RELATIONS BETWEEN PHYSICALS PROPERTIES OF SOLID FUELS AND ITS REACTIVITY

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Abstract. The purpose of this work is to analyze concepts and assumptions adopted in most of mass transfer models of solid fuel burning, mainly of biomass fixed carbon. It is briefly presented some physical and chemical parameters like chemical structure, mineral matter specific area and porosity; that could influence the reactivity of solid fuels. Experimental burning data of charcoals and graphite are presented. They are examined with reference to classical Arrhenius diagram for control of reactions in a porous solid fuel. Above 1100K, experimental data do not converge to a diffusional controlled regime, as expected. It is proposed an alternative approach to explain how the solid porosity affects the reaction rate. The suggested idea is as follows: in the lower temperature region, porosity and specific area increase the exposed area for the reactions, while in the higher temperature region they affect the heat transfer and modify the effective emissivity of the fuel's surface, thus promoting higher rates for lower emissivities.

Keywords: carbon properties, carbon burning rate, carbon emissivity, solid fuel.

1. Introduction

Traditionally the studies on solids burning are focused in the kinetic and mass transport aspects, (Smith, 1982), (Bar-Ziv and Kantorovich, 2001), (Liu et al. 2000), (Hurt, 1998). A porous solid fuel can be oxidized in three regimes: I – a kinetically controlled regime, with low temperatures, the mass transfer of oxygen is greater than its consumption by chemical reaction; the O_2 concentration inside the pores is about the same of that in gas stream, II- a mixed regime partially kinetic and partially diffusion controlled; increasing temperatures promotes a augment in the velocity of chemical reactions with consequent internal gradient in O_2 concentration, null at particle center and equal to that in gas stream at surface, III - a diffusion controlled regime, the reactions are very fast and the diffusion transport of O_2 is the slower step, creating a O_2 gradient at boundary layer (δ) ; as shown in the Fig.1 in a Arrhenius diagram obtained from (Mulcahy and Smith, 1969).
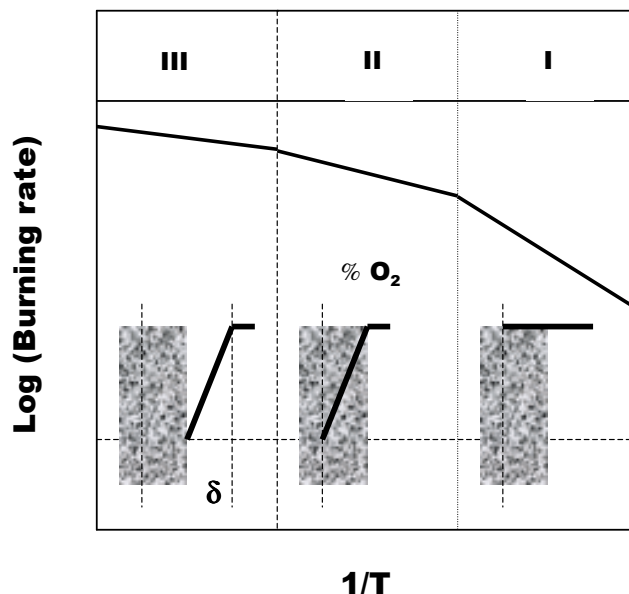

Figure 1. Arrhenius diagram: Burning rate versus (Temperature)$^{-1}$.

It is consensual that despite the many studies the fundamental surface kinetics of solid carbon oxidation and their interaction with diffusion process in a complex porous media are still poorly understood. This occurs mainly due the

great variety in the form, size and physicochemical properties of solid fuels. From the works of Kanury (1994), with a theoretical study of pyrolysis and combustion of biomass; Hurt (1998) with a review on the structure, properties and reactivity of solid fuels and Jenkins et al. (1998) analyzing the relations between biomass characteristics and its burning; it is evident the need for more research work in this area.

There are several operational parameters for a burner and various physical and chemical properties of solid fuels that can modify the effective reactivity of fuels, besides the fundamental parameters like temperature, $\%O_2$, gas velocity, and the reactor environment. It is worth to mention the influence of chemical structure, mineral matter and porosity as discussed by Laurendeau (1978). The chemical structure of char and the degree of crystalline order depends on the heat treatment and final temperature of the sample as showed in Fig. 2. The tendency of reactivity is to decrease with increasing crystalline order Hurt et al. (1995) and the presence of sp^2 and sp^3 bonds. The heat treatment of char could produce another mechanism of reactivity loss with the sintering and deactivation of inorganic catalysts presents in carbon.
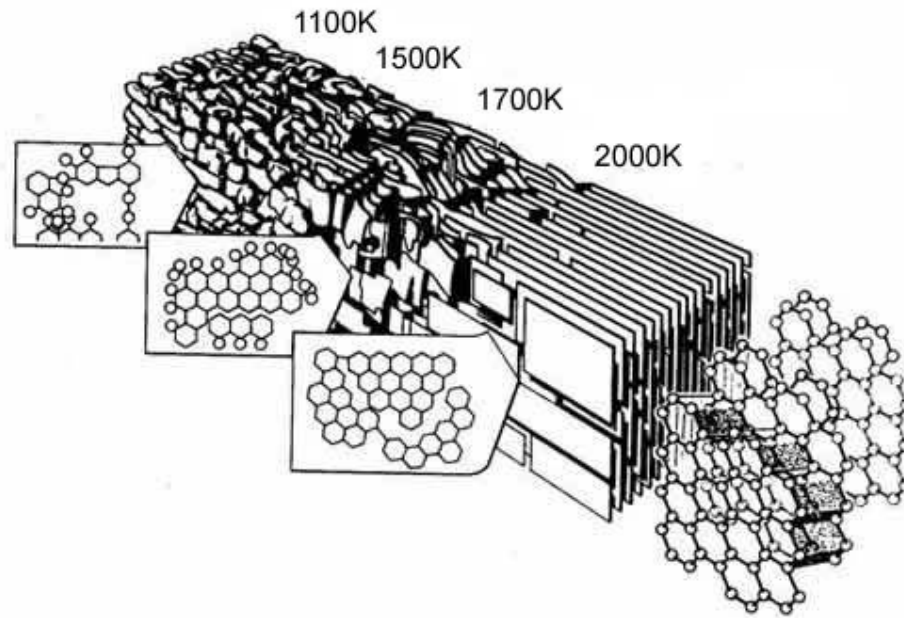

Figure 2. Changes in the structure of the carbon due to the thermal treatment (Savage, 1993).

Fuels with similar porosities may present differences in pores distribution, inducing different rates. As example is show in Fig. 3, a variation of specific area in a solid sample with constant porosity. Supposing that cylindrical pores constitute porosity, the figure below shows a strong growth of area with decreasing of pore diameter.
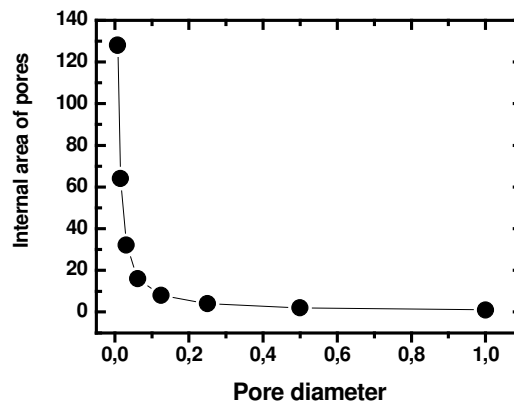

Figure 3. Simulation of specific area variation as function of pore diameter for constant porosity.

When a porous solid fuel burns at high temperature, the reactions are very fast, the control is diffusional and one can expect that properties like porosity, tortuosity, specific area, mineral matter and others factors related to reactivity of solid fuels do not act anymore on the burning rate. This must happen due to mass transport of oxygen being the slower step in the reaction process. As consequence it could be expected that solid carbon fuel even with different porosities and different values of specific area; reach essentially the same burning rate.

Experimental data of (Santos, 1999), Fig. 4, do not show the expected tendency. Different fuels exhibit different rates at high temperature, above 1100K.
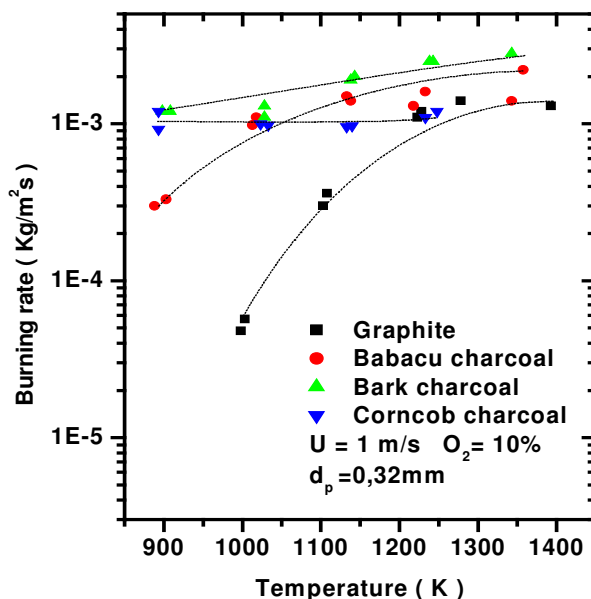

Figure 4. Burning rate (kg/m^{2}s) versus Temperature (K), (Santos, 1999).

Figure 4 shows that for graphite, the temperature interval 1000 – 1200K promotes a variation of the burning rate of more than a order of magnitude; thus characterizing a prevalence of kinetic control of the reaction. For the same temperature interval bark charcoal shows features of diffusion control with little temperature influence, and Babaçu charcoal presents mixed pattern in the range 900 – 1100K. Above 1200K, all the fuels follow a diffusion pattern, although with different levels of burning rates.

For temperatures below 1100K, the charcoal group presents burning rates an order of magnitude greater than graphite. These values can be attributed to the greater porosity and specific area of charcoals, making more surface available for chemical reaction. This reasoning is coherent with the data of the Table 1, where the group of charcoals has greater values of porosity than graphite and except for corncob charcoal also presents greater values of specific area. However, only these two physical properties are not enough to explain differences in reactivity among the several charcoals for temperatures over 1200K

Table 1. Physicals properties of graphite and charcoals

Properties	Graphite	Bark charcoal	Babaçu charcoal	Corn cob
Apparent density (kg/m^3)	1800	500	1200	280
Specific area (m^2/kg)	1200	4400	2000	1000
Ash (% mass)	0,2	17,8	6,2	3,3
Volatiles(% mass)	1,6	13,7	4,0	5,8
Fixed carbon (% mass)	98,2	68,5	89,9	90,9
Heating value (kJ/kg)	34099	23400	29600	31380
Porosity (% volume)	18	76	30	80

Figure 5 extracted from (Santos, 1999), shows a graphic representing the three ways for carbon oxidation: with chemical control (•), diffusion control (✕) and a mixed mode of chemical and diffusion control (O). At 1050K we observe the same values for both chemical kinetics and diffusion contributions, for the burning rate. This temperature is labeled T_r (transition temperature). For temperatures values higher than T_r, we have prevalence of diffusion control; and inversely, for smaller temperatures there is prevalence of chemical kinetics control. Although between 900 and 1200K, there is a mixed control mechanism; T_r is a reference value for analyzing fuel reactivity; smaller value of T_r indicates that the fuel is more reactive. Comparing this figure with data in Fig. 4, it is verified that for charcoals T_r has smaller values when compared to graphite, the change in the reaction control happens around or less than 1000K, while T_r for graphite occurs around 1120K.
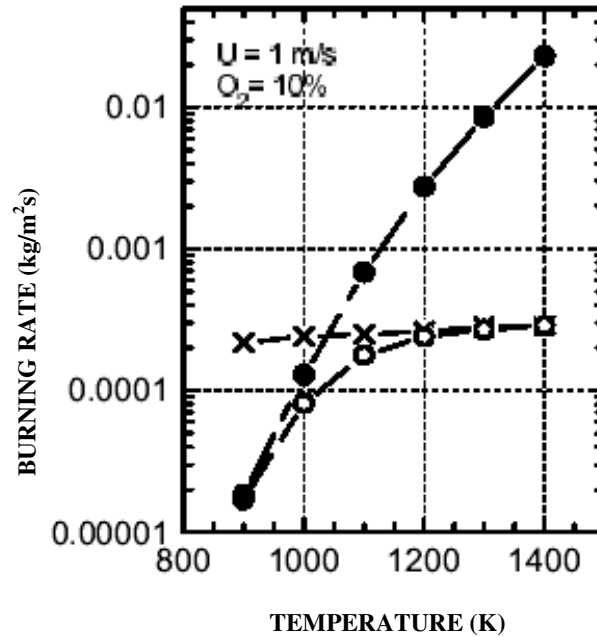

Figure 5. Effective burning rate versus temperature.

Interesting to notice that the form of the mixed mode curve (O) in Fig. 5, represents well the behavior of the data in the Fig.4, giving confidence that the combustion above 1200K is diffusion controlled.

The motivation for this paper is to discuss the reason for the unexpected differences in specific burning rates for burning solid fuels, in the diffusion-controlled regime. This work constitutes an initial attempt to explain the results.

2. Experimental methods

Charcoals were made from wood samples of Jatobá, Garapeira, Cumaru, Maçaranduba, Marfim, Canafístula and Peroba Rosa. The carbonization process was made in a horizontal tubular oven, atmosphere of nitrogen, with heating rate of 1K/min from 373K up to 1273K. After carbonization, some SEM photos were made of transversal cuts of charcoals samples. These pictures were used to study the pore distribution of the samples. Measurements have been made of pore structure for some biomass char samples, using Imago software for image analysis, and the results are presented below in Fig 6 - 9. The proximate analyses of the wood samples were made according to the norm ASTM – D1762. The same group of biomass samples was characterized for specific area using BET method, and porosity using He method. The results are presented at Tab.3. and Tab. 4.

The measurements of emissivity were done with Pyrotek infrared pyrometer coupled to a type K thermocouple. The emissivity value shown in the pyrometer was changed until that the temperature registered by the pyrometer was the same registered by the thermocouple. Measurements were made normal to sample surface.

3. Results and discussion

Table 2 shows normal values of volatiles and fixed carbon contents, varying inside an acceptable range for woods. The measurements of porosity and specific area in Tab. 3 and Tab. 4 show very close porosities values and great

differences between results for specific areas. These differences are due to different pore distribution, showed in Fig. 6 – 9.

Table 2. Proximate analysis of wood

Wood species	Volatiles (%)	Fixed Carbon (%)	Ash (%)
Canafístula	76,51	22,97	0,52
Marfim	83,37	15,53	1,10
Peróba Rosa	81.89	17,63	0,48
Jatobá	75,88	23,33	0,79
Garapeira	84,83	14,31	0,86
Cumarú	81,18	18,42	0,40
Maçaranduba	80,09	19,59	0,32

Table 3. Specific area measurement (m^2/g) of charcoals

	Cumaru charcoal	Garapeira charcoal	Jatobá charcoal	Maçaranduba charcoal
BET (N_2) (m^2/g)	4.00	2,30	16,40	1,00

Table 4. Porosity measurement (% volume) of charcoals

Method	Property	Cumaru charcoal	Garapeira charcoal	Jatobá charcoal	Maçaranduba charcoal
He	Real density(Kg/m^3)	1960	1940	2150	1950
	Bulk density(Kg/m^3)	750	630	730	640
	Porosity	62%	67%	66%	67%

Analysis of pore histograms shows predominance of smaller pores in sequence of Jatoba, Cumaru, Garapeira and Maçaranduba charcoals, coherent with results of Tab. 3.

Observing in the Fig. 4, growth of internal area for smaller pores, the specific area measurements in Tab. 3 and porosity values in Tab. 4; it is correct to associate the importance of pore distribution, for reactivity in regions I and II, with kinetic and mixed control regime of chemical reactions. It can be concluded that porosity is clearly important, and for fuels with similar porosities; the enhancement of reactivity comes from predominance of smaller pores.
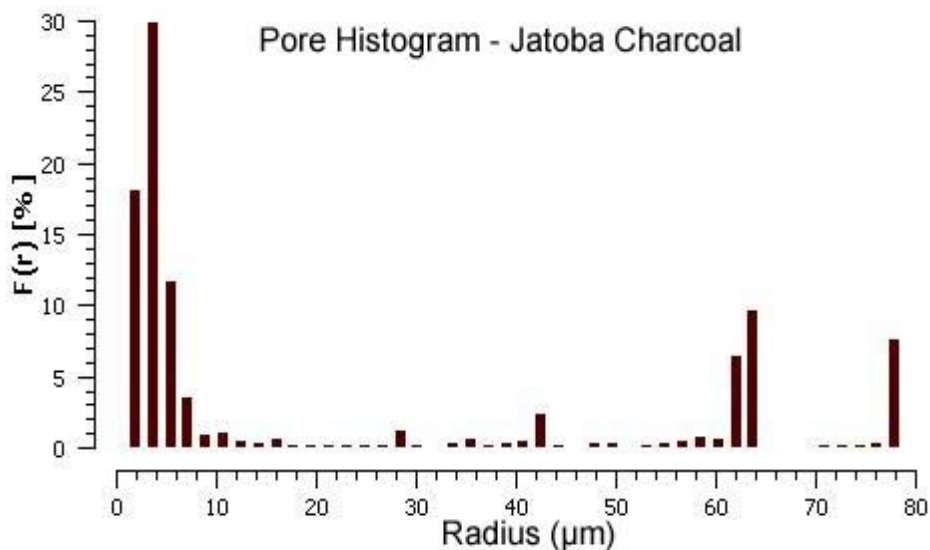
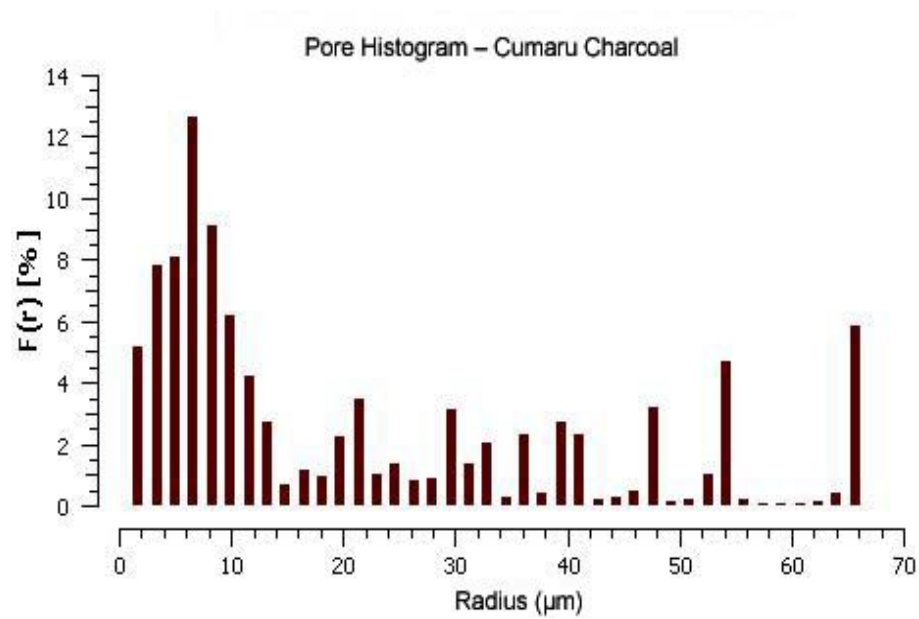

Figure 6. Pore histogram for a Jatobá charcoal.

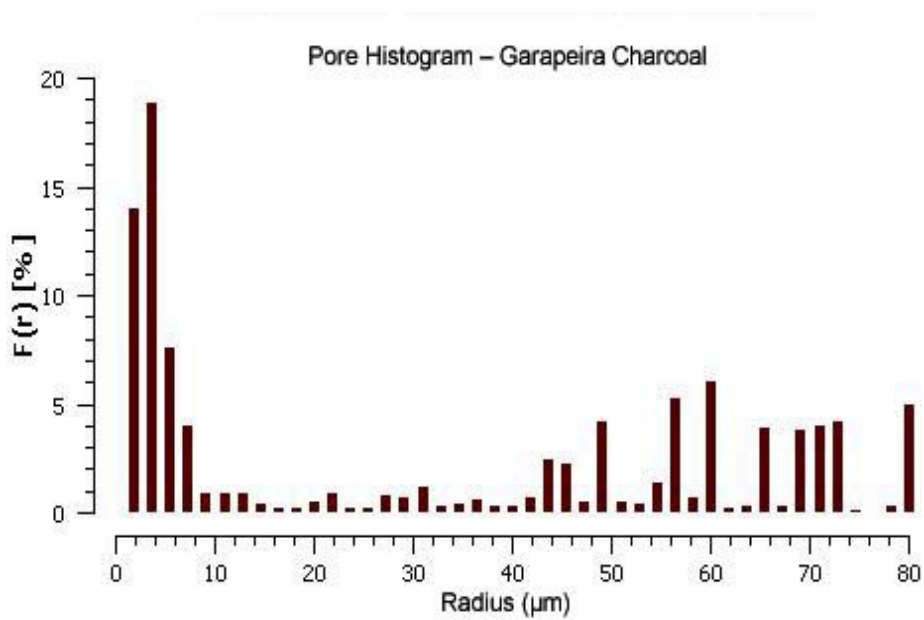Figure 7. Pore histogram for a Cumaru charcoal.
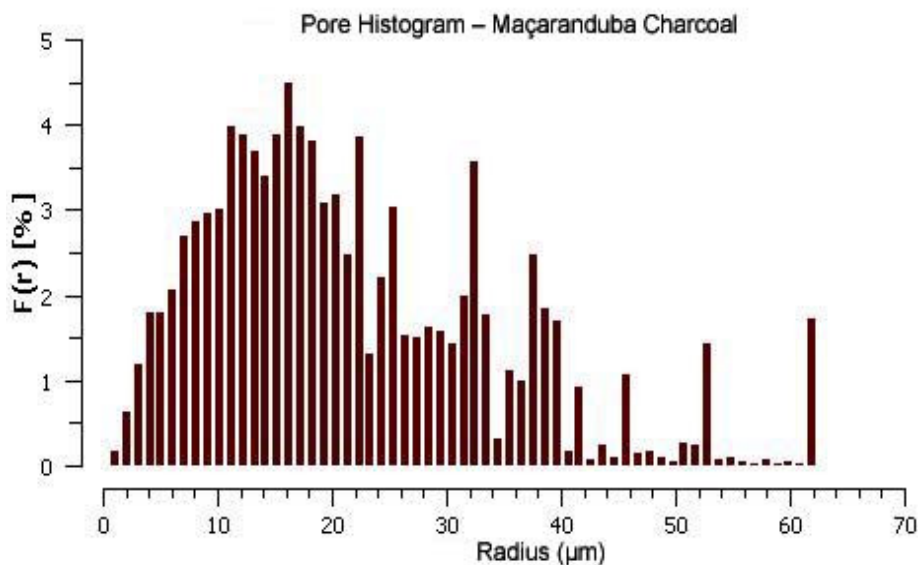

Figure 8. Pore histogram for Garapeira charcoal.

Figure 9. Pore histogram for Maçaranduba charcoal.

3.1. Equilibrium temperature during solids combustion

The temperature of a solid carbon burning in a reactor is a function of the combustion medium and of fuel type. For each condition, we can express the surface temperature of fuel as resulting from thermal equilibrium; the rate of heat generation is equal to rate of heat loss. Considering the radiation losses as the principal factor controlling the final temperature of fuel particle, the value of surface emissivity (ε), may be responsible for the variations in the fuel particle temperature. Fig. 10, show the measurement of ε, as function of temperature for some charcoals and graphite.
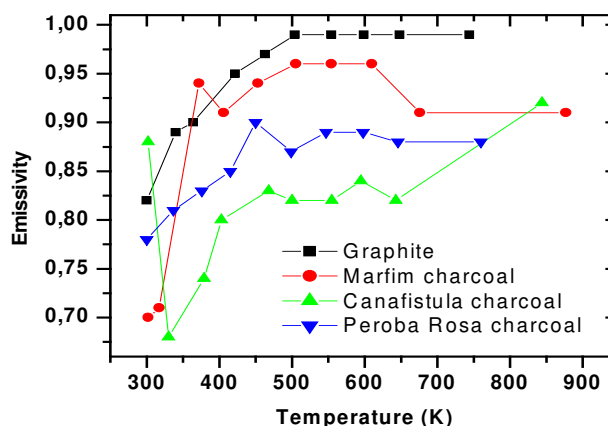
Figure 10. Emissivity of graphite and charcoals.

The data in Fig. 10 show that for the temperature interval 300K to 900K, emissive values of graphite are greater than for charcoals. The physical meaning of these results is that for the same rate of heat generation at the fuel surface, graphite emits more efficiently and reaches thermal equilibrium at particle temperature lower than for charcoals. Consequently, if charcoal temperature is augmented, the diffusion coefficient of mass transport increases, and promotes major burning rates even at the diffusion-controlled regime.

4. Conclusions

Here it was studied the influence of the solid physical properties on its reactivity. The analysis was based on characterization and burning rate data for graphite and some charcoals. Comparing the values of porosity, specific area and pores distribution, it is concluded that in the temperature range for kinetic and mixed controlled regimes, the porosity and specific area acts by increasing internal surface exposed to chemical reactions. Measurements of the emissivity for graphite and charcoals suggest that final temperature in solids fuel burning is an inverse function of porosity, promoting higher rates for lower emissivities.

5. References

Bar-Ziv, E., Kantorovich, I.I., 2001, "Mutual effects of porosity and reactivity in char oxidation", Progress in Energy and Combustion Science, Vol 27, pp 667-697

Hurt, R.H., Davis, K. A., Yang, N. Y. C., Headley, T. J., and Mitchell, G. D., 1995, "Residual carbon from pulverized-coal-fired boilers 2. Morphology and physicochemical properties", Fuel, Vol. 74, N_o. 9, pp 1297-1306.

Hurt, R.H., 1998, "Structure, properties, and reactivity of solid fuels", Topical review paper for the 27th International Symposium on Combustion.

Jenkins, B.M., Baxter, L.L., Miles Jr.,T.R., Miles. T.R., 1998, "Combustion properties of biomass", Fuel Processing Technology, Vol 54, pp 17-46.

Kanury, A.M., 1994, "Combustion Characteristics of biomass", Combustion Science and Technology, Vol 97, pp 469-491.

Laurendeau, N. M., 1978, "Heterogeneous kinetics of coal char gasification and combustion", Progress in Energy and Combustion Science, Vol. 4, pp. 221-270.

Liu, G., Benyon, P., Benfell, K.E., Bryant, G.W., Tate, A.G., Boyd, R.K., Harris, D.J., Wall, T.F., 2000, "The porous structure of bituminous coal chars and its influence on combustion and gasification under chemically controlled conditions", Fuel, Vol 79, pp 617-626.

Mulcahy,M.F.R., and Smith, I.W., 1969, "Kinetics of combustion of pulverized fuel: A review of theory and experiment" Reviews of Pure and Applied Chemistry, Vol 19, pp 81–107.

Santos, F.J., 1999, "Control mechanisms of solid fuel combustion", Proceedings of the 15th Brazilian Congresso of Mechanical Engineering.

Savage, G., 1993, "Carbon – carbon composites" Ed. Chapman & Hall, London, pp 136.

Smith, I.W., 1982, "The combustion rates of coal chars: A review", 19th Symposium (International) on Combustion/ Combustion Institute, pp 1045-1065.

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