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PREPARATION AND CHARACTERIZATION OF ADSORBENTS/CATALYSTS FROM FOREST BIOMASS FLY ASH

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Abstract

This paper deals with the production of materials, known as adsorbents/catalysts, from forest biomass fly ashes. The ashes were subjected to different pre-treatments to generate two kinds of precursors. Via an agglomerative process using domestic residual oils and a dry sieving method. Both precursors, after an activation process using potassium hydroxide, were characterized in terms of BET surface area. The adsorbent/catalyst obtained from the precursor subjected to dry sieving exhibited a developed porosity, which in turn gave rise to surface areas in the range of 2000m²/g.

Keywords: *biomass, fly ash, adsorbent/catalyst, chemical activation.*

INTRODUCTION

Like fossil fuels, e.g. coal and petroleum, biomass contains different proportions of inorganic elements depending on its origin. After the combustion of biomass, two solid wastes are obtained (fly ash or slag). Both consist principally of inorganic matter.

The energy production from biomass is considered to have a net zero CO₂ impact, because the emissions produced counteract the carbon dioxide fixed by the biomass during its growth.

ENCE-Navia, located in Asturias, is a paper mill industry that employs bark eucalyptus (*eucalyptus globules*), producing 1.25 GWh/year of electrical power. The furnace operates at 750°C and as a subproduct, the company generates around 1.500 t/year of fly ashes, which are commonly dumped.

Typical activated carbons have surface areas ranging from 600 to 1200 m²/g[1], although materials with values higher than 2000 m²/g have also been reported. The main advantage of activated carbons over other adsorbents is the possibility of

generating them from a variety of industrial wastes, that is, from low cost materials [2-4].

The aim of this work is to valorize this waste for the preparation of adsorbents/catalysts. Two chemical activation processes with KOH were tested in order to convert the unburned fly ashes into materials with specific characteristics including a high porosity and a suitable superficial chemistry.

EXPERIMENTAL

2.1 Materials

The fly ashes were obtained from the pulp and paper industry ENCE-Navia (Asturias), in a biomass plant which uses eucalyptus bark for energy production. These fly ashes are referred to as CVBE.

The CVBE were subjected to different pre-treatments to obtain the precursors: agglomeration with used domestic oils [5, 6] and dry sieving. Oil agglomeration experiments were conducted in a commercial blender equipped with a glass vessel. For each agglomeration test, 400 ml of distilled water and 16 g of fly ashes were placed in the blender and mixed for 5 min. A specific amount of oil, ranging from 2 to 50 wt% of CVBE, was then added and mixed for 60 s to produce agglomerates.

The resultant agglomeration product was separated from the refuse by froth flotation. The results of the agglomeration process were evaluated according to the percentage of organic matter recovered and percentage of ash rejected (Table 1).

The most suitable precursor was obtained with 10% oils and labelled P1.

And other procedure involved dried sieving. The fraction greater than 500 m was found to be the best precursor due to its low ash percentage and this was called P2 (Table 2).

Table 1. Oil percentage, efficiency and content of agglomerated samples.

% OIL	% Wt ORGANIC	% ASH	% UNBURNED
2	1,7	25,34	74,66
5	1,7	27,86	72,14
10	4,7	67,92	32,08
20	24,6	77,42	22,58
40	36,1	77,02	22,98
50	54,7	76,55	23,45

Table 2. Characteristics of the different fractions obtained through dried sieving.

FRACTION (m)	% UNBURNED	% Wt ASH
> 500	77,37	22,43
500 - 212	6,96	93,04
<212	16,34	83,66

Both the original CVBE and the two precursors were analysed in a thermal gravimetric analyser (TA Q600 thermobalance). All the samples were heated from 30 to 1000 °C under nitrogen atmosphere at a flow rate of 10°C/min (Fig.1).

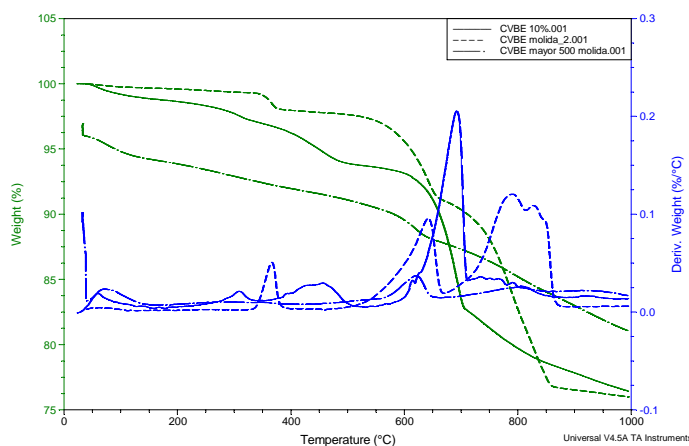


Fig. 1 Thermogravimetric analysis of the CVBE and its precursors at different temperatures.

The mineral composition and the elemental analysis of CVBE and its precursors appear in Table 3. The ashes after calcination at 900°C are also presented.

2.2 Experimental methods

The activation process of both precursors was carried out in a tubular horizontal furnace (Carbolite CTF 12/65/550), heated up to 750°C for one hour, at a heating rate 5°C min⁻¹. Nitrogen flow rates of 150ml min⁻¹ and 500ml min⁻¹ were selected during the heating treatment, and KOH was used as activating agent in different proportions, its efficiency having been demonstrated in previous works [7, 8].

After the activation process, the activating agent or other inorganic species formed during the process may block the porosity of the final material. These products must be eliminated in order to reopen the porous structure.

The sample was first washed with solutions of HCl 5M to remove any possible residues and then with Milli-Q water until all the chlorine ions had been eliminated and pH become the water (pH=5,40).

Once the final materials (adsorbent/catalyst) had been processed, their final surface areas were calculated.

RESULTS AND DISCUSSION

3.1 Characterization of the precursors

According to the elemental analysis shown in Table 3, CVBE present the highest percentages of carbon and lowest ash contents.

This is very important to obtain materials with adsorbent/catalyst of properties and high surfaces areas. In the case of the precursor with 10 wt% agglomeration (P1) it is noticed a high content of S was observed.

The mineral composition studied by atomic absorption and X-ray diffraction (Fig. 2) confirmed the presence of Ca and Si as major elements. Different forms of Ca were detected: CaCO₃, CaSO₄ or CaO [9].

3.2 Chemical activation with potassium hydroxide

Table 4 presents the characteristics of the precursors for different activating conditions.

The precursor P1 exhibits a greater ash content and a smaller amount carbon than the one resulting from dry sieving, P2. As a result the surface area of P1 is a smaller than of P2.

However, an increase in the proportion of activating agent gives rise to higher surface areas, the P1 precursor rising from 600²/g to 1000m²/g and P2 precursor rising from 1000m²/g to around 2000m²/g. Both of these surface area increases were accompanied by an increase in the KOH ratio:150ml/

min flow rate of N₂ and 500ml/min flow rate for P1 and P2.

Table 3. Characteristics of CVBE and its precursors

% Wt	CVBE	P1	P2
Ash (900°C)	85,85	67,92	22,43
Unburned	14,15	32,08	77,57
C	3,93	18,62	59,65
H	0,27	0,92	0,72
N	0,09	0,13	0,46
S	1,99	1,72	0,4
CaO	30,11	23,41	4,45
SiO ₂	25,01	26,08	8,07
Al ₂ O ₃	5,37	5,26	5,97
Fe ₂ O ₃	2,56	1,98	0,87
MgO	3,92	3,9	0,93
Na ₂ O	0,95	0,78	0,87
K ₂ O	2,41	1,04	0,77

Table 4. Activating conditions, characteristics of adsorbents/catalysts and surface areas

PRECURSOR/KOH ratio	FLOW RATE								BET					
	N ₂ (ml/min)		ASH	C	H	N	S	BET (m ² /g)	ASH	C	H	N	S	BET (m ² /g)
1:1	150		33,7	44,31	0,85	0,6	4,61	601	6,15	82,78	0,44	1,00	0,38	1056
1:2	150	10%	31,58	44,48	0,76	0,5	2,20	1026	6,71	78,52	0,45	0,98	0,27	1982
1:1	500		36,27	43,01	0,72	0,52	3,77	671	4,06	86,92	0,32	0,75	0,31	
1:2	500		43,47	38,68	0,83	0,5	2,32	1135	14,13	77,28	0,40	0,65	0,35	

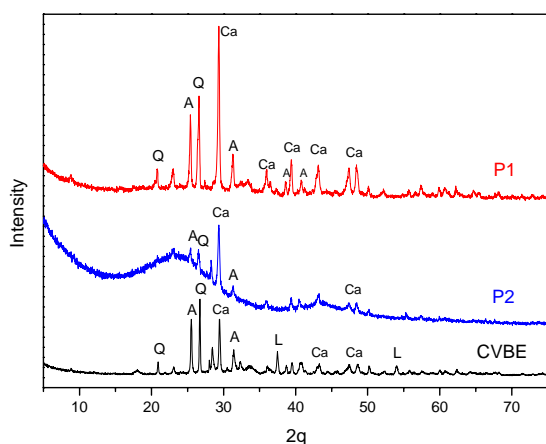


Fig. 2 X-ray diffraction patterns of CVBE and its precursors (P1 and P2): Ca-calcite, Q-quartz, A-Anhydrite, L-Lime.

The adsorbents/catalysts of P1 have a high S percentage; X-ray diffraction shows consequently that this S is in form of CaSO_4 , the KOH can not attack the sulfate.

CONCLUSIONS

Of the two concentrated unburned processes, the more effective precursor (P2) was obtained by means of dry sieving. Firstly because of the simplicity of this method and also because of the precursor's characteristics.

In relation to chemical activation, an increase in the precursor/hydroxide ratio leads to enhanced surface areas.

The most suitable precursors for producing in good adsorbents/catalysts have a high carbon and low inorganic material content.

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