_0) and the activation energy (E_a) were estimated for the two studied reactions. The kinetic parameters obtained in this study are presented in Table III.

Thus, the C-O_2 and C-CO_2 reaction rates (molC./cm².min) can be calculated by equations (7) and (8) respectively, where *R* is the universal constant (cal/mol.K) and the activation energy is given in cal/mol.

$$(-r_A) = 1.14 \times 10^{10} \exp\left(-\frac{31{,}790}{RT}\right)C_{O_2}^n \qquad (7)$$

$$(-r_A) = 5.40 \times 10^{6} \exp\left(-\frac{47{,}992}{RT}\right)C_{CO_2}^n \qquad 8)$$

As can be observed in Figures 8 and 9, there is a strong fit between the data and the Arrhenius equation. The value of the activation energy found for the C-O_2 reaction was 31.79 kcal/mol and for the C-O_2 reaction was 47.99 kcal/mol.

In recent years, several papers tried to determine the kinetic parameters of the C-O_2 reaction with biomass. Table IV

TABLE IV
Kinetic Parameters for the C-O_2 and C-CO_2 Reactions Found in Literature

T(K)	fuel	E_a (kcal.mol^{-1})	n (reaction order)	Ref
C-O_2 reaction				
non-isothermal	biomass	31.1 - 35.9	0.62 - 1.61	16
1,023-1,173	biomass	32.0 - 34.0	0.9 - 1.1	17
non-isothermal	biomass	31.8	0.81 - 1.0	18
C-CO_2 reaction				
1,113-1,373	coal	59.31	1	5
1,213*	coal	49.97	1	12
1,023-1,173	coal	50.80	0.74	19

* Maximum temperature of the experiments

presents the kinetic parameters (activation energy and reaction order) obtained by some authors for this reaction. As can be observed, the values obtained in this study for both reactions are compatible with those found in literature.

The Progressive-Conversion model

In the progressive-conversion model, the reacting gas penetrates the particle and reaction occurs simultaneously in the entire volume. The solid is, therefore, consumed continuously and progressively throughout the particle in an uniform manner. This model was developed for the case where the diffusion of the reacting gas is fast, compared to the chemical reaction rate. Under these conditions, the experimental results of conversion (X_C) and time (t) applied to equation (9) should present a linear behavior, where the slope represents the reaction rate ($-r_A$). Figures 10 and 11 show the experimental results compared to the progressive-conversion model.

$$-\ln(1-X_c)=(-r_A)t \quad (9)$$

As can be observed in Figures 10 and 11, the Progressive-Conversion model does not adequately describe behavior of C-O_2 and C-CO_2 reactions occurring with the char from leather shavings.

CONCLUSIONS

Based on the experimental results obtained in this study, at different temperatures and partial pressures of the reacting gas and at atmospheric pressure, we may reach the conclusion that:

- The Shrinking Unreacted-Core model reproduces the experimental results for both the O_2 and CO_2 reacting gases, establishing that the process is being controlled mainly by the chemical reaction;
- Progressive-Conversion model does not adequately describe the behavior of the reaction of char from leather shavings with oxygen and carbon dioxide;
- The activation energy of the C-O_2 reaction is 31.79 kcal/mol. The reaction order varied from 0.99 to 1.24;
- The activation energy of the C-CO_2reaction is 47.99 kcal/mol. The reaction order varied from 0.41 to 0.54.

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