ACTIVATED CARBON PELLETS FROM EUCALYPTUS CHAR AND TAR
TG studies

A. Amaya[1], J. Píriz[1], N. Tancredi[1*] and T. Cordero[2]

[1]Universidad de la República, Facultad de Química, DETEMA, Cátedra de Fisicoquímica y Laboratorio de Fisicoquímica de Superficies, Gral. Flores 2124, CC 1157, 11800 Montevideo, Uruguay
[2]Universidad de Málaga, Escuela Técnica Superior de Ingenieros Industriales, Departamento de Ingeniería Química Campus de El Ejido, 29071, Málaga, Spain

Char and tar derived from pyrolysis of Uruguayan Eucalyptus wood has been evaluated as raw materials for the preparation of high mechanical resistance activated carbon pellets. Thermogravimetric analysis was used as the main technique for studying tar and char pyrolysis in N_2 and CO_2 atmospheres, and to determine the best conditions for CO_2 activation of the carbon pellets. Results indicated that activated carbon pellets with high surface area and good mechanical resistance were obtained by CO_2 gasification at 1098 K. Pellets properties can be explained as due to the independent contribution of each component.

Keywords: activated carbon, gasification, pelletization, wood tar

Introduction

Activated carbon is a commercial adsorbent, which can be prepared from a variety of raw materials [1–3]. Some of them such as coconut shell are adequate for a direct preparation of granular carbon, used in flow treatments, with the advantage of regeneration and re-using. Others, such as wood wastes and soft carbonaceous materials [4–6] produce powder activated carbons (commonly used as a disposable adsorbent) and can be transformed in granular carbon or carbon pellets by binding or agglomeration techniques [7–12]. The use of wood tar as the binder and wood char as the carbonaceous material, to be agglomerated, is particularly interesting, because both are products in wood pyrolysis [13, 14].

Biomass carbonization (pyrolysis) produces about a 20% of residual tars, which are frequently used as fuels. The use of these residual tars as a binder increases the value of this thermochemical process either on an economical as on an environmental point of view.

Thermogravimetric analysis (TG) and derivative thermogravimetric curves (DTG) has been frequently used in the study of wood pyrolysis and char-carbon gasification [4, 14, 15–25]. On the other hand, un-catalysed wood charcoal CO_2 gasification has been the subject of several studies in the past [26, 27].

Wood wastes are the main source of carbonaceous materials in Uruguay, and several studies were accomplished for the preparation of powdered activated carbon from it [4–6, 19, 27]. In previous works we have studied the preparation of activated carbons

by CO_2 partial gasification of biomass and the kinetics of the gasification process [19, 27] as well as the possible application of these carbons in the adsorption of polluting agents and its relation with the preparation methods [4–6]. In this work, char and tar derived from pyrolysis of Uruguayan Eucalyptus wood has been used as raw materials for the preparation of activated carbon pellets. Thermogravimetric method has been used as the main technique for studying the processes occurring in tar and char pyrolysis and activation, and to determine the activation conditions.

Experimental

Materials

A commercial char prepared by pyrolysis of Eucalyptus wood has been used as carbonaceous raw material. Tar was obtained from pyrolysis of *Eucalyptus Grandis* sawdust, by condensation at room temperature (298 K) of the produced gases.

Pyrolysis was performed in a horizontal tubular furnace (Carbolite Furnaces CTF 12/75), at 723 K and under N_2 flow of 500 cm^3 (STP) min^{-1}.

Carbon pellets were obtained by adding tar on the char, drop by drop, until a homogeneous paste was formed (final ratio char:tar 40:60). This wet paste (water content 25%) was extruded, obtaining cylindrical pellets, which were dried at 378 K for 2 h and stored in dry atmosphere.

---

*   Author for correspondence: nestor@fq.edu.uy

Activated carbon pellets were prepared in the TG system and carbon pellets were pyrolysed under N_2 atmosphere until 1098 K; then the gas was changed to CO_2, until a specified burnoff was achieved. Flows were of 50 cm^3 (STP) min^{-1} and a platinum pan was used in all the experiments. Other conditions are specified in the results and discussion section, as they were a result of thermogravimetric studies.

Methods

Thermogravimetric studies were performed in a thermogravimetric analyser Shimadzu TGA-50, using platinum pan, and heating rate of 5 K min^{-1}, from ambient temperature until 1098 K (activation studies) or until 1173 K (other studies). Gas flow was 50 cm^3 (STP) min^{-1}, and the gases used were N_2 99.998% and CO_2 99.996%. N_2 was passed through traps to retain humidity.

Ultimate analysis of wood, char, tar (dried 298 K-fraction), carbon pellets and activated carbon pellets was performed with a Carlo Erba, EA 1108 CHNS-O model. Char and tar treated in the same conditions than carbon pellets (to obtain activated carbon pellets) has been also analysed; these samples were named treated char and tar.

Water content for all the samples was determined by drying at 378 K, until constant mass. Ash content was determined by TG with a flow air of 50 cm^3 (STP) min^{-1}, heating up to 1223 K at 5 K min^{-1} and maintaining this temperature during 1 h.

The resistance to impact of pellets and activated carbon pellets were determined by analyzing whether the pellet maintained its integrity after dropping it from a height of 1 m. The drop number, defined as the average number of drops to cause fracture of the pellet, was the resistance indicator [28, 29]. Granulates with drop numbers higher than 10 were considered resistant to impact. Different samples were analyzed: 1) dry carbon pellets; 2) dry carbon pellets, pyrolysed in the TG system in N_2 atmosphere, at 15 K min^{-1}, from ambient

temperature to 1098 K; 3) dry carbon pellets, pyrolysed in the TG system in N_2 atmosphere, at 15 K min^{-1}, from ambient temperature to 1098 K and then activated by CO_2 partial gasification, at 1098 K, until a burnoff of 10% and a burnoff of 20% with respect to the initial mass at 1098 K. Some additional experiments were performed with carbon pellets activated with air at 673 K, in order to compare their properties with those of carbon pellets activated with CO_2.

Nitrogen adsorption–desorption studies at 77 K were carried out in an automatic volumetric sorption analyser Autosorb-1 (Quantachrome Corp.), after overnight outgassing at 150°C. BET specific surface areas of samples were determined from these data, and micropore volumes were calculated by applying t and Dubinin Radushkevich methods (V_t and V_{DR}, respectively). Mesopore and part of macropore volumes were determined as the difference between adsorbed volume at a relative pressure of 0.95 ($V_{0.95}$) and V_t [30].

Results and discussion

Table 1 shows the results for the ultimate analysis and ash contents of the studied samples. From the comparison of the char and carbon pellets analysis, it is seen that pelletization produces an increase in oxygen and hydrogen contents, and a decrease of carbon content, presumptively due to the tar contribution in C, N, H and O. With CO_2 activation, carbon and ash content increase, meanwhile the H and O contents decrease.

Carbon and carbon dioxide activated carbon pellets showed good resistance to impact with drops numbers higher than 10, meanwhile air activated carbon pellets had a very low resistance, with drop numbers of 1. From these results, no additional tests were carried out on air activated carbon pellets.

Thermogravimetric results are presented as derivative of mass loss percent *vs.* temperature (DTG curves in Fig. 1).

Table 1 Ultimate analysis and ash content in dry basis of wood, char, carbon pellets, activated carbon pellets and char and tar treated in the same way as activated carbon pellets

Sample	C/%	H/%	N/%	S/%	O/%[1]	Ash/%
Eucalyptus wood	47.1	5.9	0.1	0.0	46.6	0.3
Char	82.4	2.6	0.0	0.0	11.6	3.4
Tar (dry 298 K-fraction)	53.6	6.4	0.4	0.0	39.1	0.5
Carbon pellets	76.1	3.8	0.3	0.0	19.4	0.4
Activated carbon pellets (burnoff=20%)	90.5	0.0	0.4	0.0	5.0	4.1
Treated tar	96.0	0.0	0.5	0.0	0.0	3.5
Treated char	92.0	0.0	0.3	0.0	3.0	4.7

[1]by difference

Curves were carried out up to a temperature of 1173 K. At this point the yields obtained were: for tar 14% (CO_2 and N_2 atmospheres); for char, 74% in N_2 and 63% in CO_2.

For char, DTG curves in N_2 and CO_2 were similar (Fig. 1, curves a and b), with a small increase in the mass loss rate which started at 650 K. It could be explained as a consequence of a char preparation temperature lower than 650 K: at higher temperatures, pyrolytic carbon formed during carbonization of biomass to char would decompose. In CO_2 atmosphere, reaction was detected for temperatures higher than 1000 K (activation). As the burnoff is low, the catalysis due to the main mineral components (Na, K) can be neglected [19], therefore this reaction may be attributed to uncatalysed gasification. For tar, both DTG curves were almost coincident (Fig. 1, curves c and d); mass loss began at ambient temperature, as volatile compounds were vaporized, and continued up to 700 K, as a consequence of tar charring. There was no evidence of reaction with CO_2 at higher temperatures. These facts may be explained taking into account that tar is a mixture of compounds, all of them with different volatilities and reactivities [20]. Those compounds with a high reactivity or volatility would be lost at lower temperatures, remaining a charred solid,
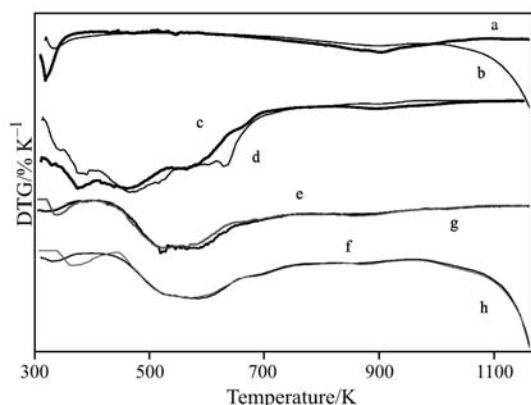

Fig. 1 DTG for different materials at different atmospheres:
a – char, N_2; b – char, CO_2; c – tar, N_2; d – tar, CO_2;
e – pulverized pellet, N_2; f – pulverized pellet, CO_2;
g – pellet, N_2; h – pellet, CO_2

formed during the heating, very resistant to impact and with lower reactivity than char.

Carbon pellets and pulverized carbon pellets were studied for determining whether diffusional effects are important in pyrolysis (Fig. 1, curves e and g) and gasification (Fig. 1, curves f and h). From the results of the gasification of carbon pellets in CO_2 atmosphere the better conditions for pellets activation were obtained. Comparison between DTG curves, for raw materials and carbon pellets, allowed to establish the consequences of pelletization on pyrolysis and gasification.

DTG curves for carbon pellets and pulverized carbon pellets were coincident in N_2 atmosphere (Fig. 1, curves e and g) and CO_2 atmospheres (Fig. 1, curves f and h). Pyrolysis and CO_2 gasification rates are therefore independent of particle size, revealing that diffusion at the interior of the pores of the pellets was not important neither for pyrolysis (N_2) nor for CO_2 gasification. Therefore, in the experimental conditions for gasification, diffusion is not a controlling step neither for pellets nor for pulverized carbon. The chemical reaction for CO_2 gasification must then be the rate controlling step.

The main peak for pellet pyrolysis (in N_2 as well as in CO_2) was a wide one, placed mostly in the range 400–700 K; this peak appeared also in tar DTG curves but not in char DTG curves: in conclusion, the mass variation in this range may be explained by volatilisation or decomposition and reordination of tar components. For tar, the peak began at a lower temperature than pellets because the tar was not dried before thermal analysis, meanwhile carbon pellets were previously dried at 378 K. In CO_2 atmosphere and beyond 1000 K, CO_2 gasification occurred, and the DTG curves for pellets and char presented a very similar shape, showing that CO_2 reactivity is mainly due to char content.

From curve h (Fig. 1), it was possible to determine the activation temperature in CO_2 for the pellets: 1098 K was selected, because it is higher enough to get a high gasification rate, but it is well far from the highest (and uncontrollable) rate. This temperature is in good agreement with previous works [19]. Useful information in relation to activated carbon pellet regeneration (reactivation) can also be obtained from these curves, taking into account that regeneration implies a new gasification. Probably the gasification of carbon pellets begins in the char components, as CO_2 reactivity observed for the tar at high temperature was low. This fact is also important from the point of view of structural consistence of activated carbon pellets.
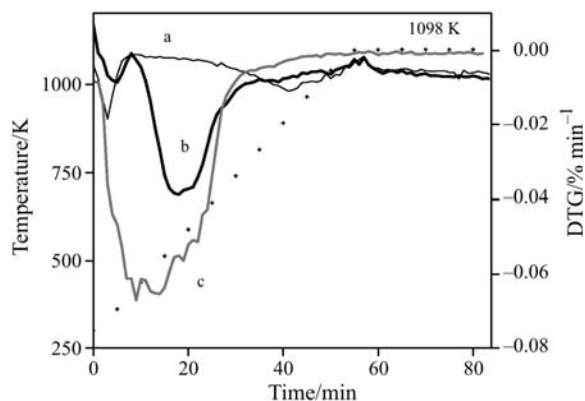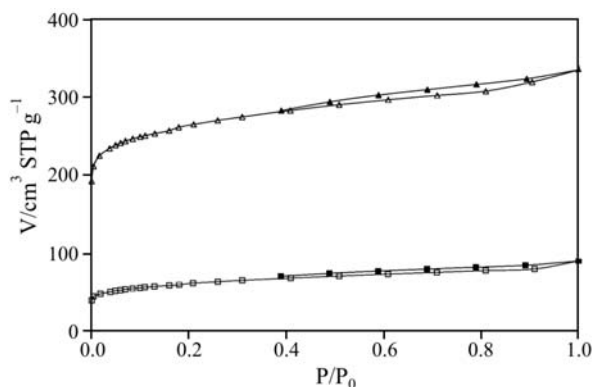
Figure 2 shows the DTG curves of dry carbon pellets, tar and char during activation process. Gasification rate was adequate, and the burnoff achieved was 20%, corresponding to a yield of 50% with respect to the initial dry mass (the corresponding curve for a burnoff of 10% is not shown, since it did not provide additional information).

Tar did not change at 1098 K in CO_2 atmosphere, so it can be supposed that all changes in carbon pellet activation are a consequence of char reaction. DTG curves of char and carbon pellets were similar during CO_2 activation at 1098 K.

Porosity and surface parameters of all the studied samples were determined from N_2 adsorption–desorp-

Table 2 Porosity and surface parameters for CO_2 activated carbon pellets

Burnoff of the sample/%	BET area/m^2 g^{-1}	V_t/cm^3 g^{-1}	V_{DR} N$_2$/cm^3 g^{-1}	$V_{0.95}$/cm^3 g^{-1}	Difference $V_{0.95}-V_t$/cm^3 g^{-1}
10	220	0.11	0.08	0.13	0.02
20	990	0.40	0.38	0.51	0.11

Fig. 2 Activation in thermobalance, carbon dioxide atmosphere. Nitrogen flow (50 cm^3 min^{-1} up to 1098 K) and carbon dioxide flow (50 cm^3 min^{-1} at 1098 K) during 31 min (corresponding to 20% burnoff): a – char DTG; b – carbon pellet DTG; c – tar DTG; + – temperature (K)

Fig. 3 Nitrogen adsorption–desorption isotherms at 77 K for carbon pellets activated with carbon dioxide at 1098 K: □ – adsorption, 10% burnoff, ■ – desorption, 10% burnoff, △ – adsorption, 20% burnoff, ▲ – desorption, 20% burnoff

tion isotherms at 77 K; Fig. 3 and Table 2 show the results obtained for carbon pellets activated with CO_2 at 1098 K. BET area of unactivated carbon pellets was found to be very low: 10 m^2 g^{-1}.

BET specific surface area and micropore volumes significantly increased with burnoff. Both samples passed the pellet mechanical resistance test. Mesopore volume increased for the higher burnoff, as it is seen in the higher adsorption slope at medium P/P_0 and the higher difference $V_{0.95}-V_t$ (Table 2) for 20% sample.

Conclusions

Carbon activated pellets were obtained by partial gasification with CO_2 of pellets prepared by agglomeration of char and tar derived from Eucalyptus wood pyrolysis. Thermogravimetric analysis showed that in N$_2$ and CO_2 atmospheres the more important changes in carbon pellets up to 800 K could be attributed to the tar components decomposition and reordination; on the contrary, char is the more reactive component over 1000 K. The products presented high specific surface area and good mechanical resistance.

Acknowledgements

References

1 R. C. Bansal, J. P. Donnet and F. Stoeckli, Active Carbon, Marcel Dekker, Inc., New York 1988.
2 H. Jankowska, A. Swiatowski and J. Choma, Active Carbon, Ellis Horwood Limited, New York 1991.
3 F. Rodríguez Reinoso, Carbons, in Handbook of porous solids, Edited by F. Schütz, K. S. W. Sing and J. Weitkamp, Wiley & Sons, New York 2002, Vol. 3, Chapter 4.8.
4 N. Tancredi, T. Cordero, N. Medero, F. Möller, J. Píriz and C. Plada, J. Colloid Interface Sci., 279 (2004) 357.
5 T. Cordero, J. Rodriguez-Mirasol, N. Tancredi, J. Piriz, G. Vivó and J. J. Rodriguez, Ind. Eng. Chem. Res., 41 (2002) 6042.
6 P. Milich, F. Möller, J. Píriz, G. Vivó and N. Tancredi, Separation Sci. Technol., 37 (2002) 1453.
7 F. Rodríguez Reinoso, M. Molina Sabio and J. C. González, Letters to the editor/Carbon, 39 (2001) 771.
8 K. Miura, H. Nakagawa and H. Okamoto, Carbon, 38 (2000) 119.
9 J. Kurihara, K. Sakata and G. Harada, US 6031712 Patent. NGC Corp., Tokyo, Japan, February 29, 2000.
10 M. Anglès, J. Reguant, D. Montané, F. Ferrando, X. Farriol and J. Salvadó, J. Appl. Polym. Sci., 73 (1999) 2485.
11 B. Rubio, M. Izquierdo and E. Segura, Carbon, 37 (1999) 1833.
12 J. Miller, US 5736485 Patent. Westvaco Co., New York, April 7, 1998.

13 T. Cordero, Ph.D. Thesis, University of Malaga, Spain 1987.

14 T. Cordero, F. García-Herruzo, C. Gómez-Lahoz and J. J. Rodríguez, Anales de Química, 85 (1989) 445.

15 J. Adam, M. Blazsó, E. Mészáros, M. Stöcker, M. Nielsen, A. Bouzga, J. Hustad and G. Oye, Fuel, 84 (2005) 1494.

16 R. López Fonseca, I. Landa, M. Gutiérrez Ortiz and J. González Velazco, J. Therm. Anal. Cal., 80 (2005) 65.

17 Q. Liu, C. Ly, Y. Yang, F. He and L. Ling, J. Mol. Struct., 733 (2005) 193.

18 E. Mészáros, E. Jakab, G. Várhegyi, P. Szepesváry and B. Marosvölgyi, J. Anal. Appl. Pyrolysis, 72 (2004) 317.

19 N. Tancredi, T. Cordero, J. Rodríguez Mirasol and J. J. Rodríguez, Fuel, 75 (1996) 1505.

20 M. Prauchner, V. Pasa, C. Otani and S. Otani, Energy Fuels, 15 (2001) 449.

21 F. Márquez-Montesino, T. Cordero, J. Rodríguez-Mirasol and J. J. Rodríguez, Fuel, 81 (2002) 423.

22 J. Tascón, J. Therm. Anal. Cal., 79 (2005) 525.

23 H. Barkia, L. Belkbir and S. Jayaweera, J. Therm. Anal. Cal., 76 (2004) 623.

24 A. Pappa, K. Mikedi, N. Tzamtzis and M. Statheropoulos, J. Therm. Anal. Cal., 84 (2006) 665.

25 M. Gonçalves, D. Ribeiro, D. Da Mota, A. Teixeira and M. Teixeira, J. Therm. Anal. Cal., 80 (2005) 387.

26 E. M. Suuberg, Preprints of Symposia – American Chemical Society, Division of Fuel Chemistry, 44 (1999) 162.

27 N. Tancredi, T. Cordero, J. Rodríguez Mirasol and J. J. Rodríguez, Fuel, 75 (1996) 1701.

28 J. Gelman, Farmacotecnia teórica y práctica, Vol. VI, 1st Edition, México 1981, p. 1749.

29 D. Perry and R. Green, D. Perry's Chemical Engineers' Handbook, 6th Edition, New York: Mc Graw Hill, 1984, Sec. 8.

30 S. J. Gregg and K. S. W. Sing, Adsorption, Surface Area and Porosity, New York: Academic Press Inc., 1982, Chap. 3–4.