Extension of preparation methods employed with ceramic materials to carbon honeycomb monoliths

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Honeycomb monolithic catalysts are being used to reduce the emissions of pollutants resulting from the combustion of fossil fuels [1]. At present, commercial catalysts include noble metals (Rh, Pt, Pd) and oxides of different elements such as V, Cr, Cu or Ti which are able to catalyze the transformation of atmospheric pollutant species into others with lower toxicity, so diminishing their concentration in the air to below allowed tolerance levels. Usually, active components are deposited over supports to obtain well dispersed phases that maintain high accessibility to the species that need to be transformed. As regards the supports, if compared with more conventional designs as those based on particle beds, monolithic structures offer several advantages such as a lower pressure drop in gas flows with high space velocity -so enhancing the catalyst's performance-, together with lower weight and space requirements for filters and catalytic converters [2]. Currently, technology to make ceramic and metallic monoliths is already available. Several studies have pointed out the convenience of using carbon as raw material to make monolithic catalysts, both with and without deposited active phase [3]. Nonetheless, the plastic properties of carbon make it an inappropriate material for processing through extrusion [4]. In this sense, carbon-containing catalysts are prepared mainly as beds of powdered or granulated materials or, in the case of monoliths, by further deposition of carbon or a carbon's precursor on a ceramic monolith and not before extrusion. Although studies of honeycomb monoliths of activated carbons in the literature are available, they do not indicate how extrudibility of the carbonaceous paste is finally achieved [5]. The originality of this work lies in using a simple methodology developed for ceramics by Casagrande and Atterberg [6] to predict the extrudibility of a carbon-based paste. As far as we know, no similar approach has been described in the bibliography devoted to the technology of carbonaceous solids.

We used two different carbon samples in this study, a commercial powdered activated carbon (Norit SX1) provided by Campi y Jové, and a type of natural coal, also in the form of powder, kindly supplied by the National Institute of Carbon of Spain, characterized by containing 30 wt% of volatiles and less than 6 wt% of ashes, and 75 vol.% of vitrinite phase in its maceral composition. Elemental analysis of both samples was performed using a Leco CHNS-932 determinator providing the following results (wt%): 72.7, 1.8, 0.3 and 0.1 in the activated carbon, and 83.8, 5.4, 2.0 and 0.5 in the natural coal, for C, H, N and S, respectively. To obtain doughs with adequate rheological properties different additives, besides water, were incorporated. Table 1 shows a list of compounds that might be employed according to their respective function. As inorganic binder, a silicate clay, Argi-2000, from VICAR S.A., was also used. This additive allows to improve the handling characteristics and rheological properties of the paste during the kneading and extrusion operations and to give greater mechanical strength to the final heat-treated product. All the components of the pastes were well premixed to ensure homogeneity. In order to check the validity of the optimized doughs according to the criterion proposed here, tests were carried out using a extrusion machine capable of making honeycomb square section monoliths with a cell density of 4 cells cm^{-2}, in 2x2 and 4x4 configurations, and a wall thickness of 1.3 mm.

In the case of the monoliths prepared from the natural coal, it is necessary to include a final preparation step consisting on a preoxidation [7], carbonization and activation, after drying the green monoliths, in order to improve the porous structure of the final products. Preoxidation consisted in heating at 250 ºC under flowing air during 24 h. Carbonization was carried out under flowing Ar (60 cm^3 min^{-1}) at 840 ºC for 1 h, while activation was done at 860 ºC using an Ar flow of 120 cm^3 min^{-1} bubbling through water (P_{H2O}=205 Torr) during the time needed to reach a burn-off degree of 15 wt%. Texture characterization of the starting materials and the coal-based monoliths was carried out by measuring true and apparent densities (mercury at 0.1 MPa), mercury porosimetry and physical adsorption of N_2 and CO_2 at –196 ºC and 0 ºC, respectively (Table 2 and Figure 1). For this study, a Micromeritics 1320 Autopycnometer, a Macropores Unit 120 from Carlo Erba, and a Micromeritics ASAP 2010, were used, applying the methods and experimental protocols indicated elsewhere [7].

According to Casagrande and Atterberg [6], any ceramic paste whose liquid limit (LL) is included in the interval 40-60% and simultaneously has a plasticity index (PI) between 10 and 30% is extrudable (Figure 2). In order to understand the effect of different additives on the properties of a carbonaceous paste with a specific composition, a series of experiments were performed in which each additive was added separately to the carbon/clay paste (Table 3). Additionally, the effect of the amount of each additive was also studied (hereafter expressed at % in respect of the weight of the mixture of carbon and clay employed). This methodology allowed us to optimize the composition of the carbonaceous paste to be extruded. First, a 1:1 (per weight) activated carbon/clay mixture was studied, obtaining LL=113% and PI=11%, thus giving rise to a point in Casagrande's diagram far away from the extrudibility zone (point AC1 in Figure 2). Successive tests with the selected additives were performed, employing at least one for each type of function. Position in Casagrande's diagram of the different pastes prepared, as obtained from their respective plastic properties, is indicated in Figure 2. Three groups of additives affecting differently LL and PI have been selected; methylcellulose (AC2), glycerine (AC3) and aluminium phosphate dissolved in o-phosphoric acid (AC7) being good representatives for each group, which is why they were usually considered in subsequent tests. An increase in the amount of activated carbon (case of a 9:1, per weight, carbon/clay paste) leads to an increase in the liquid limit, reaching a value higher than 150%. Thus its corresponding point in Casagrande's diagram moves away from the extrudibility area. In order to correct this undesirable effect, and using the above information, the aluminium phosphate dissolved in o-phosphoric acid, which induces a clear fall in LL (Figure 2), was chosen as the indispensable additive. Again, the amount of this and other additives was successively changed according to the effect induced in Casagrande's diagram until a paste was obtained the properties of which matched the stated requirements. The composition of some of these pastes is detailed in Table 3 (A1-A4) whereas their possibility of extrusion consistent with their respective plastic properties can be rationalized in Figure 2. In the case of the so-called A4 paste, as it possessed the plastic conditions dictated by Casagrande, extrusion tests were successfully carried out confirming the predictions. A similar study was performed to formulate an extrudable paste containing a 9:1 (in weight) natural coal/clay. As was the case with the activated carbon, the preliminary step was that of preparing a paste composed only of coal and clay, finding that, this time, their intrinsic plastic properties were on the left of the extrudibility area in Casagrande's diagram (LL<40%). Therefore, the additive used was methylcellulose, capable to displace the point to the right, along with glycerine as plasticizer to avoid union between the agglomerates, and a small amount of aluminium phosphate dissolved in o-phosphoric acid to diminish the PI slightly. As before, successive tests were performed until a paste was found that matched the requested criteria (N1 in Table 3). As predicted (Figure 2), the N1 paste was successfully extruded, the resulting monolith being further dried at 80 ºC. Therefore, the results exposed in this work confirm the validity of the pattern developed by Atterberg and Casagrande for ceramic materials and their possible application for the extrusion of carbonaceous materials.

In the case of the coal-based monoliths, as expected (Table 2), activation of the green monolith gives rise to a development of the porous structure, the total open pore volume increasing considerably. Also, a huge increase in the BET surface area is observed with regard to the starting carbon material. Concerning the pore volume distribution (Figure 1), the microporosity clearly increases from complete absence in the coal up to 45% of the total porosity. The volume of narrow micropores is also enhanced as detected by CO_2 adsorption (W_o DR data in Figure 1). In consequence, the resulting monoliths might be interesting for their further use as adsorbents or catalytic supports.

References

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Table 1

Additives that can be used to make extrudable a carbonaceous paste

Function	Additive
Agglomerant	Methylcellulose, Starch, Polyvinyl alcohol, Hydroxyethyl cellulose, Dextrine from potato starch
Plasticizer	Polyethilene glycol, Glycerine
Defloculating	Glycerine, Ammonium poliacrylate, Oleic acid
Lubricant	Oleic acid, Aluminium stearate, Stearic acid
Dispersant	Aluminium phosphate hydrate dissolved in ortho-phosphoric acid, Gelatine from porcine skin
Humidifying	Etanol, Kerosene
Drying	Gelatine from porcine skin, Ferric chloride hexahydrate, Aluminium chloride

Table 2

Textural study of the monolith precursors and the activated coal-based monoliths

	Activated carbon	Natural coal	Natural coal-based monolith after activation
True Density (g cm^{-3})	2.190	1.440	2.040
Apparent Density (g cm^{-3})	-	0.857	0.836
Pore Volume (g cm^{-3})	-	0.470	0.706
Porosity (%)	-	40	59
S_{BET} (m^2 g^{-1})	942	3	487

Table 3

Composition of the carbonaceous pastes prepared for extrusion

Composition		Sample Name
Starting material [a]	Additives [b]	
Activated carbon, 50% + Clay, 50%	None	AC1
	Methylcellulose, 0.5%	AC2
	Glycerine, 5%	AC3
	Ethanol, 20%	AC4
	Aluminium stearate, 1%	AC5
	Gelatine from porcine skin, 1%	AC6
	Aluminium phosphate [*], 1.5%	AC7
Activated carbon, 90% + Clay, 10%	Aluminium phosphate, 2%	A1
	Glycerine, 2% + Aluminium phosphate [*], 2%	A2
	Glycerine, 4.6% + Aluminium phosphate [*], 2.5%	A3
	Glycerine, 4.6% + Methylcellulose, 0.5% + Aluminium stearate, 1% + Aluminium phosphate [*], 2.5%	A4
Natural coal, 90% + Clay, 10%	Glycerine, 2.6% + Methylcellulose, 2% + Aluminium phosphate [*], 0.3%	N1

[a] Percentage per weight

[b] Data related to 100 g of the starting material

[*] Dissolved in o-phosphoric acid

Figure Captions

Fig. 1. Pore volume distribution of the A) activated carbon, B) natural coal and C) natural coal-based monolith after activation.

Fig. 2. Casagrande’s diagram showing the position respect the extrudibility area of the carbonaceous pastes prepared for extrusion, name samples being listed in Table 3.

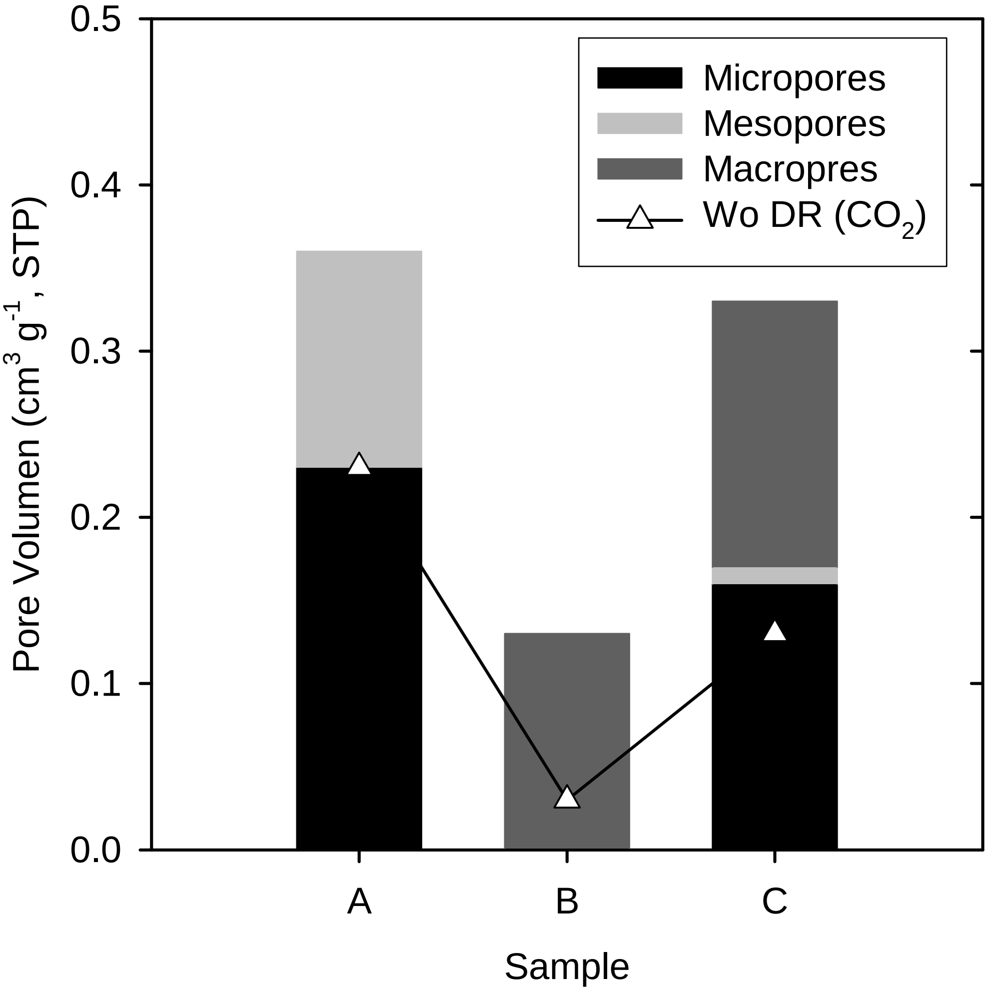
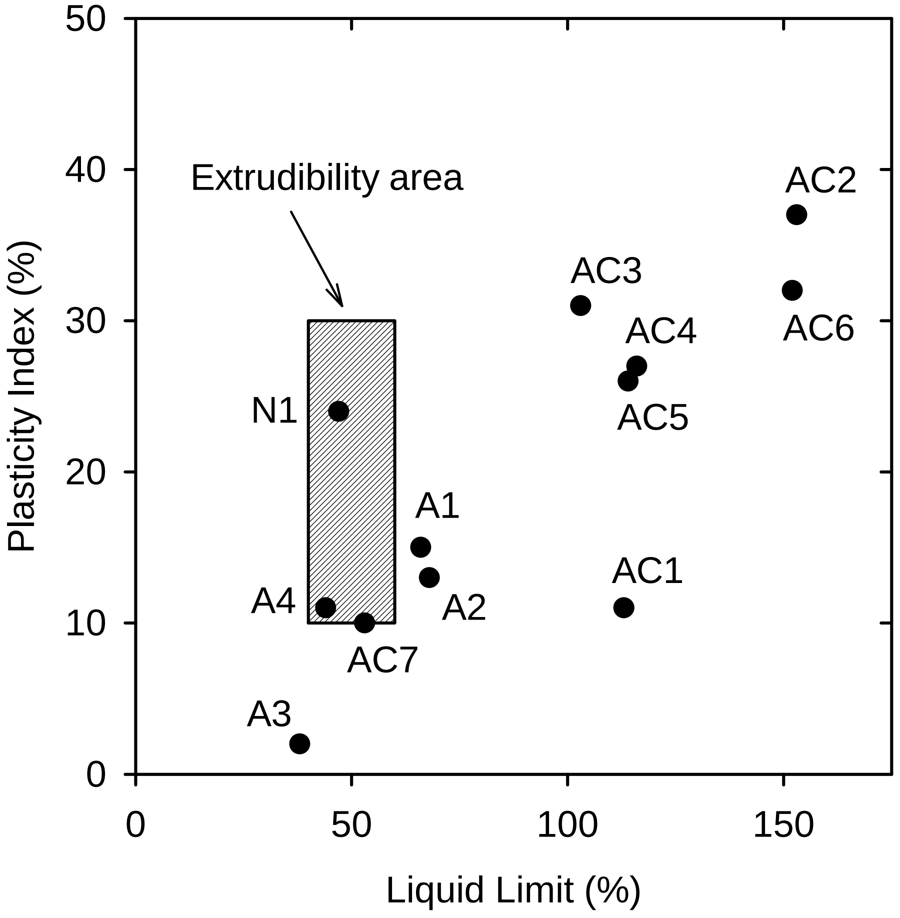

0.5
0.4
0.3
0.2
0.1
0.0
Pore Volumen (cm^3 g^{-1}, STP)
Micropores
Mesopores
Macropres
Wo DR (CO_2)
A
B
C
Sample

Figure 1



50
40
30
20
10
0
0
50
100
150
Plasticity Index (%)
Liquid Limit (%)
Extrudibility area
AC2
AC3
AC4
AC6
AC5
N1
A1
AC1
A4
A2
AC7
A3

Figure 2