

Coal-Based Carbon Foams. Influence of the Precursor Coal

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Abstract

Carbon foams were obtained from several bituminous coals with different plasticity and volatile matter content by a two-stage thermal process. The first stage, a controlled carbonisation treatment under pressure at 450-500 °C, is responsible for the final textural properties of the foam. In the second stage the carbonisation product was baked at 1100 °C. The foams produced display a macroporous texture with plasticity, volatile matter content and maceral composition of the precursor coals having an influence on the apparent density and the pore size of the resultant porous products.

Keywords

Carbon materials, Pore structure, Macerals

INTRODUCTION

Carbon foams are lightweight ($0.2\text{-}0.8\text{ g cm}^{-3}$) and exceptionally strong cellular materials that have thermal and electric conductivity adjustable by the foaming thermal treatment. Their low production costs and flexible physical properties make them ideal for a wide range of applications, including thermal management, electromagnetic interference, acoustic shielding and batteries and fuel cell components (Gallego and Klett, 2003; Jang et al., 2006; Min et al., 2007).

Carbon foams were first developed as reticulated glassy carbons (Ford, 1964) from thermosetting organic polymer foams through a thermal treatment. In the 1990's, research focused primarily on producing carbon foams from alternative precursors such as pitches and coals. Graphitized carbon foams are most appropriate to produce high strength and thermal and electrical conductivity because of the interconnected graphitic ligament network (Gallego and Klett, 2003; Jang et al., 2006; Klett et al., 2000; Min et al., 2007). However, carbon foams made from coal have hardly been studied (Calvo et al., 2005; Chen et al., 2006; Rogers et al., 2001), in spite of being an attractive more economical alternative to traditional materials since their structural properties made them perfectly useful in numerous applications, when very high conductivity is not required.

In this work, carbon foams were obtained from ten bituminous coals through a simple thermal procedure. Unlike previous works, not only high volatile bituminous coals were used as feedstock, but also medium and low volatile ones. Neither previous modification of coals nor further stabilization step of the green foams was carried out. This leads to a faster and cheaper production process as compared to foams prepared from other feedstock. The aim of this study is to find correlations between the raw coal properties (including the maceral composition) and the morphology and properties of carbon foam.

EXPERIMENTAL

Precursor characterization

Ten coals were used as precursors to produce carbon foams (Table 1). The Gieseler plasticity test and the crucible swelling test were used to measure the fluidity and dilatation characteristics of each precursor. Thermogravimetric analysis was carried out with a TA Instruments equipment, Mod. SDT 2960, at a heating rate of 2 °C min⁻¹ from ambient temperature to 1000 °C using 15 mg of sample. The mean random vitrinite reflectance measurement (%Ro) and maceral analysis (Table 2) were carried out on a MPV-Combi Leitz microscope in accordance with the ISO 7404/05 and ISO 7404/03 standard procedures, respectively.

TABLE 1: Analytical data of the bituminous coal used as precursors for carbon foams.

Coal	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
<i>Gieseler Plasticity Test</i>										
Softening Temperature (°C)	414	388	441	387	380	393	432	446	389	393
Solidification Temp. (°C)	470	476	500	467	482	470	498	502	476	486
Plastic Range (°C)	56	88	59	80	102	77	66	56	87	93
Maximum Fluidity Temp. (°C)	444	436	474	427	442	438	470	475	436	439
Fluidity (ddpm)	43	1696	30	3019	26695	7307	80	15	11883	13037
<i>Swelling Index</i>	7.75	5.75	8	3.5	6.5	6	7.5	6.75	5	6.5
<i>Volatile Matter (% d.b.)</i>	34.1	26.6	17.8	34.5	32.5	34.8	19.0	17.6	34.1	30.8
<i>Ash (% d.b.)</i>	5.74	5.28	9.7	7.5	8.4	6.6	7.0	5.6	6.1	6.1
<i>ATG</i>										
Inicial Weight Loss Temp. (°C)	370	370	395	345	368	365	384	400	354	374
Max. Weight Loss Temp. (°C)	444	436	477	429	438	432	473	477	436	446
Final Weight Loss Temp. (°C)	537	540	571	558	522	525	626	585	552	525

TABLE 2: Petrographic analysis data.

Carbón	Vitrinite Reflectance (%Ro)	Coal Rank	Maceral composition (%)			
			Vitrinite	Liptinite	Inertinite	Mineral Matter
C1	0.90	HVM	83.3	2.3	3.4	11.0
C2	0.97	HVM	73.7	9.0	13.7	3.6
C3	1.49	LVM	71.4	0.0	23.5	5.1
C4	0.73	HVM	36.8	10.5	45.7	7.0
C5	0.89	HVM	64.7	6.6	24.1	4.6
C6	0.86	HVM	64.1	8.8	22.0	5.1
C7	1.43	MVM	71.1	0.1	24.8	4.0
C8	1.57	LVM	75.2	0.0	21.0	3.8
C9	0.88	HVM	62.8	7.7	23.6	5.9

C10	0.99	HVM	66.3	3.4	24.4	5.9
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Foaming process

In these experiments, the precursor coal (80 g), pulverized at $< 212 \mu\text{m}$, was pressed into a cylinder and fed into a 50 x 100 mm stainless steel reactor. Then, it was purged with argon to provide an inert atmosphere and heated at $2 \text{ }^\circ\text{C min}^{-1}$ up to the temperature of highest volatile matter release ($470 \text{ }^\circ\text{C}$ for C2 and C4, and $450 \text{ }^\circ\text{C}$ for the rest), that was held for 2 h. The pressure was kept at 1 bar until the highest volatile release starting temperature was reached (Table 1) by leaving the outlet valve open. At that moment, the valve was closed and the pressure increased due to the release of volatile matter. The green foams thus obtained were carbonized under argon flow at $1100 \text{ }^\circ\text{C}$ with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ and a soaking time of 2 h. The final carbon foams are designated with an F followed by the same number as the precursor coal.

Carbon foams characterisation

The foams were analysed by scanning electron microscopy (SEM) using a Zeiss microscope, Mod. DSM-942, provided with an EDS detector OXFORD, Mod. Link-Isis II. The true density, determined by He displacement, was measured by using a pycnometer, Accupyc 1330 from Micromeritics. Apparent density and pore volume distributions were evaluated with a mercury porosimeter (AutoPore IV, from Micromeritics), which provides a maximum operating pressure of 227 MPa. The percentage of open cells was calculated by equation [1], where ε is the open porosity (%), and ρ_{Hg} and ρ_{He} are the apparent and true densities (g cm^{-3}) determined in Hg and He, respectively. Similarly, the total open pore volume, V_T , was obtained by equation [2].

$$\varepsilon = \left(1 - \frac{\rho_{Hg}}{\rho_{He}} \right) \cdot 100 \quad [1]$$

$$V_T = \left(\frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \right) \quad [2]$$

RESULTS AND DISCUSSION

Visual examination reveals that all the precursor coals produced good quality foams except C3 and C8. Foams F3 y F8 exhibit several cracks, maybe due to an incomplete agglomeration. In fact, these are the coals with the lowest fluidity (30 and 15 ddpm, respectively, Table 1) and without liptinite in their maceral composition (Table 2).

The properties of the carbon foams carbonized at $1100 \text{ }^\circ\text{C}$ are listed in Table 3. Apparent density ranges from 0.50 to 0.87 g cm^{-3} . Previous results (Calvo et al., 2005) indicate that the bulk density of the foam decreases with the increasing fluidity of the precursor coal. The results of this study follow the same trend, but only if low and high fluidity coals are considered separately. Figure 1 displays two bulk density vs. fluidity plots: one for the coals with fluidity >3000 ddpm (high and medium volatile bituminous coals) (Figure 1A) and the other for those with values <100 ddpm (low volatile bituminous coals) (Figure 1B). In both cases, the bulk density of the resultant foam

decreases significantly with the increasing fluidity of the precursor coal, reaching a plateau at high fluidity values. The drop is more pronounced in the lower rank coals (Figure 1A), with bulk density decreasing from 0.87 to 0.61 g cm⁻³ as fluidity rises from 3000 to 27000 ddpm.

As coal is heated under inert atmosphere, cracking reactions producing free radicals take place, but, simultaneously, some of the latter are involved in the condensation of aromatic molecules. The hydrogen rich species present in the coal are able to stabilise the fragments and convert them into “solvating” species, which make larger size molecules dissolve easier with a concomitant increase of fluidity. If there is not enough hydrogen available, the radical fragments join each other generating larger molecules and, then, high density foams. However, conversely to the expected, the low volatile bituminous coals produce the lowest-density foams, despite having very low fluidity.

TABLE 3: Properties of carbon foams

Foam	True density (ρ_{He} , g cm ⁻³)	Apparent density (ρ_{Hg} , g cm ⁻³)	Open porosity (ϵ , %)	Total pore volume (V_T , cm ³ g ⁻¹)	Major pore size (μ m)
F1	1.84	0.51	72.3	1.42	19
F2	1.81	0.84	53.7	0.64	97
F3	1.70	0.56	67.4	1.21	21
F4	1.70	0.87	48.5	0.56	132
F5	1.82	0.61	66.6	1.10	107
F6	1.84	0.71	61.4	0.86	107
F7	1.74	0.50	71.2	1.42	4
F8	1.64	0.60	63.6	1.06	11
F9	1.71	0.63	62.9	0.99	108
F10	1.79	0.67	62.5	0.93	60

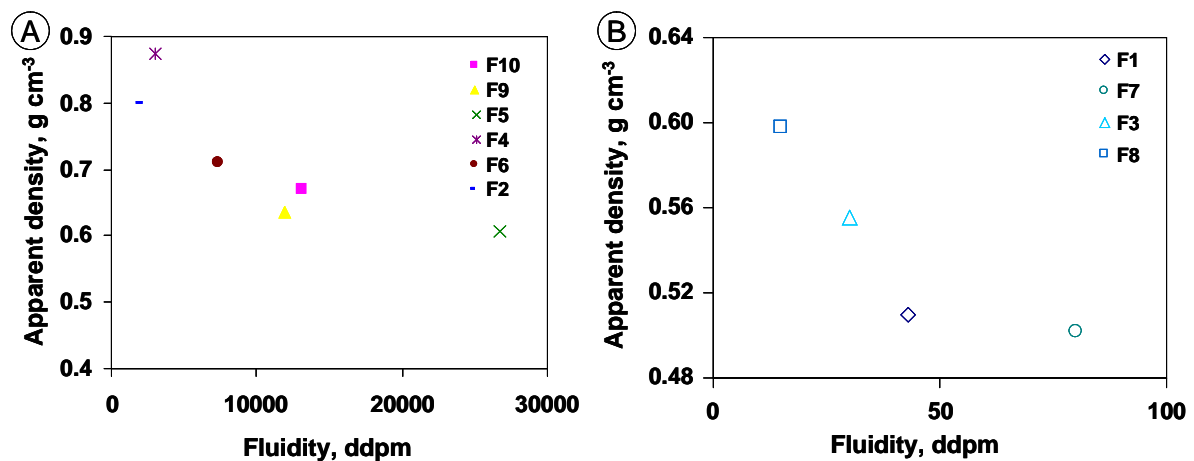


FIGURE 1: Variation of the apparent density of the carbon foams with the fluidity of the precursor coals. A) Low-rank coals, B) High-rank coals.

Liptinite is the maceral group with the highest hydrogen content, then, it is expected that coals with more liptinite show more fluidity and produce lower density foams. However, C1, C3, C7 and C8, in spite of having very low contents of liptinite macerals in their composition and displaying low fluidity, produce foams with the lowest apparent density. Liptinite, consisting mainly of aliphatic compounds, contribute more to the volatilized fraction than to the final structure of the foams and, therefore, to the increase of pressure in the reactor during the foaming. As pressure increases, the volatile matter will be released with more difficulty than at the beginning of the heating process. As a consequence, polymerization reactions will occur in a larger extent and high-density foams will be generated. (Figure 2).

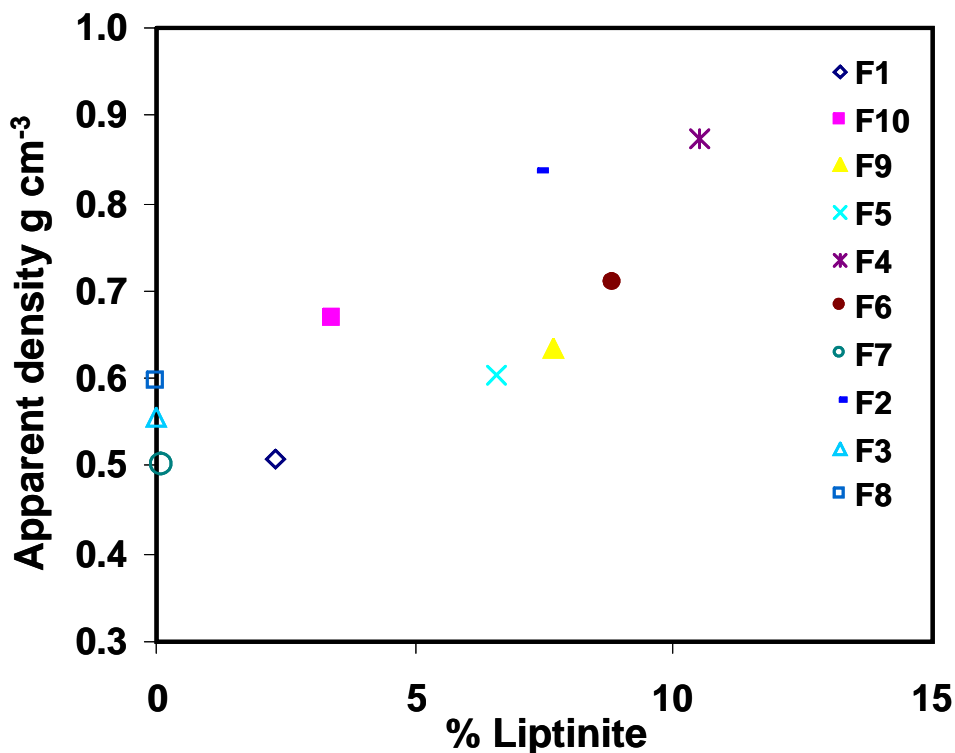


FIGURE 2: Variation of the apparent density of the carbon foams with the liptinite content of the precursor coal.

Table 3 shows the most abundant pore diameter of every foam, obtained from the pore size distribution graphics determined by mercury intrusion up to 227 MPa. On the whole, carbon foams have quite a homogeneous cell size, spherical structure and open interconnected pores in most of the cells. Most of the samples display macropores of around 100 μm , except F1, F3, F7 y F8, whose pore size is closer to 20 μm . These samples also present high values of open porosity and total pore volume. All of that is corroborated by the SEM microphotographs displayed in Figure 3).

It was found a trend between the pore size and the liptinite content (Figure 4). High liptinite content coals seem to produce higher macropore diameter foams. This can be explain if we consider that, as it was mentioned above, compounds that make up liptinite group make large size molecules dissolve easier and, in addition, the pore coalescence, eased by the fluidity increase, is at least partially responsible for the growth in pore size.

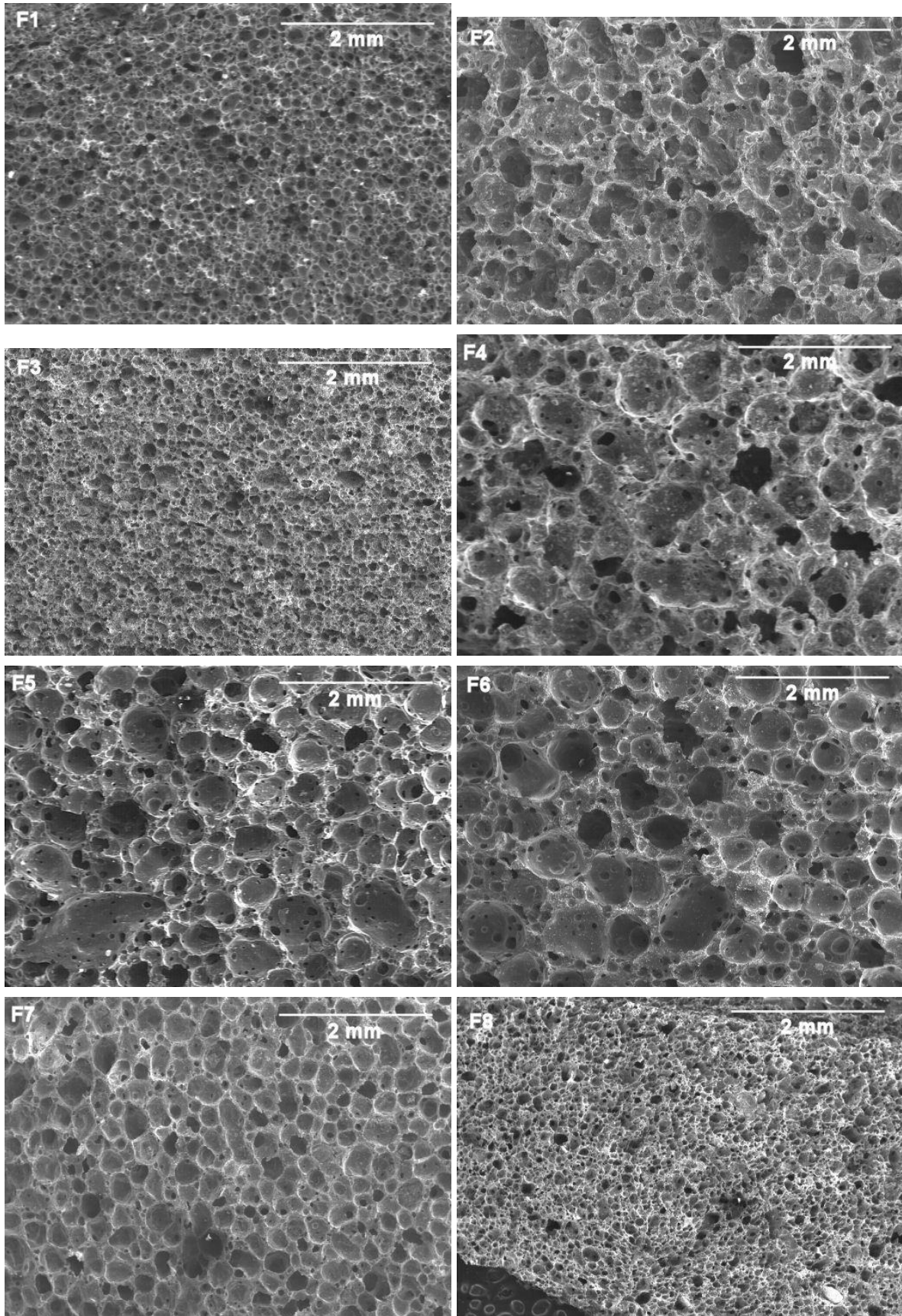


FIGURE 3: SEM microphotographs of the carbon foams obtained from the different coals.

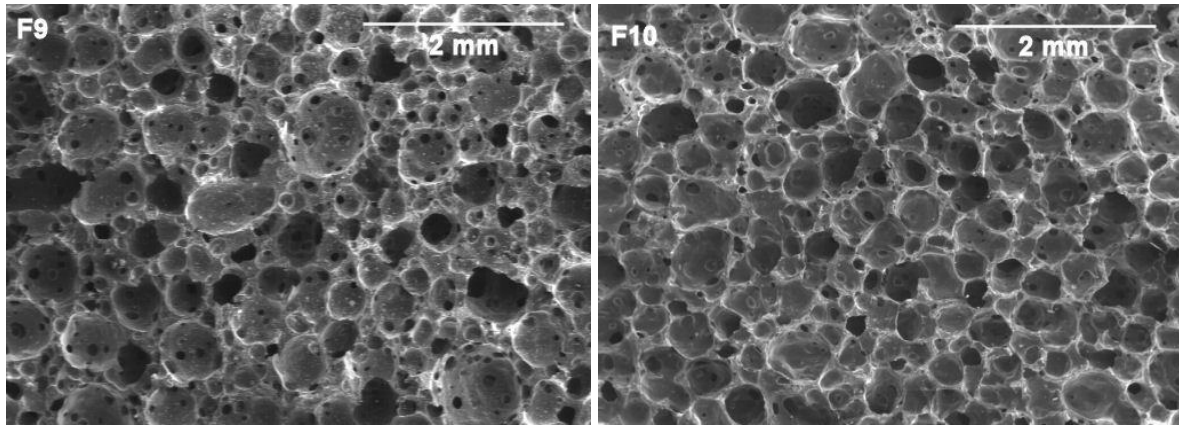


FIGURE 3 (cont.): SEM microphotographs of the carbon foams obtained from the different coals.

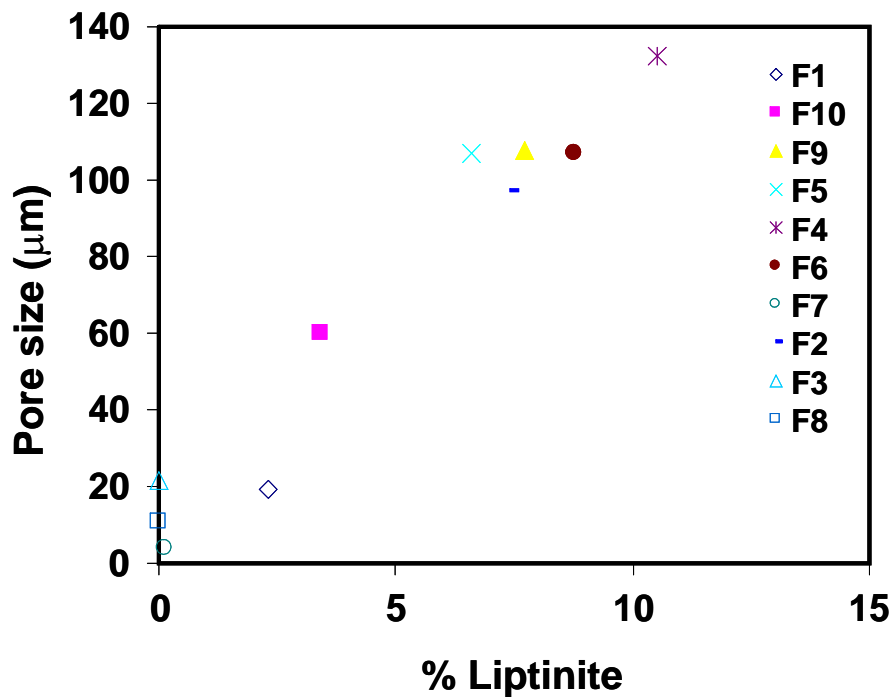


FIGURE 4: Variation of the pore size of the carbon foams with the liptinite content of the precursor coal.

CONCLUSIONS

Carbon foams have been obtained from several coals ranging from high-volatile to low-volatile bituminous coals. The textural characteristics of the resultant foams are influenced by the properties of the precursor coals, with fluidity and maceral composition playing a significant role in determining the density, the pore size and the pore volume of the products. The increasing fluidity gives rise to foams of lower apparent densities when considering coals of similar volatile matter content. The high hydrogen content of the liptinite maceral group promotes an increase of the pore size, but, also, an increase of the apparent density as a consequence of condensation reactions being favoured by the increased pressure.

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