Handbook on Emerging
Trends in Scientific Research
ISBN: 978-969-9952-07-4

Kinetic of the Thermal Conversion Processes of Tropical Biomasses

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ABSTRACT

The growing demand of carbonaceous adsorbents, fundamentally for environmental applications, has motivated the use of different resources of biomass unknown until now. In the present work, the characteristic kinetic parameters of the pyrolisis and activation processes corresponding to different tropical renewable precursors (Anoncillo, Brasilete, Marabou barks and coconut shell) were determined by using a simple mathematical model, frequently employed in similar systems. Thermogravimetric tests (TGA) were done in nitrogen atmosphere for the pyrolisis process and N_2-steam water for the activation one up to 1000°C employing a heating rate of 10°C*min^{-1}. Also, the crystallinity degree (η) of the precursors, employed as raw material, was determined by X-ray diffraction analysis (XRD). The characterization of the activated carbons prepared was accomplished through the determination of a parameter that provides an indirect estimation of the impact resistance and wear resistance. The reached results allowed inferring a correlation between the crystallinity degree of the studied renewable precursors and the analyzed thermal conversion processes.

Keywords: Activated carbon precursor, Kinetics parameters, Pyrolisis-activation, Thermal conversion, Thermogravimetric analysis, X ray diffraction.

1. Introduction

Numerous studies about the morphological and textural characterization during the thermal conversion of biomasses resources have been reported. These studies were fundamentally referred at employ of coconut shell and olive stones (Gonzalez, *et al*(1994); Gonzalez, *et al*(1997); Satya Sai, *et al*(1997)). However, other resources that are nowadays fully available and of little competency in other applications in tropical areas, have been barely studied (Villegas Aguilar, *et al*; 2004). In particular, some anthropogenic exotic woods compose one of the resources that increasingly reach more ground in cultivated field. In the last years, important efforts have been accomplished in order to find different alternatives to reduce the negative environmental impact produced by that great amount of biomass. Moreover, the possibility to add them aggregate value could allow achieving a sustainable agricultural development. In this manner, the preparation of activated carbon, expensive adsorbent highly demanded in the international market, constitutes an interesting way (Deiana, *et al*; 2004), (Jaguaribe, *et al*; 2004).

Several raw materials can be used to produce carbonaceous adsorbents (Macías García, *et al*; 2005). The inorganic matter and volatile mass contents, handling easiness and stability during the storage of the raw materials are aspects that should be taken into account for their selection. Moreover, independently of the vegetable precursor, is important to know the thermal cycle since to which will be subjected because of the mass losses are determined by the specific features of its cellular structure that define the final microstructure of their respective activated homologous. Another outstanding aspect to be considered is the activation methods. A basic problem in the development of an activated carbon from a determined precursor is the great diversity of physical and chemical parameters involved. In addition, the efficiency of the developed final product is determined in relation to its application and therefore it defines the final process (Rodriguez-Reinoso, 2002).

In the present work, characteristic the kinetic parameters of the pyrolisis and activation processes of different tropical renewable precursors were determined in order to prepare carbons to be used in specific environmental applications. In addition, a correlation level between the crystallinity degree of the studied precursors and the mass losses during the analyzed thermal conversion processes was also inferred.

2. Materials and Methods

Four tropical vegetable precursors (Table 1), evaluated in the synthesis of adsorbents (Satya Sai, *et al*; 1997), (Villegas Aguilar, *et al*; 2004), were studied. The coconut shell –endocarp- (*Coconuts nucifera*) was included with comparative purposes.

Table-1. Vegetable precursors studied

Precursors	Scientific name
Anoncillo bark	*Lonchocarpus Domingensis*
Brasilete bark	*Caesalpinia Bahamensis*
Marabou bark	*Leptoptilus Crumeniferus*
Coconuts shell	*Cocos Nucifera*

2.1.Chemical-Physical and Activation Studies

The chemical-physical study of the pyrolisis and activation processes consisted in the determination of the kinetic parameters that characterize these processes: activation energy, rate constant and reaction order. For it, the non-isothermic thermogravimetric tests (Shimatzu-TGA 50) were accomplished in similar experimental conditions at the employed in preliminary tests previously accomplished with others biomasses that allow minimizing possible diffusive effects (Villegas Aguilar, 2000).

In the pyrolisis tests, before heating of the sample (10mg; granulometric fraction: 0,03- 0,10µm) was circulated a N_2 current at 80mL*min^{-1} for 30min in order to shift the air of the enclosure and it was stayed during the heating step at 10°C*min-^{1} up to 1000°C. The activation tests were performed in equals conditions that in the pyrolisis ones, but in this case a N_2 current saturated with water vapor was used in order to guarantee the occurrence of the activation process.

2.2. Kinetics' Parameters Evaluation

The evaluation of the kinetic parameters was carried out through the application of a simple mathematical model denominated as transciente kinetic model in non-stationary state (Lizzio, *et al*; 1990). Its employ in the kinetic characterization of the heterogeneous catalysis and ´chars´ activation of the carbonaceous materials, in particular with CO_2, O_2 and H_2O has been reported. For this reason, its utilization in the study of the kinetic of carbonaceous adsorbents preparation was suggested (Di Blasi, *et al*(1998); (Luo and Stanmore (1992); (Roberts and Harris (2000). This model considered the thermochemical conversion reactions of the biomasses as processes that occur in a single global stage. This condition allows realize the mathematical modeled of the experimental with a reduced number of parameters employing the following expression:

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

where: X is the solid conversion:

$$X = \frac{m_0 - m}{m_0} = 1 - w \qquad (2)$$

t, the time; k, the kinetic constant of the global reaction of pyrolisis or activation and **n** the reaction order with respect to solid.

By replacing (1 – X) for w, the expression (1) result:

$$\frac{dX}{dt} = k\,w^{n} \qquad (3)$$

The adjustment of the experimental data w *vs.* t was accomplished by non lineal regression. The characteristics parameter of the model was estimated by minimizing the objective function FO:

$$FO = \sum_{i=1}^{N}\left(\left.\frac{dX}{dt}\right|_{exp_i} - \left.\frac{dX}{dt}\right|_{cal_i}\right)^2 \qquad (4)$$

where: N is the experimental data number considered for fit; $\left.\frac{\mathrm{dX}}{\mathrm{dt}}\right|_{\mathrm{exp}}$ are refer to the experimental reaction rate, obtained of the thermograms and $\left.\frac{\mathrm{dX}}{\mathrm{dt}}\right|_{\mathrm{cal}}$ is the reaction rate calculated with the model. The optimization was realized for k > 0 y n > 0.

For considered model, it was calculated the standard deviation, D.S. as follows:

$$\mathrm{D.S.} = 100\left[\sqrt{\frac{\mathrm{FO}}{\mathrm{N-P}}}\right] \qquad (5)$$

where: P is the number of estimated parameters. Moreover, it was calculated the variation coefficient, C.V. with:

$$\mathrm{C.V.} = 100\left[\frac{\mathrm{FO}}{\overline{\mathrm{W}}_{\mathrm{exp}}}\right] \qquad (6)$$

where: $\overline{\mathrm{W}}_{\mathrm{exp}}$ is the average value of the experimental data.

The kinetic energy, EA of the studied processes was determined by Arrhenius equation:

$$\mathrm{k} = \mathrm{k}_0 \exp\left\{-\frac{\mathrm{EA}}{\mathrm{RT}}\right\} \qquad (7)$$

where: k_0 is the pre-exponential factor; EA is the activation energy of the global reaction and R the gases universal constant.

2.3. X-Ray Diffraction Study

The raw materials were characterized by X-ray diffraction analysis (Philips) employing radiation of Co (λ=1,78897Å), 40kV, 30mA and 1°2θ*min^{-1}. For these tests, granulometric fractions < 62μm of the powdered samples were obtained by grinding in agate mortar and sieving (mesh N° 230), and they located on a glycerin film deposited on the sample holder.

The measurement of the intensities and positions of the diffracted beams in XRD spectrum, and the employ of structure factor equations F_{hld} (Alexander, 1969), (Vainshtein, 1966) are necessary in order to determine the atoms distributed in the unitary cells. The vectorial characteristics of the network and those of the diffracted rays are related to each order through the spatial magnitude, ρ_{hkl} of the network vector and diffracted beam vector, s by means of the following equation:

$$\mathrm{s} = \left|\vec{\mathrm{s}}\right| = \rho_{\mathrm{hkl}} = \frac{2\mathrm{sen}\theta_{\mathrm{hkl}}}{\lambda} - \frac{\mathrm{s}}{2\pi} \qquad (8)$$

where: λ is the employed wave-length.

The integrals on the total reciprocal space and the corresponding to its orderly fraction of both, **I(s)**: intensity of the coherent radiation diffused by the sample at point s in the reciprocal network and **I_0(s)**: intensity at point s where the reflexes corresponding to crystalline part were expressed as follows:

$$\int_0^\infty \mathrm{I(s)d}\upsilon_{\mathrm{I}} - 4\pi\int_0^\infty \mathrm{s}^2\mathrm{I(s)ds} \qquad (9)$$

and

$$\int_0^\infty \mathrm{I}_0\mathrm{(s)d}\upsilon_{\mathrm{I}} - 4\pi\int_0^\infty \mathrm{s}^2\mathrm{I}_{\mathrm{c}}\mathrm{(s)ds} \qquad (10)$$

I(s) and I_c(s) were referred to the dispersion intensities by solid angle unit in the radial distance **s** in the reciprocal space.

For a first approach, the crystalline fraction of the substance in the sample irradiated is expressed in the following way:

$$X_C = \frac{\int_0^\infty s^2 I_c(s)ds}{\int_0^\infty s^2 I(s)ds} \qquad (11)$$

X_C value, experimentally determined, tends to be smaller than the true crystalline fraction due to the fact that a part of the X-ray peak intensity that is diffused by crystalline zone gets lost and appears as diffuse dispersion associated with the background radiation. This radiation arises from the thermal vibrations and network defects.

Therefore, in order to determine the crystallinity of the precursors was considered: $\sum I_c(s)$ as all the intensities of the peaks and $\sum \mathbf{I_{amorf}(s)}$ as the intensities of the beam below the background line.
Taking into account that the energy involved in the diffraction keep constant, it can be affirm that the sum of the dispersed radiation and diffracted one is constant possibility the determination of the crystallinity through the following expression:

$$\%\eta = \frac{I}{It}\ 100 \qquad (12)$$

where: I is the dispersed radiation and It is the total intensity of the radiation. In order to evaluate the crystallinity from the equation 11, firstly, the area below the wide band in the range 10 to 45 °2θ was determined. XRD patterns of the studied precursors present a wide band in this interval indicating the presence of high amount of non crystalline substances (Magnaterra et al., 1994).
The activated carbons obtained from studied precursors were characterized by determining a parameter that provides an indirect measure of the impact resistance and wear resistance. A similar method to employed one by Lovera was used. A known material mass was fragmented by impact and friction of six glass balls in the semispherical container of stainless steel. The perceptual relation between the fragmented mass retained in mesh N° 35 (0,5 mm) and the initial mass was considered as a measure of the mechanical resistance of the activated carbons (Heschel and Klose, 1995).

3. Results and Discussion

Non-isothermal thermo-grams that characterize the pyrolisis process of the studied raw materials are shown in Figure 1.

The thermo-gravimetric curves of the four precursors presented similar characteristics: up to ~220°C, the weight losses were associated with the elimination of both the adsorbed water in the samples and the volatile composites removed by dragging of the water steam flow disinterested of the biomass during the evaporation process.

In all the materials, at temperatures higher than 220°C, a strong weights loss (significative change of slopes in the range 20-35 min.) attributed to beginning of the carbonization process produced by volatile composites elimination, was registered. Between 220 and 330°C, the higher weight loss rates of the biomasses produced. In this manner, solid residues practically volatilized but with incomplete carbonization inside the samples were obtained, like one was observed visually.

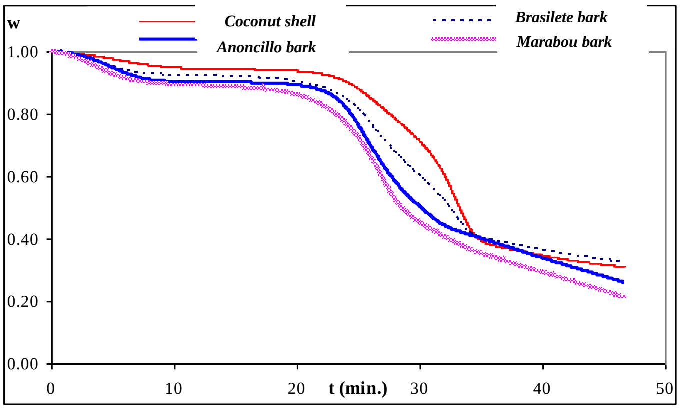

Figure-1. Thermo Gravimetric Curves of The Pyrolysis Process Corresponding To The Studied Renewable Precursors.

The weight loss rates registered between 220 and 330°C were smaller for the Coconut shell and the Brasilete bark than for the Anoncillo and Marabou barks, registering in all the cases a loss of 60-80% of total mass.

With the increment of the temperature, the fixed carbon content in the charred residual product increased lightly, being obtained a solid, more and more, porous.

Starting from these obtained results, it can infer that pyrolisis temperatures higher than 330°C originate charred with appropriate conditions for the later synthesis of adsorbents.

Nevertheless, the employment of low heating rates is advisable in order to avoid drastic morphological damages during the pyrolisis process and later activation (Rodriguez-Reinoso, 2002).

Based on the obtained results from the thermogravimetric tests, it was considered the interval of temperatures between 220 and 330°C (temperatures range where occurs the greatest elimination of volatiles) in order to value the kinetics of the thermal decomposition process.

The kinetic parameter values determined are presented in the Table 2.

Table-2. Characteristic kinetic parameters of the precursor pyrolysis (EA: activation energy; K: kinetic constant; n: reaction order regarding the solid)

Precursor	EA (kJ*mol1)	K (min-1)	n	DS* (%)	VC* (%)
Anoncillo bark	84.42	5.43x106	1	0.12	0.13
Brasilete bark	85.93	5.00x106	1.07	0.16	0.2
Marabou bark	76.6	8.00x105	0.97	0.03	0.03
Coconut shell	115.4	1.21x106	0.97	0.2	0.23

* SD: standard deviations; VC: variation coefficient.

The low values obtained for standard deviations (< 0,25%) and the variation coefficients (0,50%) seem to indicate that the method used to estimate the kinetic parameters is appropriate and that the obtained values of this estimate are reliable. The process of the studied precursors, pyrolisis, was characterized to possess activation energy values in the range of those reported in the literature for similar precursors, from 23,6 up to 166 kJ*kmol^{-1} and, relatively low, with regard to those reported for other biomasses (Villegas Aguilar *et al*., 2004), (Villegas Aguilar, 2000).

The highest activation energy and, consequently, the smallest reactivity for the pyrolisis process was obtained for the Coconut shell, being the order of reactivity of the process Marabou > Anoncillo > Brasilete > Coconut shell. In all the cases the obtained reaction orders are near to the unit.

The resulting thermograms of the activation process with water vapor of the obtained solid products of the pyrolisis of the studied vegetable precursors are shown in Figure 2.

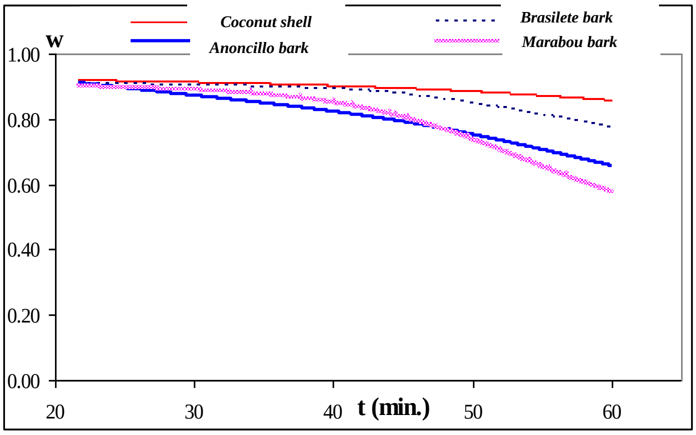

Figure 2. Thermo gravimetric curves of the activation process with water vapor corresponding to the solid products obtained from pyrolysis of the studied renewable precursors.

It is observed that the curves experience a softer fall (they present a smaller weight loss rate that in the pyrolisis process) in agreement with the fact that this process occurs more slowly.

Applying of the previously defined mathematical model, the kinetic parameters involved in this process were estimated (Table 3).

Table-3. kinetic parameters of the activation process (ea: activation energy; k: kinetic constant; n: reaction order regarding the solid) and yield of the precursor pyrolysis reaction (ra).

Precursor	EA (kJ*mol1)	K (min-1)	n	DS* (%)	Ra
Anoncillo bark	109.52	9.94x106	1	0.22	50
Brasilete bark	116.18	4.82x106	1	0.2	50.7
Marabou bark	100.52	1.04x105	1	0.37	46
Coconut shell	141.88	9.38x106	1.15	0.19	51.7

* S.D.: standard deviations

The activation of the studied precursors was characterized to possess relatively superior activation energy values to the obtained ones in the respective pyrolisis processes (the higher value was obtained for the Coconut shell according to this precursor's drop reactivity), were in the interval of those reported for this type of process (Villegas Aguilar *et al*., 2004); (Villegas Aguilar, 2000).

The most reactive precursor was the Marabou bark, while the Coconut shell evidenced the smallest reactivity (the lowest loss of mass into the analyzed time).

The reactivity order was similar to that of the pyrolysis process: Marabou > Anoncillo > Brasilete>> Coconut shell.

For all the precursors, reaction orders near to the unit were determined. The kinetic constants were next to each other, to exception of the obtained one with the Marabou bark. This precursor presented an inferior order of magnitude to that of the remaining precursors. The obtained yields for the activation process were appropriate and similar to the values reported in the literature (Villegas Aguilar *et al*., 2004); (Villegas Aguilar, 2000). (Heschel and Klose, 1995).

From the difractograms of the original precursors, the crystallinity degree of each one of the raw materials was evaluated (η) (Table 4).

The crystalline of each precursor was determined in order to correlate this parameter with the weight loss that takes place during the pyrolisis and activation events.

Significant differences significant differences were appreciated in the crystallinity degree for the analyzed precursors.

The lowest values were registered in the Marabou and Anoncillo barks, while the Brasilete bark and the Coconut shell presented higher values, in relative agreement with the reactivity order observed for the different precursors.

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.

Table-4. Volume parameters for atoms, groups, and fragments

Precursor	η (%)	Rm (%)
Anoncillo bark	39.1	94.4
Brasilete bark	47.3	90.2
Marabou bark	35.1	86.6
Coconut shell	55.4	99

In relation to the mechanical characteristics of the obtained products, all the activated carbons presented appropriate values of the analyzed mechanical parameter (Rm).

The Coconut shell showed the highest value of Rm while those values obtained for the rest of the precursor were lightly smaller. In addition, the precursors that evidenced low reactivity in pyrolisis and activation processes (e.g. Coconut shell) developed activated carbons with the highest Rm. However, the different Rm values can be justified keeping in mind the different structural composition of the products of vegetable origin employed.

The considered Rm parameter result of utility when is sought to evaluate differences in the precursor reactivities.

It is known that the diffusion of weak oxidative reagents, in the structure of precursors of high hardness is hindered; consequently so much the necessary energy to favor the reactions of controlled gasification or of activation is superior. In addition, the mechanisms of thermochemistry conversion differ from a sample to the other one, since during this complex process, different arranging of the carbon chains take place with the increment of temperature, which will be conditioned as much by the operational variables employed as the mechanical properties of the treated material.

4. Conclusions

The employment of a simple model, as the one considered study presently, was an appropriate tool for the determination of the kinetic parameters in both the pyrolisis and activation processes of the studied renewable precursors.

Starting from the X-ray diffraction analysis, the crystallinity degree of the precursors was determined being inferred a certain correlation between their reactivity and the analyzed thermal conversion processes.

In the synthesis of activated carbons starting from the thermal conversion of the different studied biomasses, the kinetic parameter values allow to anticipate the feasibility of the employment of these precursors in the production of activated carbons, as alternative to the obtained one from the coconut shell.

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