

## ACTIVATED CARBONS FROM LIGNOCELLULOSIC WASTES FROM THE EXTRACTION OF TANNINS

E. Ruisánchez<sup>1</sup>, R.P. Girón<sup>1</sup>, R. R. Gil<sup>1</sup>, B. Ruiz<sup>1</sup>, M. S. Lozano<sup>2</sup> and E. Fuente<sup>1</sup>

<sup>1</sup>Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe, 26, 33011 Oviedo, Spain

<sup>2</sup>Asociación de Investigación de las Industrias del Curtido y Anexas (AIIICA), Avda. Pla de la Massa, s/n, 08700 Igualada (Barcelona), Spain

---

### Abstract

This paper studies the possibility of obtaining activated carbons from lignocellulosic wastes. Three types of residues, obtained from chestnut shells, acacia pods and grape pips, were studied. To achieve our aim, several parameters commonly used in thermo-chemical processes (pyrolysis, alkaline activation) were evaluated: heating rate, final temperature and maintenance time of final temperature in the pyrolysis, final activation temperature, inert gas flow and the ratio between the activating agent and the sample.

*Keywords:* activated carbon, lignocellulosic wastes, tannins, pyrolysis, alkaline activation.

### INTRODUCTION

In recent years our research at the INCAR has focussed on methodologies for valorising residues (sewage disposal muds, fly ashes, etc.) by means of thermo chemical processes. Adsorbent materials commonly used to retain contaminants at source were obtained [1, 2]. The residues that most recently have been studied were taken from leather containing vegetal tannins rather than chrome which is highly contaminant.

The use of commercial vegetal tannins (Mimosa, Chestnut tree, Quebracho) poses a serious problem for the environment since the search for this type of tannins leads ultimately to deforestation. As an alternative to this source of tannins AIIICA is exploring the possibility of extracting tannins from residues (grape pip and the fruit of acacia). In the case of grape pips, the tannins are chemically extracted, whereas in the case of acacia they are obtained by sieving the ground pod from the fruit of acacia. The tannins in the residues from the chestnut shells were extracted prior to the experiments.

In all three cases, the extraction of the tannins gave rise to a lignocellulosic residue which appeared to be suitable for obtaining activated carbons [3, 4].

By means of thermo chemical processes, pyrolysis and activation with alkaline hydroxide (KOH, NaOH), activated carbons with a suitable surface chemistry and textural development were obtained. These materials are appropriate for retaining contaminants from the leather industry and other possible applications.

### EXPERIMENTAL

#### 1. Chemical and textural characterization

The elemental analysis was carried out on LECO CHN-2000 and LECP Sulphur Determination S-144-DR instruments. The ash content was determined according to the UNE 32004 norm.

Textural characterization was carried out by measuring the N<sub>2</sub> adsorption isotherms at -196 °C on an automatic (ASAP 2420-Micromeritics) equipment. Before the experiments, the samples were outgassed under vacuum at 120 °C overnight. The isotherms were used to calculate the specific surface area, S<sub>BET</sub>. The results are presented on dry basis.

#### 2. Pyrolysis

In order to establish the optimal conditions for the pyrolysis of the sample, several parameters were studied in a thermo-balance (Q5000IR): heating rate (5, 10 y 15 °C/min), final temperature (650, 750, 850, 900 °C), maintenance time of final temperature (60, 120 min) [5].

As can be seen in Figure 1, above 750 °C there was almost no loss of weight in the three materials, so this temperature in the furnace

(Carbolite CTF 12/65/550) was maintained for one hour, the effect being similar to that obtained at higher temperatures.

Once the optimal conditions were established, the sample was pyrolyzed. As a consequence of the pyrolysis, the materials obtained presented a carbon content value higher than that of the original sample, which in all cases exceeded 80 % (Tables 1 and 2).

### 3. Chemical activation

In the next stage, a chemical activation was carried out in order to increase the porosity of the sample. The pyrolyzed sample (roughly 5 g) was impregnated with the activating agent, potassium hydroxide. This mixture was introduced in a conventional tubular furnace where the following parameters have been changed: final activation temperature (from 700 to 900 °C), inert flow gas (150 and 500 ml/min) and proportion of the potassium hydroxide to the sample (1:1 and 2:1).

When the sample was activated, the porosity was not effective because it was blocked by different activation products; therefore, these products had to be removed. The samples were washed, using hydrochloric acid and Milli-Q water, until water. Finally, the sample was dried first in a heater (105 °C) and then in a vacuum heater (65 °C).

## RESULTS AND DISCUSSION

The elemental analysis of the original material is presented in the Table 1. These results show that they are good original materials (C≈50%), especially considering that they are merely residues.

Table 1. Elemental analysis and ash content of the original material

Sample	C (%)	H (%)	N (%)	S (%)	Ash (%)
Acacia pod	50,57	4,77	1,45	0,26	5,53
Chestnut shell	49,08	4,89	0,97	0,17	2,11
Grape pip	53,32	5,68	1,05	0,23	2,07

Table 2. Analysis of the pyrolyzed materials

Pyrolyzed sample	C (%)	Ash (%)	Yield (%)
Acacia pod	82,86	12,60	38,02
Chestnut shell	91,32	4,78	34,14
Grape pip	92,54	5,34	39

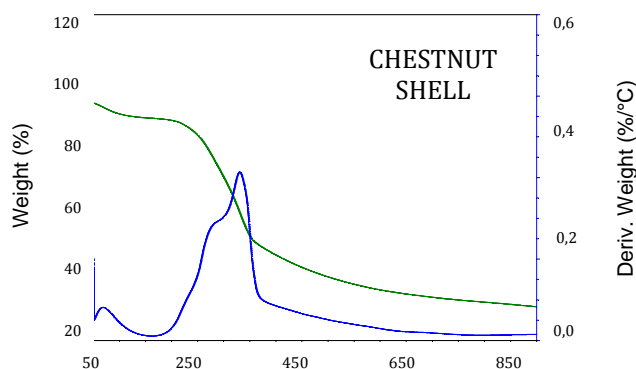
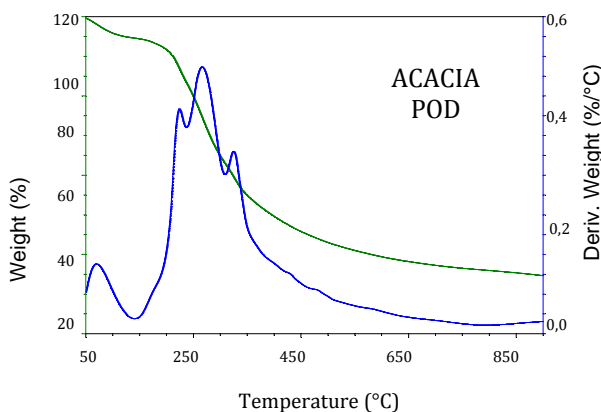
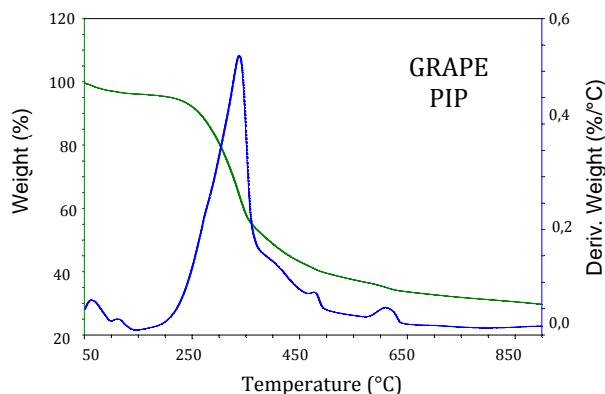


Figure 1. TG-DTG lignocellulosic wastes

The ash composition of the original material was studied by atomic spectrometry and is presented in Figure 2.

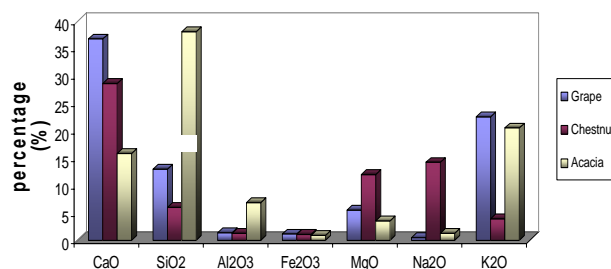


Figure 2. Ash composition by AE

The chemical composition of the carbonized materials is shown in Table 2.

In order to increase the specific surface area,  $S_{BET}$ , chemical activation was carried out by changing several parameters while maintaining the activating agent (KOH), maintenance time of final temperature (60 min) and heating rate (5 °C/min) constant. The results for the Acacia residue are shown in Table 3. These samples have low sulphur, oxygen and nitrogen contents. The nitrogen content decreases, from 1,5 % at 700 °C to 0,99 % at 900 °C, as the activation temperature increases.

Table 3. Activated carbons from acacia residue

KOH Ratio	T <sup>a</sup> (°C)	Flow (ml/min)	Ash (%)	C (%)	S <sub>BET</sub> (m <sup>2</sup> /g)
1:1	700	150	0,04	92,64	1187
1:1	750	150	0,12	98,03	1243
2:1	750	150	-	97,73	1888
1:1	750	500	0,42	94,37	1160
1:1	800	150	0,08	93,96	1360
1:1	900	150	0,47	95,49	1684

Table 4. Activated carbons from chestnut residue

KOH Ratio	T <sup>a</sup> (°C)	Flow (ml/min)	Ash (%)	C (%)	S <sub>BET</sub> (m <sup>2</sup> /g)
1:1	700	150	2,81	92,91	1130
1:1	750	150	3,60	87,48	1159
2:1	750	150	0,86	94,93	1973
1:1	750	500	3,22	92,14	1256
1:1	800	150	2,26	93,63	1339
1:1	900	150	3,43	91,84	1667

The chestnut residue was activated using the same conditions as for the Acacia residue. The results obtained are presented in Table 4. The hydrogen, nitrogen and sulphur contents in this residue are analogous to those above. The nitrogen content also decreases when the activation temperature rises.

In the case of residues from the grape pips, the activation results are shown in Table 5. From this table it can be seen that the hydrogen, sulphur and nitrogen contents continue to be low for the grape pip waste with nitrogen values close to 1%.

Figure 3 shows the increase in specific surface area ( $S_{BET}$ ) with the change in activation temperature.

Table 5. Activated carbons from grape residue

KOH Ratio	T <sup>a</sup> (°C)	Flow (ml/min)	Ash (%)	C (%)	S <sub>BET</sub> (m <sup>2</sup> /g)
1:1	700	150	0,07	93,26	970
1:1	750	150	0,07	92,60	1003
2:1	750	150	0,09	92,61	1746
1:1	750	500	0,06	95,76	1054
1:1	800	150	0,09	96,24	1080
1:1	900	150	0,10	94,62	1540

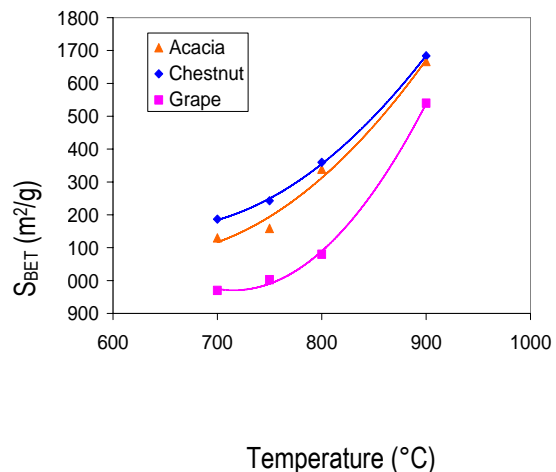


Figure 3. Specific surface area of activated carbons

## CONCLUSIONS

From the residues of the lignocellulosic material, activated carbons without heavy metals and with an ash content between 0,1 % and 3 % were obtained. The adsorbents obtained reach specific surface areas,  $S_{BET}$ , of approximately 2000 m<sup>2</sup>/g.

These areas increased when the concentration of activating agent and the final activation temperature were increased.

The obtained materials were essentially microporous.

## REFERENCES

- [1] A.Anfruns, C. Canals-Batlé, A. Ros, M. A. Lillo-Ródenas, A. Linares-Solano, E. Fuente, M. A. Montes-Morán, M. J. Martín (2009) Removal of odour-causing compounds using carbonaceous adsorbents/catalysts prepared from sewage sludge. *Water Science & Technology* 59, 1371-1376
- [2] A. Ros, M. A. Lillo-Ródenas, A. Linares-Solano, E. Fuente, M. A. Montes-Morán, M. J. Martín (2009) Further insights into the activation

process of sewage sludge-based precursors by alkaline hydroxides. *Chem. Eng. J.* 142, 168-174

[3] Suhas, P.J.M. Carrot, M.M.L. Ribeiro Carrot (2007) Lignin – from natural adsorbent to activated carbon: A review. *Bioresource Technology* 98, 2301–2312.

[4] Khezami L., Chetouani A., Taouk B., Capart R. (2005) Production and characterization of activated carbon from wood components in powder: cellulose, lignin, xylan. *Powder Technology* 157, 48-56.

[5] I.V. Perezdrienko, T.B. Molodozhenyuk, B.E. Shermatov, M.P. Yunusov (2001) Effect of carbonization temperature and activation on structural formation of active lignin carbons *Russian J. of Applied Chemistry* 74, 1650-1652.

#### ACKNOWLEDGEMENTS

We wish to thank the group of the University of Santiago de Compostela (GI-1612) for supplying us with chestnut shells residue.