PERFORMANCE ANALYSIS OF PILOT ROTARY KILN FOR ACTIVATED CARBON MANUFACTURE, USING A STEADY STATE MATHEMATICAL MODEL

O. A. ORTIZ, N. D. MARTÍNEZ, C. A. MENGUAL and L. M. PETKOVIC

Instituto de Ingeniería Química, Univ. Nac. de San Juan, 5400 – San Juan, Argentina.
rortiz@unsj.edu.ar

***Abstract*— The physical activation of charcoal from eucalyptus wood has produced excellent results in laboratory tests. The obtained activated carbons have good adsorbent properties with surface areas over 500 m^2/g, low density and moderate attrition resistance. The activation process is strongly endothermic and involves gasification of the carbonaceous char by oxidation with either water vapor or carbon dioxide in the temperature range of 1073 – 1373 K. This process is carried out in either directly or indirectly fired activators, such as rotary kilns. The goal of this work is to describe the performance analysis carried out on a pilot rotary kiln, using a previously developed steady state mathematical model. The comparison between simulated and experimentally data has been reported in a previous paper. The model accounts for the complex transfer and reaction phenomena, which occur inside the kiln. The model was solved by a finite difference method. The solution predicts solid, freeboard gas, and wall temperature axial profiles, as well as the mass variations in the solid and freeboard gas, due to activation reaction and solid drying. The performance of the activator can be measured through its production rate, burn off, and solid temperature profile. To analyze the influence of different operating conditions on the equipment performance, the main operating variables (i.e., gas, steam, and solid flow rate, residence time, and solid temperature) have been studied. The results obtained from the sensitivity analysis allow for the identification of the operation variables that can be optimized.**

***Keywords*— Performance Analysis, Rotary Kiln, Activated Carbon.**

I. INTRODUCTION

Activated carbon (AC) is a well known adsorbent material, which finds its use mainly in chemical, mining and food industries, and also in other important applications as purification and deodoration processes, water treatment, medicine, etc. (Yehaskel, 1978, Bansal et al. 1988). In Argentina, large volumes of AC are imported from China, USA, Japan and Brazil. Therefore, there is an increasing interest in the development of technology to cope with the local demand.

Studies of physical activation at laboratory scale have been performed on charcoal samples obtained from various raw materials, for example, eucalyptus wood (which is an abundant and low-cost material in the Cuyo region, Argentina), fruit stones, residues from the manufacture of olive and grape oils, poplar wood, olive tree wood and grape stalk (Deiana et al. 1998). Using these data, approximate kinetic expressions were also developed (Martínez, 1998). Furthermore, a pilot-scale rotary kiln has been built for experimental studies of the physical activation process of charcoal obtained from raw materials of the region.

Rotary kilns are used by almost all important AC world manufacturers (i.e. Norit & Co.). Although Boateng and Barr published in 1996 a general thermal model for a rotary kiln that included heat transfer within the bed, studies about the modeling of the activation process of charcoal with water vapor in rotary kilns are lacking in the open literature. On the other hand, there is abundant literature of studies about the process physical chemistry at laboratory scale, and also about physical and chemical characterization of the product (Tancredi et al. 1996). Due to the specificity arising from each raw material, there are not published studies on the activation reaction kinetics, because of the difficulties associated with proposing general-type kinetics for the process. The majority of published papers on the activation and re-activation processes at pilot scale are empirical (Smith, 1979; Laine et al. 1991), and a mathematical model to predict the steady state and dynamic behavior of rotary kilns for the activation of charcoal is not available at present.

The present work describe the performance analysis carried out on a pilot rotary kiln, using a previously developed steady state mathematical model (Ortiz et al. 2003), aiming to obtain valuable information for the proper selection of operating conditions and design parameters.

II. ROTARY KILN MODELING

The rotary kiln under study basically consists of a cylindrical shell, which rotates about a slightly inclined, horizontal axis. The hot gases and carbon flow counter currently in direct contact with each other in the shell. Water vapor is injected in counter current with the solids, at the discharge end. See Figure 1 for an outline of the rotary kiln and Table 1 for nominal operation conditions. Raw material is carbonaceous material from regional resources such as eucalyptus wood. This material had been tested in laboratory, using a fixed bed furnace to activation with water vapor (Deiana et al. 1998).

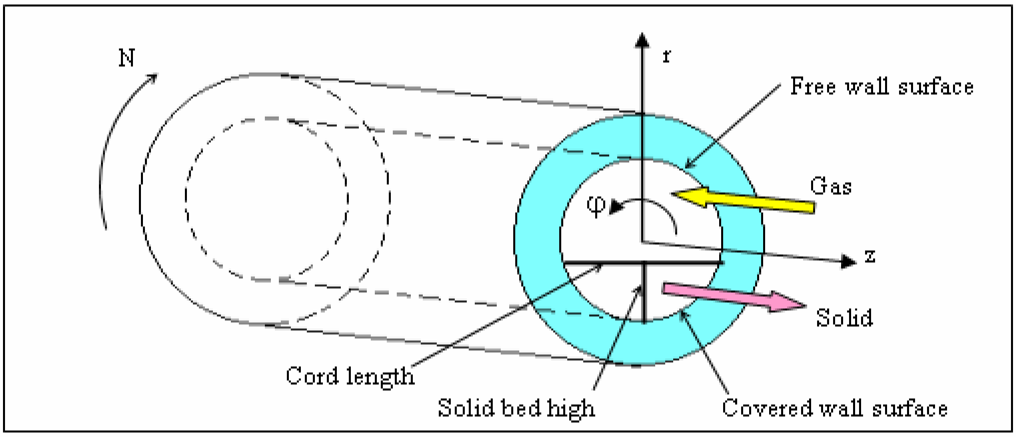

Fig. 1. Reactor scheme and cross section.

Table 1. Equipment characteristics and nominal operation conditions.

Length and Internal Diameter	3.7 m and 0.30 m
External Diameter	0.60 m
Raw Material	solid carbonaceous material
Moisture Content	5 – 10 %
Particles Size	0.002 m [(-6+20) # ASTM]
Input Flow Rate of Solids	$2.78 \cdot 10^{-3}$ Kg/s
Activation Gas	water vapor
Water Vapor Flow Rate	$3.53 \cdot 10^{-3}$ Kg/s
Reaction Temperature	1073 – 1273 K
Heating	direct from natural gas combustion
Gas Flow Rate	≅ 6.5· [Input Flow Rate of Solids]
Cylinder Rotation Velocity	1 – 3 rpm
Rotary Kiln Inclination	2 – 6 %
Residence Time	< 7200 s
Solid Input Temperature	room temperature

A. Mathematical Modeling

The following assumptions were made in order to develop the model:

- Solids and gas velocity are constant along the longitudinal axis of the rotary kiln.
- There is no variation of parameters in radial direction.
- Axial heat transfer due to conduction and radiation is insignificant, including the conduction in the axial direction of wall.
- Mixing of solids in axial direction is negligible.
- Coefficients of convection, emissivities, specific heats, latent heat, and heat of reaction are independent of temperature.
- There is no drag of solids particles by the flue gas.
- The kiln operates at thermal equilibrium (temperatures will be steady over time).
- The activation reaction follows Arrhenius' law.

B. Chemical Reaction

The main objective of the rotary kiln under study is to carry out the activation reaction of charcoal with water vapor to produce activated carbon, according to the following reactions:

$$C + H_2O \implies CO + H_2 \quad [130 \text{ kJ / mol}] \qquad (1)$$

Even though secondary reactions also occur at high temperature (1173 K) and atmospheric pressure, reaction 1 is the predominant one. When the activation process is carried out with an excess of water vapor, the main occurring reaction is 1, and assuming that water partial pressure is constant, according to Arrhenius´ law, the rate of carbon activation can be written down as equation 2 in Table 2 (Martínez, 1998).

The mathematical model (Ortiz et al. 2003) accounts for the complex transfer and reaction phenomena, which occur inside the rotary kiln. The main processes in the kiln are: heat and mass transfer (drying zone), heat transfer (heating zone) and heat and mass transfer associated to the reaction (reaction zone) (Barr et al. 1989). The momentum transfer has not been incorporated in the model, due to its negligible influence on the thermal behavior. The equations that constitute the steady state model are shown in Table 2.

Table 2. Steady State Model of Rotary Kiln.

Activation Rate: $$r_s = -\frac{\partial Q_s}{\partial z} = \frac{6.005\left[\exp\left(-8033/T_s\right)\right]Q_a\ Q_s}{V_s} \quad (2)$$

Free Moisture Mass Balance: $$\frac{\partial Q_h}{\partial z} = -\frac{h_t \cdot A \cdot (T_g - T_s) \cdot Q_h}{H_v \cdot (0.1 \cdot Q_s)} \quad (3)$$

Solid Mass Balance: $$\frac{\partial Q_s}{\partial z} = -k_e \cdot e^{-\left(\frac{8033}{Ts}\right)} \cdot Q_a \cdot \frac{Q_s}{V_s} - \frac{h_t \cdot A \cdot (T_g - T_s) \cdot Q_h}{H_v \cdot (0.1 \cdot Q_s)} \quad (4)$$

Gas Mass Balance: $$\frac{\partial Q_g}{\partial z} = -k_e \cdot e^{-\left(\frac{8033}{Ts}\right)} \cdot \frac{Q_s}{V_s} \cdot Q_a \cdot \frac{30}{12} - \frac{h_t \cdot A \cdot (T_g - T_s) \cdot Q_h}{H_v \cdot (0.1 \cdot Q_s)} \quad (5)$$

Gas Energy Balance: $$\frac{\partial (Q_g \cdot C_g \cdot T_g)}{\partial z} = -C_3 \cdot (T_g - T_s) - C_4 \cdot (T_g^4 \cdot e_g - T_s^4 \cdot A_v) - C_5 \cdot (T_g - T_w) - C_6 \cdot (T_g^4 \cdot e_g - T_w^4 \cdot A_v) + \frac{\partial Q_h}{\partial z} \cdot C_v \cdot (T_s - 373) \quad (6)$$

Solid Energy Balance: $$\frac{\partial \left(Q_s \cdot C_s \cdot T_s\right)}{\partial z} = C_3 \cdot (T_g - T_s) + C_4 \cdot (T_g^4 \cdot e_g - T_s^4 \cdot A_v) + C_7 \cdot (T_w - T_s) + C_8 \cdot (T_w^4 \cdot e_g - T_s^4 \cdot A_v) - \frac{\partial Q_h}{\partial z} \cdot H_v - k_e \cdot e^{-\left(\frac{8033}{Ts}\right)} \cdot \frac{Q_s}{V_s} \cdot Q_a \cdot \Delta H \quad (7)$$

Inner Wall Temperature:

$$T_w = \frac{\left[\frac{T_a}{h_i \cdot R_i} + T_g \cdot \left[\frac{1}{\left[\left[1 + \frac{T_a}{T_{w0}} + \left(\frac{T_a}{T_{w0}}\right)^2 + \left(\frac{T_a}{T_{w0}}\right)^3\right] \cdot e_{w0} \cdot \sigma \cdot \left(T_{w0}\right)^3 + h_o\right] \cdot R_e}\right] - \frac{\ln \frac{R_i}{R_e}}{K_w}\right]}{\frac{1}{h_i \cdot R_i} + \frac{1}{\left[\left[1 + \frac{T_a}{T_{w0}} + \left(\frac{T_a}{T_{w0}}\right)^2 + \left(\frac{T_a}{T_{w0}}\right)^3\right] \cdot e_{w0} \cdot \sigma \cdot \left(T_{w0}\right)^3 + h_o\right] \cdot R_e} - \frac{\ln \frac{R_i}{R_e}}{K_w}} \quad (8)$$

Outer Wall Temperature: $$T_{w0} = T_w - \frac{\left[T_w - T_a\right] \cdot 0.693}{0.693 + \frac{k_w}{h_o \cdot R_e}} \quad (9)$$

The parameters C3,…, C8 in the model given in Table 2 are shown in Table 3. More details about the model developed and its solution method can be found in Ortiz et al. (2003)

III. PERFORMANCE ANALYSIS

The rotary kiln performance can be described by production rate, burn off, and activation temperature. On the other hand, burn off and activation temperature can be correlated with different quality indexes, such as mechanical strength, pore volume, and microporous to mesoporous ratio (Tancredi et al. 1996). Laboratory tests have shown that activation temperature, residence time, flow rate and composition of gas phase, and the presence of alkaline additives determine such a performance (Wigmans, 1989). Therefore, the sensitivity of burn off, production rate and solid activation temperature respect to the main operating variables has been estimated using the proposed steady state model.

The operating variables are: residence time, flow rate and inlet temperature of solid phase, gas flow rate, vapor flow rate, and moisture contents. The analysis was done at nominal conditions, varying one variable and maintaining the others constant. The combined effect of two or more variables will be addressed in a future work once the process optimization is analyzed.

The plots of Figs. 2 to 9 illustrate the mentioned above sensitivity.

Table 3. Equation parameters.

$$C_3 = h_{gs} \quad L_{cu}$$

$$C_4 = \frac{\sigma \cdot L_{cu} \cdot e_s}{[1 - (1 - e_s)(1 - A_v)]}$$

$$C_5 = h_{gw} \quad L_{li}$$

$$C_6 = \frac{\sigma \cdot L_{li} \cdot e_w}{[1 - (1 - e_w)(1 - A_v)]}$$

$$C_7 = h_w \cdot L_{es}$$

$$C_8 = \sigma \cdot L_{cu} \cdot \phi_{sw} \cdot e_w \cdot e_s$$

$$\phi_{sw} = \left\{ \frac{1}{1 - e_g} - (1 - e_w) \cdot \left[\frac{L_{cu}}{L_{li}} \cdot (1 - e_s) + \left(1 - \frac{L_{cu}}{L_{li}}\right) \right] \right\}^{-1}$$

A. Sensitivity Analysis

The residence time, vapor flow rate, gas flow rate and solid flow rate, play an important role on the production, as can be observed in Fig. 2, 3, 4, and 5. The first three produce an increment in the burn off. The mesoporous to microporous ratio depends on the activation temperature level. A raise in solid flow rate, keeping constant the other variables, produces a decrease in burn off and therefore a minor pore volume. The influence on the production rate has similar characteristics, although inverse.

Considering the residence time, vapor flow rate, input gas flow rate, and input solid flow rate, an increase of two times in the manipulated variable conducted to a change of above 20 % in production.

On the other hand, for both input solid temperature and moisture content, the change in production was below 10 % for an increase of about two times in the manipulated variable (see Fig. 6 and 7).

The average between the starting activation temperature (1073 K) and the solid temperature at the discharge end has been considered as the activation temperature. This is due to the solid temperature is not constant along the longitudinal axis.

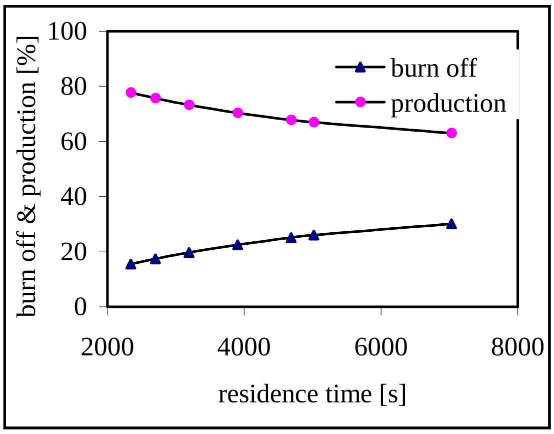

Fig. 2. Burn off and Production vs. Residence Time.

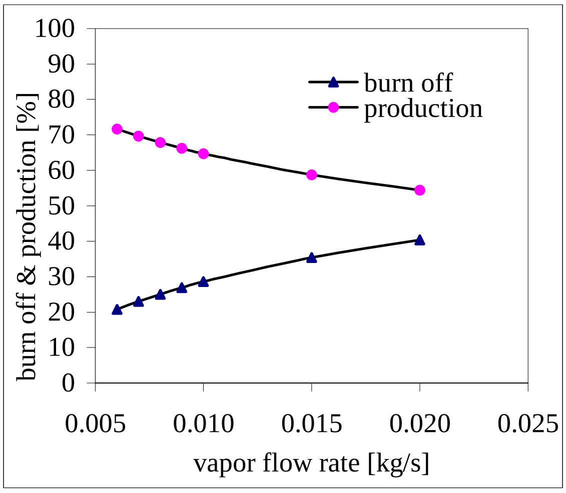

Fig. 3. Burn off and Production vs. Vapor Flow Rate.

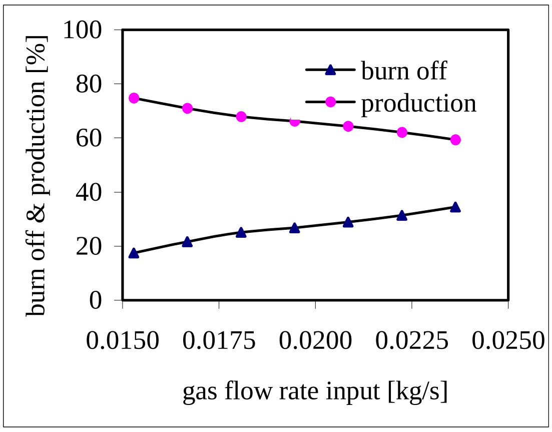

Fig. 4. Burn off and Production vs. Gas Flow Rate Input.

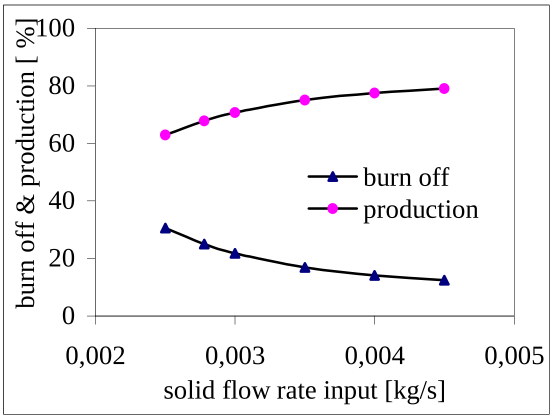

Fig. 5. Burn off and Production vs. Solid Flow Rate Input.

The activation temperature decreases with an increment in residence time (Fig. 8), as it could be expected for an endothermic reaction. Similar behavior in the sensitivity of activation temperature respect to an increase in vapor flow rate has been observed (Fig. 9).

The input solid flow rate has the greater influence on the activation temperature. The higher input solid flow rate the lower activation temperature. By other hand a decrease in activation temperature produces a decrease in the burn off (Tancredi et al. 1996). The input solid temperature and moisture contents have less influence on activation temperature.

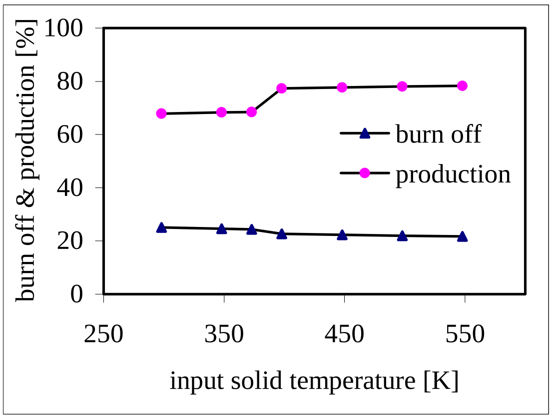

Fig. 6. Burn off and Production vs. Input Solid Temperature.

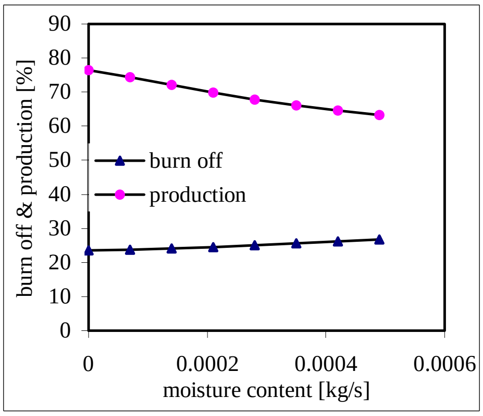

Fig. 7. Burn off and Production vs. Moisture Content.

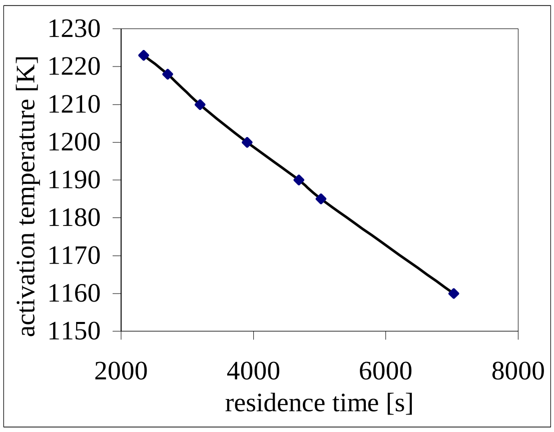

Fig. 8. Activation Temperature vs. Residence Time.

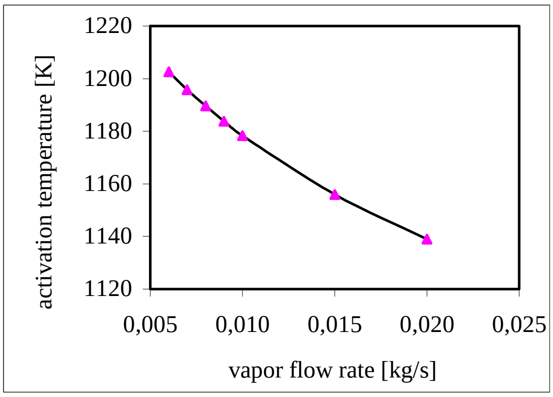

Fig. 9. Activation Temperature vs. Vapor Flow Rate.

IV. CONCLUSIONS

The simulation of the rotary kiln under different operating conditions and the sensitivity analysis show that residence time, vapor flow rate, gas flow rate input, and solid flow rate input, have a significant influence on the performance of the activation process in the pilot plant. Therefore, these operating variables can be considered as optimization variables. These conclusions are in agreement with laboratory tests reported by Wigmans (1989). To solve the model more easily, the composition of gas phase and presence of alkaline additives were not considered in this first contribution.

The results obtained allow for the identification of operating variables that can be manipulated to optimize the rotary kiln performance. Furthermore, they contribute to a better understanding of the activation process. As a next step, optimization studies will be developed to obtain data that help in the improvement of the pilot rotary kiln operation.

Finally, the development of design and control strategies is also needed and it will be addressed in future work.

NOMENCLATURE

A	Gas-solid surface per unit of length [m^2/m]
Av	Absorptivity
Cg	Average specific heat of gas [kJ/kg · K]
Cs	Average specific heat of solid [kJ/kg · K]
Cv	Average specific heat of steam [kJ/kg · K]
eg	Gas emisivity
es	Solid emisivity
ew	Emisivity of internal surface of wall
ewo	Emisivity of external surface of wall
hgs	Heat transfer coefficient between the solid and gas [W/m^2 · K]
hgw	Heat transfer coefficient between the wall and gas [W/m^2 · K]
hou	Heat transfer coefficient between the wall and surrounding [W/m^2 · K]
ht	Heat transfer coefficient for drying process [W/m^2 · K]

hw Heat transfer coefficient between the solid and wall [$W/m^2 \cdot K$]
Hv Latent heat of vaporization of water [kJ/kg]
ΔH Heat of reaction [kJ/kmol]
ke First order reaction rate constant [s^{-1}]
kw Thermal conductivity of wall [$kW/m \cdot K$]
L_{cs} Covered wall surface [m^2]
L_{cu} Cord length [m^2]
L_{li} Free wall surface [m^2]
Qg Gas flow rate [kg/s]
Qh Moisture flow rate [kg/s]
Qs Solid flow rate [kg/s]
Qa Steam flow rate [kg/s]
Re External radius of the cylinder [m]
Ri Internal radius of the cylinder [m]
rs Activation reaction rate (coal) [$kg/s \cdot m$]
Ta Surrounding temperature [K]
Tg Gas temperature [K]
Ts Solid temperature [K]
Tw Temperature of internal surface of the wall [K]
Two Temperature of external surface of the wall [K]
Vs Solid velocity [m/s]
z Longitudinal coordinate [m]
ϕsw Radiation number
σ Boltzman constant $5.57.10^{-8}$ [$W/m^2 K^4$]

REFERENCES

Bansal, R. C., J. B. Donnet and F. Stoeckli. *Active Carbon*, Ed. M. Dekker (1988).

Barr, P. V., J. K.Brimacombe and A. P. Watkinson, "A Heat Transfer Model for the Rotary Kiln. Part I. Pilot Kiln Trials", *Metallurgical Transactions*, **20B**, 391-402 (1989).

Boateng, A. A. and P. V. Barr, “A Thermal Model for the Rotary Kiln Including Heat Transfer within the Bed”, *Int. J. Heat Mass Transfer*, **39**, 10, 2131-2147 (1996).

Deiana, C., L. M. Petkovic and , S. E. Noriega. "Carbón Activado a Partir de Materias Primas Regionales", *Información Tecnológica*, **9**, 5 (1998).

Laine, J., S Simoni and R.Calles, "Preparation of Activated Carbon from Coconut Shell in a Small Scale Cocurrent Flow Rotary Kiln", *Chem. Eng. Comun.*, **99**, 15 – 23 (1991).

Martínez, N.D.. “Internal Report” (not published), Universidad Nacional de San Juan, (1998).

Ortiz, O. A., N. D. Martinez, C. A. Mengual, and , S. E. Noriega, “Steady State Simulation of a Rotary Kiln for Charcoal Activation”, *Lat. Am. Appl. Res.* **33**, 51-57 (2003).

Smith, S. B., “Activated Charcoal for Water Purification from Florida Woods”, Final Report Project A-2214, Prepared for United States Department of Agriculture, Southeastern Forest Experiment Station, Asheville, North Carolina 28802, Georgia Institute of Technology, available in: http://www.acrl.org/db/paper/JohnAdams_C-103.pdf. (1979).

Tancredi, N., T. Cordero, J. Rodrigues-Mirasol and J. J. Rodríguez, “Activated Carbons from Uruguayan Wood”, *Fuel*. **75**, 1701-1706 (1996).

Wigmans, T., “Industrials Aspects of the Production and Use of Activated Carbons”, *Carbon*, **27** 1, .13-22 (1989).

Yehaskel, A. *Activated Carbon, Manuf. and Reg.*, Noyes Data Corp., Par Ridge, N. .Jersey (1978).

Received: September 16, 2001.
Accepted for publication: February 20, 2003.
Recommended by Guest Editors: J. Cerdá, S. Díaz and A. Bandoni.