Mol2Net, **2015**, 1(*Section C*), pages 1-7, *Proceeding*
http://sciforum.net/conference/mol2net-1

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Kinetic Study of Activated Carbon Synthesis from Marabou Wood

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Received: 28 September 2015 / Accepted: 28 September 2015 / Published: 2 December 2015

Abstract: In the last years the demand of activated carbons for environmental remediation and medical applications has been growing. This situation has stimulated the study of new precursors for the synthesis of these adsorbents. This work shows the kinetic parameters of activation process of Marabou Wood (*Leptoptilus Crumeniferus*) using a simple mathematical model. These parameters were compared with ones corresponding to other tropical biomasses studied under similar conditions. To conduct the study, a thermo-gravimetric analysis was carried out in steam water. The study was carried on from room temperature to 1000°C with a heating rate of 10°C/min, additionally; the crystallinity was determined by X-rays diffraction analysis. The characterization of the activated carbon was carried out through parameters that provide an indirect measure of the mechanical resistance. Interesting correlations for the analyzed thermal conversion processes were also obtained.

Keywords: biomass, activated carbons, thermo-gravimetric study, kinetic parameters, X-ray, mechanical resistance.

1. Introduction

Various studies about the morphological and textural characterization during the thermal conversion of biomasses resources have been reported. These works studied mainly coconut shell and olive stones as raw materials. (5, 6, 13, 16) However, other resources that are nowadays widely available in tropical areas, with less competence in other applications, have been barely studied. (13, 17, 19)

Marabou is an exotic wood that is increasingly infecting cultivated fields of Central American Countries. In the last years, important efforts have been conducted, in order to find different alternatives to reduce the negative environmental impact of these great amounts of biomass that is difficult to manage.

Moreover, the possibility to valorize them could allow the achievement of a sustainable agricultural development. The preparation of activated carbon, an expensive adsorbent highly demanded in the international market, could be an interesting alternative. (2, 4, 8)

In this work, the kinetic parameters of the activation processes of Marabou Wood were determined. These parameters were compared with those obtained for other woods studied under similar conditions. Besides, some useful correlations between the mechanical properties and the kinetic parameters were also inferred.

2. Materials and Methods

Marabou (*Leptoptilus Crumeniferus*) was the biomass precursor studied in this work. Other nine woods were also included with comparative purposes. (19)

2.1. Physical- chemical and activation studies

The physical-chemical study of the activation processes consisted in the determination of some kinetic parameters such as: activation energy, kinetic constant and reaction order. To conduct the study, non-isothermal thermo-gravimetric registers were executed using a Shimatzu-TGA 50 equipment.

The experimental conditions were similar to those used in previous studies with others biomasses what minimize possible diffusive effects, time and money. The final temperature used in this study was 1000°C and the heating rate of 10°C/min. (18)

2.2. Kinetic parameters evaluation

For the evaluation of the kinetic parameters, a simple model known as "*Transient kinetic model in non-stationary state*" was used. This model has been widely used to study chemical reactions between gas and solid products. (9) There are various works that used this model in the kinetic characterization of the heterogeneous catalysis and the carbonaceous materials activation with CO_2, O_2 and/or H_2O. (3, 11, 15)

For these reasons, this model should be adequate to study the kinetic of carbonaceous adsorbents preparation.

This model considers the thermo-chemical reactions of biomasses as processes that occur in a single global stage. This assumption allows the mathematical modeling of the experimental data with a reduced number of parameters using a single following expression:

$$\frac{dX}{dt} = k\,(1 - X)^{n} \qquad [1]$$

Where: **X** is the solid conversion: $X = \frac{m_0 - m}{m_0}$ [2]

t, the time; **k**, the kinetic constant of the global reaction of activation and **n** the reaction order with respect to solid. The experimental data **X** *vs.* **t** was modeling by non-lineal regression. The characteristics parameter of the model was estimated by minimizing the objective function OF:

$$OF = \sum_{i=1}^{N} \left(\left.\frac{dX}{dt}\right|_{exp_i} - \left.\frac{dX}{dt}\right|_{cal_i} \right)^2 \qquad [3]$$

Where: **N** is the experimental data amount; $\left.\frac{dX}{dt}\right|_{exp}$ is the experimental reaction rate, obtained from the thermo-gravimetric registry and $\left.\frac{dX}{dt}\right|_{cal}$ is the reaction rate calculated by the model.

The kinetic energy, AE was calculated by Arrhenius equation: $k = k_0 \exp\left\{-\frac{AE}{RT}\right\}$ [4]

Where: $\mathbf{k_0}$ is the pre-exponential factor; **AE** is the activation energy of the global reaction and **R** the gases universal constant.

2.3. X-Ray Diffraction study

Marabou was characterized by X-ray diffraction analysis using Philip equipment with the following characteristics: radiation of Co (λ=1,78897Å), 40kV, 30mA and $1°2\theta*\mathrm{min}^{-1}$. The particles size was below 62µm obtained by grinding in agate mortar and sieving and then located on a glycerin film.

The measurement of the intensities and positions of the diffracted beams in X-Ray Diffraction (XRD) spectrum, and the use of structure factor equations are necessary in order to determine the atoms distributed in the unitary cells. (1, 20)

In order to determine the crystallinity (η) of the precursors was considered that the energy involved in the diffraction keep constant. Then it can be affirmed that the sum of the dispersed radiation and diffracted one is constant allowing the calculation of the crystallinity through the following expression:

3. Results and Discussion

Non-isothermal thermo-gravimetric registry that characterizes the activation of the raw material is shown in Figure 1. In this Figure **w** is the conversion that can be calculated by: w = (1 - X)*100.

The thermo-gravimetric curve is divided in 3 sections. In section one, up to 220°C it can be clearly observed that the weight loss is minimal. This first loss can be associated with the elimination of absorbed water and the removing of some volatile compounds. In section 2, temperatures higher than 220°C and up to 380°C, a strong weight loss can be observed. This loss is attributed mainly to the pyrolysis o de-volatilization process; in this process a loss of 50% of total mass was registered.

$$\%\eta=\frac{I}{It}*100 \qquad [5]$$

Where: **I** is the dispersed radiation and **It** is the total intensity of the radiation. In order to evaluate the crystallinity using equation 5, firstly, the area under the curve in the angular range from 10° to 45° was determined. The XRD pattern of the studied precursor presents a wide band in this interval indicating the presence of high amount of non-crystalline substances. (12)

Finally, the mechanical resistance of the activated carbon obtained from Marabou was measured. (10) This simple method used a known mass of the granular material that is impacted by six glass balls into a semispherical container of stainless steel. The perceptual relation between the fragmented mass retained in a 0.5 mm mesh and the initial mass is used to estimate the mechanical resistance of the activated carbon. (7)

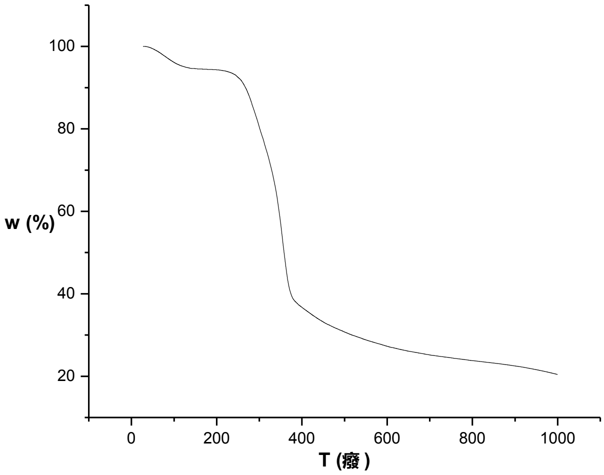

Figure 1. Thermo-gravimetric registry of Marabou.

In section 3, temperature above 380°C the carbon content increased significantly obtained a more porous solid product. This last section is considered, in the majority of revised works, as the activation process.

The carbonized product increases the porosity with the temperature, producing an excellent adsorbent. Furthermore, it is advisable to use low heating rates to avoid undesirable morphological damages during the activation process. It is also necessary to point out that temperature higher than 800°C, significantly affects the yield without notable increase of the micro-porosity. Hence to obtain a better product, it is advisable temperatures near 800°C or below. (6, 18)

Taking into account previous observations derived from Figure 1, the temperature interval from 380°C to 800°C was used to estimate the kinetics parameters of the thermo-chemical reaction studied. The previously defined mathematical model (Equation 1) was used. The results are reported in Table 1.

Table 1. Kinetics parameters of Marabou activation compared with other woods under similar conditions

Sample	AE (kJ/mol)	k(min^{-1})	n	S.D.(%)	V.C.(%)
Iron Wood (Schinosis Balansae)	101.88	$9.38*10^{6}$	1.15	0.19	0.25
Holy Wood (Bulnesia Sarmientoi)	96.18	$4.82*10^{6}$	1.00	0.20	0.23
Teak (Tectona Grandis)	89.52	$9.94*10^{6}$	1.00	0.22	0.26
River Oak (Casuarina Cunninghamiana)	90.52	$1.04*10^{5}$	1.00	0.37	0.44
Eucalyptus (Eucalyptus Robusta)	85.93	$5.00*10^{6}$	1.07	0.16	0.20
Marabou (Leptoptilus Crumeniferus)	84.42	$5.43*10^{6}$	1.00	0.12	0.13
White Carob-tree (Prosopis Alba)	76.60	$8.00*10^{5}$	0.97	0.03	0.03
Mahogany (Jacaranda Semiserrata)	72.72	$6.11*10^{5}$	0.69	0.09	0.11
Pine (Araucaria Angustifolia)	50.00	$1.98*10^{5}$	0.74	0.21	1.04
Cedar (Cedrela Balansae)	49.50	$3.89*10^{5}$	0.98	0.05	0.15

(**AE**: activation energy; **k**: kinetic constant; **n**: reaction order; **S.D.**: standard deviation; **V.C.**: variation coefficient).

From Table 1 it can be deduced that the thermal conversion of Marabou has values similar to semi-hard woods. The reaction orders obtained are, in all cases near to one. Should be noted that the higher values correspond to the *Red Quebracho or Iron Wood*, what is attributable to its higher hardness and hence it's lower reactivity. The very low values for standard deviations (< 0,40%) and variation coefficients (≤0,45%) are indicative that the method applied to estimate the kinetic parameters is adequate.

The crystallinity degree (η) of the raw materials was evaluated from the XRD registry (Figure 2) such as the mechanical resistance. This value was compared with other materials in Table 2.

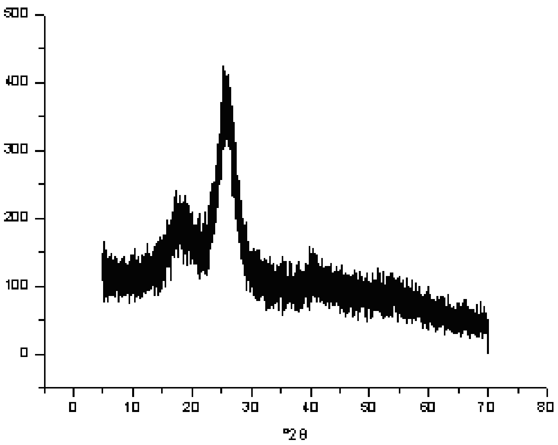

Figure 2. X-Ray Diffraction Registry of Marabou.

Table 2. Crystallinity (η), Mechanical Resistance (Rm) and Density (d) of Marabou and other Materials.

Sample	η (%)	Rm (%)	d (g/cm^3)
Iron Wood (Schinopsis Balansae)	55.36	98.97	1.200
Holy Wood (Bulnesia Sarmientoi)	53.01	96.63	1.150

Teak (Tectona Grandis)	47.32	92.72	1.100
River Oak (Casuarina Cunninghamiana)	45.53	90.15	0.900
Eucalyptus (Eucalyptus Robusta)	42.86	89.00	0.800
Marabou (Leptoptilus Crumeniferus)	39.10	86.63	0.780
White Carob Tree (Prosopis Alba)	41.84	85.76	0.764
Mahogany (Jacaranda Semiserrata)	39.72	81.04	0.850
Pine (Araucaria Angustifolia)	35.49	79.47	0.551
Cedar (Cedrela Balansae)	35.14	77.64	0.483

From Table 2 it should be noted that significant differences were appreciated in the crystallinity degree for the analyzed precursor, compared to the others. Although, in principle, it can be attributed a low reactivity to a greater crystallinity degree, it should be also considered the influence of other factors, for example the chemical composition of the precursor.

The mechanical resistance **(Rm)** of the activated carbon from *Marabou* has an appropriate value. Compared with other materials the *Iron Tree* or *Red Quebracho* has the higher value. From this table it can also be inferred that the less reactive precursors are the harder activated carbons. The differences between the **Rm** values could be due to the different chemical composition of the original products.

The mechanical resistance is very useful to evaluate differences between precursor's reactivity. It is known that the diffusion of weak oxidative reagents, in the structure of precursors of high hardness is hindered; consequently the necessary energy to favor the activation reactions would be higher. Hence, the mechanisms of thermo-chemical conversion differ from one sample to other. During this complex process, different arrangements of the carbon chains take place with the increment of temperature. The thermo-chemical conversion process will be conditioned by the operational conditions used such as the mechanical properties of the materials.

From Table 1 and 2 some correlation between physical-chemical and mechanical parameters can be obtained as show following:

$$\mathrm{Rm} = 0.373*\mathrm{AE} + 58.104\ (R^2 = 0.8762) \quad [6]$$

$$d = 0122*\mathrm{AE} - 0.1155\ (R^2 = 0.8353) \quad [7]$$

$$\eta = 0.338*\mathrm{AE} + 16.607\ (R^2 = 0.784) \quad [8]$$

4. Conclusions

The simple model used in the present study, was an appropriate tool for the determination of the kinetic parameters of *Marabou Wood* activation with steam water.

The kinetic parameters that characterize the synthesis of activated carbon from *Marabou Wood* are similar to those reported to semi-hard woods. These values assure the feasibility of this precursor in the production of this adsorbent.

The statistical parameters assure the right adaptation of the experimental results of the Theoretical Model used, what means that this study is adequate and accurate.

Some useful correlation for the analyzed thermal conversion process was also obtained.

The crystallinity degree of the precursor during the thermo-chemical process studied was determined from the X-ray diffraction analysis.

Acknowledgments

The author wishes to acknowledge Maria Andrea Camerucci and Ana Lia Cavalieri from Mar del

Plata University, Argentina, they provided a crucial help in the experiments of this work.

Conflicts of Interest

The author declares no conflict of interest.

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