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Very high methane uptake on activated carbons prepared from mesophase pitch:

a compromise between microporosity and bulk density

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Abstract

Two petroleum residues were pyrolysed under two different conditions to obtain pitches with low or high mesophase content. The effect of the KOH: precursor ratio and the activation temperature on the packing density and porous texture of the carbons have been studied and optimized. Activated carbons combining high micropore volume (>1 cm^3/g) and high packing density (0.7 g / cm^3) have been successfully prepared. Regarding excess methane adsorption capacities, the best results (160 cm^3 (STP) / cm^3 at 25 ºC and 3.5 MPa) were obtained using the pitch with the higher content of the more organized mesophase, activated at relatively low temperature (700ºC), with a medium KOH: precursor ratio (3:1). Some of the activated carbons exhibit enhanced adsorption capacity at high pressure, giving values as high as 175 cm^3 (STP) /cm^3 at 25ºC and 5 MPa and 200 cm^3 (STP)/cm^3 at 25ºC and 10 MPa (the same amount as in an empty cylinder but at half of the pressure), indicating a contribution of large micropores and narrow mesopores to adsorption at high pressure. The density of methane in pores between 1-2.5 nm at pressure up to 10 MPa was estimated to understand their contribution to the total adsorption capacity.

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1. Introduction

The use of natural gas as vehicular fuel is becoming an attractive alternative to gasoline and diesel fuel due to its clean burning and low cost. Compressed natural gas (CNG) is being used in vehicles but the high storage pressure (20 MPa) requires heavy stainless steel cylindrical storage vessels for safety. Adsorbed natural gas is an alternative that could reduce the methane storage pressure to around 1/5-1/6 of CNG at ambient temperature. Therefore, the storage vessels could be manufactured with lighter and less resistant materials than stainless steel, such as aluminum or carbon-carbon composites. Moreover, a more suitable shape for the storage tank could be employed to take advantage of the unusable space on board the vehicle.

In order to be economically viable, the Department of Energy of the United States (DOE) stablished in 1995 a volumetric objective for adsorbed natural gas value of 150 cc (STP: 0ºC, 1 bar)/cc, which was changed in 2002 to 180 cm³ (STP: 0ºC, 1 bar)/cm³ and recently revised to a value of 263 cm³ (STP: 0ºC, 1 bar)/cm³; the equivalent gravimetric value for the later would be 0.5 g/g [1]. To achieve this objective the adsorbent must have a narrow pore size distribution, between 0.8 and 1.1 nm, which is the pore width where maximum packing density of molecules of methane occurs, and an appropriate bulk density to obtain the maximum stored value per volume of adsorbent [2, 3]. Recent studies show that activated carbon can be used as a component for high pressure storage tanks provided that high-pressure compressors are available, as pressures around 10 MPa are required to reach the new DOE value [4].

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Petroleum residue is an excellent precursor material to produce graphitizable carbons but it can also be used to produce activated carbons with specific textural properties [5, 6]. The selection of the petroleum residue and the control of the experimental parameters for the subsequent pyrolysis treatment determine the characteristics of the mesophase pitch influencing the process of activation with KOH [5, 7]. Our previous investigations have shown that the pore volume increases with the pyrolysis temperature reaching a maximum value just at the transition temperature between a fluid pitch and a solid coke, the pitch with the highest mesophase content being the one developing the maximum porosity when activated with KOH [5]. On the other hand, the density of mesophase pitch and coke increases when enhancing the pyrolysis temperature and it also depends on mesophase microstructure. Therefore, to maximize the methane adsorption capacity of the activated carbons prepared from petroleum residues not only the microporosity of a specific size has to be optimised but also the density of the carbon. Thus, it is necessary to systematically study the influence of the nature of the petroleum residue precursor as well as the preparation conditions on packing density of the carbon in addition to methane adsorption.

In the present work mesophase pitches with specific characteristics obtained from different petroleum residues were used as carbon precursors for the preparation of activated carbons using KOH as activating agent. The main objective of this study is to reach a compromise between microporosity development and packing density to achieve the largest possible amount of volumetric methane storage, studying the effects at pressures up to 10 MPa. It is also important to evaluate the density of the methane adsorbed up to 10 MPa in function of the pore size of the carbon.

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2. Experimental

2.1 Mesophase pitch preparation

Two petroleum residues with different aromaticity were used as starting material: decanted oil (DO) and ethylene tar (PY). The characteristics of the petroleum residues and their treatments can be found elsewhere (DO and PY as R2 and R1, respectively) [8, 9]. The pyrolysis conditions for each residue (Table 1) were selected in order to prepare two mesophase pitches with low mesophase content (DO10 and PY56), and two with high mesophase content (DO100 and PY100). Pyrolysis was carried out in a laboratory-scale pilot plant, using 350 g of residue. The resulting mesophase pitches were ground in a ball mill to obtain a particle size lower than 500 µm.

Table 1. Pyrolysis conditions of the petroleum residues.

Petroleum residue	Temperature ºC	Pressure bar	Soaking time h	Mesophase %	Nomenclature
PY	440	10	4	56	PY56
	480	10	3	100	PY100
DO	460	10	1.5	10	DO10
	480	10	6	100	DO100

2.2 Activated carbons preparation

Four different series of activated carbons have been prepared by physical mixture of anhydrous KOH and mesophase pitch (DO10, DO100, PY56 and PY100), varying the KOH: precursor ratio from 1:1 to 4:1 (wt./wt.). In the specific case of the PY56 pitch, the precursor was also activated using a 6:1 and 8:1 ratio. Activation treatments were carried out in a horizontal furnace at 800 ºC for 2 h, under a nitrogen flow of 100 ml/min, using a heating rate of 5 ºC/min. The final materials were washed, first with a 10% HCl solution and afterwards with distilled water in a Soxhlet apparatus, until complete removal of chloride ions, and finally dried overnight at 110 ºC. New

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additional series were prepared from DO10 and PY100 by changing the activation temperature. In this new series the KOH: precursor ratio was fixed at 3:1, but the activation temperature was varied between 600 ºC and 800 ºC in order to evaluate its effect in the porosity and in the packing density on the final material. Labelling of the different samples includes: two letters to specify the type of petroleum residue, a number indicating mesophase content and finally the KOH/precursor ratio, followed by the activation temperature used (e.g., PY56-1:1_800 ºC to indicate a petroleum residue PY with 56 % mesophase, activated with a KOH: precursor ratio 1:1 at 800 ºC).

2.3 Characterization

The development of porosity on the activated carbons was evaluatedby nitrogen adsorption measurements at -196 ºC using a homemade automatic manometric equipment designed and constructed by the Advanced Materials Group (LMA), now commercialized as N2Gsorb-G (Gas to Materials Technologies (www.g2mtech.com). The samples were previously degassed for 4 h at 250 ºC. Nitrogen adsorption data were used to determine: i) the total pore volume (V_t) at a relative pressure of 0.95, ii) the BET specific surface area (S_{BET}), according to the criteria established by Rouquerol et al. [10] and iii) the micropore volume ($V_{N2,DR}$), pores < 2 nm, by the application of the Dubinin-Radushkevich equation (DR) [11]. The difference between V_t and $V_{N2,DR}$ is considered to be the mesopore volume (V_{meso}). The volume of narrow micropores, pores < 0.7 nm, was calculated by applying DR equation to the CO_2 adsorption data at 0ºC ($V_{CO2,DR}$). The characteristics curves of N_2 and CO_2 isotherms (LnV vs A^2/β^2) for representative samples can be found in the supporting information material. Pore size distribution was calculated by the application of the Quenched-Solid Density Functional Theory (slit pore, QSDFT equilibrium model) to the nitrogen adsorption isotherm data [9, 10] for pores > 1 nm and the Non-Linear Density Functional Theory (NLDFT) to the

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CO_2 adsorption isotherm data for pores < 1 nm. Packing density has been determined by pressing a given mass of activated carbon in a mold with a cross-sectional area of 1.30 cm^2 at a pressure of 500 kg/cm^2. The methane excess adsorption capacity of the synthesized activated carbons was estimated from the methane adsorption isotherms at 25 ºC and up to a pressure of 4 and/or 10 MPa. Before any adsorption measurement, activated carbons were degassed at 250 ºC for 4 h. The experiment was carried out in a homemade automatic manometric equipment (designed and constructed by the Laboratorio de Materiales Avanzados de la Universidad de Alicante (LMA), now commercialized as iSorbHP by Quantachrome Corporation). This equipment takes into account the compressibility factor (Z) calculated by the Helmholtz equation and the nonlinear behavior caused by the differences in temperature between the manifold and the cells. Helium is used to calculate the void volume. Transmission electron microscopy (TEM) observations of some of the activated carbons were performed on a JEOL JEM-2100F microscope.

3. Results and discussion

The results obtained along the study will be discussed in terms of the effect of the mesophase pitch (nature and mesophase content) and the activation conditions (temperature and KOH: pitch ratio) on the characteristics of the resulting activated carbon: i.e., microporosity development and packing density.

3.1 Effect of the KOH: precursor ratio

Mesophase pitch PY56 was selected to evaluate the effect of the amount of activating agent, using a KOH: precursor ratio ranging from 1:1 to 8:1; the activation temperature being fixed at 800 ºC. The nitrogen adsorption- desorption isotherms of the

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samples prepared are presented in Figure 1. The isotherms clearly show the effect of KOH: precursor ratio on the activation process. Nitrogen isotherms are all type I, typical of microporous solids. However, an increase in the amount of activating agent results in an enhancement of the amount of nitrogen adsorbed and in a change in the isotherm shape, thus indicating a higher porosity development.
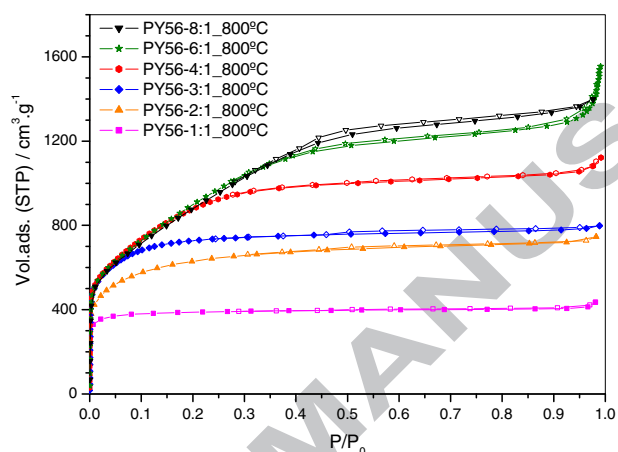

Figure 1. Nitrogen adsorption-desorption isotherm at -196 ºC up to 1 bar for the precursor PY56 activated at different KOH: precursor ratio. Closed symbols: adsorption, open symbols: desorption.

Despite the fact that N_2 adsorption isotherms follow a clear trend, it is worth analyzing them in detail. Sample activated with KOH: precursor ratio 1:1 shows a narrow knee indicating the presence of a narrow pore size distribution (PSD). The corresponding PSD estimated by applying the QSDFT method [12, 13] (Figure 2), shows the presence of only a contribution located at 0.9 nm. There is a second group of isotherms for samples activated using ratios above 2:1 which exhibit a wider knee in the nitrogen adsorption isotherm, thus suggesting the development of wider micropores. It is important to highlight the fact that for ratios above 4:1 these isotherms exhibit a linear region in the low-medium relative pressures range where the volume of nitrogen

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adsorbed increases linearly with the pressure, thus reaching a plateau afterwards (at a relative pressure between 0.3 and 0.6). The widening of the knee indicates the progressive development of wide microporosity and narrow mesoporosity. A closer look to the pore size distribution (Figure 2) shows that the peak appearing at 0.9 nm progressively decreases with the activation treatment while it is shifted to larger values (up to 1.1 nm). Additionally, there is a new wide peak appearing at 1.7-2.5 nm, which widens with an increase in the amount of KOH.
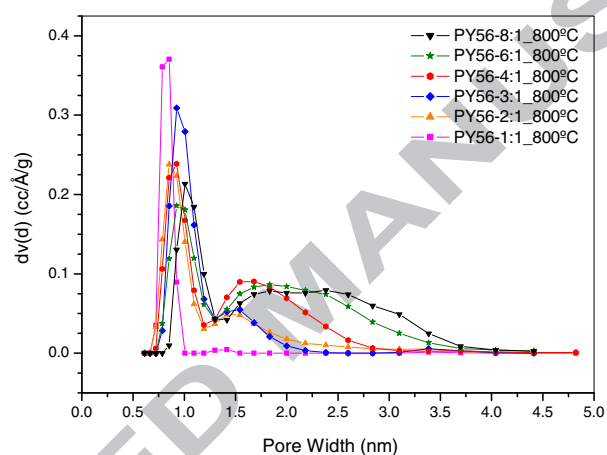

Figure 2. Pore size distribution by applying Quenched Solid Density Functional Theory analysis over nitrogen adsorption isotherm at -196ºC (QSDFT) for the precursor PY56 activated at different KOH: precursor ratio.

Table 2 summarizes the textural properties for these samples calculated from the nitrogen adsorption data and the volume of narrow micropores (size lower than 0.7 nm) calculated by the application of DR equation to the CO_2 adsorption data obtained at 0ºC. The apparent BET surface area reaches values as high as 3290 m^2/g for the activated carbon PY56-8:1_800 ºC. This value is comparable to the highest values reported in the literature for this kind of materials [14]. In accordance with previous observations, the volume of narrow micropores ($V_{CO2,DR}$) progressively increases with the amount of

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activating agent, reaching a maximum for a 3:1 ratio. On the other hand, the total pore volume (V_{total}) and mesopore volume increase with KOH ratio, reaching a maximum for 8:1 ratio, which correspond to values of 2.20 cm^3/g and 1.10 cm^3/g, respectively. Regarding the total micropore volume ($V_{N2, DR}$), values are higher than 1.0 cm^3/g for KOH: precursor ratios larger than 3:1, reaching a maximum of 1.10 cm^3/g for 8:1 ratio. Therefore, increasing the amount of activating agent implies an enlargement of the pore size distribution in the region of the wide micropores-narrow mesopores, as it is inferred from the analysis of the nitrogen adsorption isotherms. The amount of potassium hydroxide used for the chemical activation also has a notable influence on the process yield, decreasing from 76 wt% for 1:1 to 19 wt % for 8:1 ratio.

Table 2. Porous textural characteristic for samples activated at different KOH: PY56 ratios and the yield of the process.

Sample	S_{BET}	V_{total}	$V_{N2,DR}$	$V_{CO2,DR}$	V_{meso}	Yield*
	m^2/g	cm^3/g	cm^3/g	cm^3/g	cm^3/g	wt%
PY56-1:1_800ºC	1470	0.63	0.61	0.56	0.02	76
PY56-2:1_800ºC	2295	1.13	0.83	0.71	0.30	59
PY56-3:1_800ºC	2670	1.21	1.01	0.94	0.20	46
PY56-4:1_800ºC	3170	1.63	1.03	0.74	0.60	35
PY56-6:1_800ºC	3265	2.05	1.07	0.73	0.98	25
PY56-8:1_800ºC	3290	2.20	1.10	0.68	1.10	19

*Yield(wt%)= (dry carbon weigh/ precursor weigh)*100

3.2 Effect of mesophase pitch

The effect of mesophase content on the structure of the synthesized activated carbons was evaluated by selecting four mesophase pitches (PY56, PY100, DO10 and DO100), activated at 800 ºC using a variable amount of activating agent. The relationship between packing density and microporosity development for PY and DO samples is presented in Figure 3. As expected, an increase in KOH: precursor ratio gives rise to an increase in the porosity development, which is accompanied by a

decrease in the sample density. The maximum development of microporosity is achieved for the PY (Figure 3 a) and DO (Figure 3 b) residues with values as high as $V_{N2,DR}$= 1.07 cm^3/g and a packing density of 0.48 g/cm^3; and $V_{N2,DR}$=1.01 cm^3/g and a packing density of 0.53 g/cm^3, respectively are reduced. Similar values of micropore volume with a notable reduction of the density is observed when the potassium hydroxide ratio is higher than 3:1, indicating that a widening of porosity is taking place, with a lower creation of new pores.
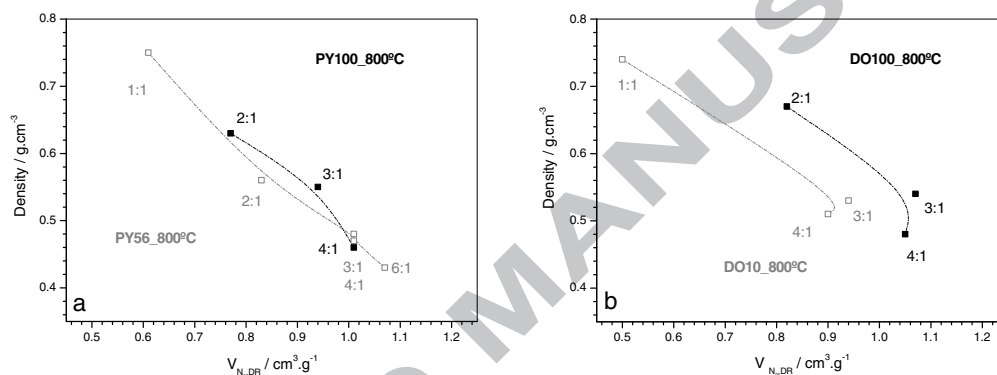

Figure 3. Evolution of the packing density as a function of nitrogen volume calculated by Dubinin-Radushkevich (DR) for precursors with high and low content of mesophase activated at different KOH: precursor ratio; a) PY56 and PY100; b) DO10 and DO100.

On the other hand, when samples with similar microporosity are compared, higher densities are achieved for the activated carbons obtained using mesophase rich carbon precursor, i.e. PY100 and DO100. As anticipated out by Martínez- Escandell et al. [8, 9] semicokes obtained from these two petroleum residues possess very similar aromaticity and produce a highly ordered mesophase, despite their significant differences in the initial aromaticity. In this case, it is reasonable to conclude that if the amount of mesophase increases, the density of the carbon precursor should also increase. As it can be observed in Figure 3, the activated carbons from semicokes

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PY100 and DO100 have higher density. Figures 4 a, b show the transmission electron microscopy (TEM) images for the activated carbons DO10-3:1_800ºC and DO100-3:1_800ºC, respectively. These micrographs compare two activated carbons derived from the same petroleum residue but with different mesophase content. Graphene-like layers with different dimensions and shapes are clearly observed, all co-bonded to create spaces between them, microporosity [15]. A more detailed observation can provide an explanation for the density of these samples. There exists a very remarkable difference when the microstructure of both samples is compared; it seems that the activated carbon prepared from the precursor with high mesophase content (DO100) has a more compact structure, whereas the one obtained from the precursor with low mesophase content (DO10) has a more open microstructure. It is clear that DO100 must be denser; nevertheless, both samples have almost the same value of packing density (0.54 cm^3/g). To explain this uncertainty it must be remembered that the volume occupied by a carbon is a result of adding the non-microporous contribution (space between particles and macro-mesopores), the carbon skeleton and the micro-plus mesopore volume. The best materials for methane storage application should minimize the first and second ones and enhance the last one [16]. Apparently the carbon skeleton of sample DO100-3:1-800 ºC occupies less volume whereas it has a larger micropore volume (more than 1 cm^3/g) than DO10-3:1_800 ºC (closed to 0.95 cm^3/g).
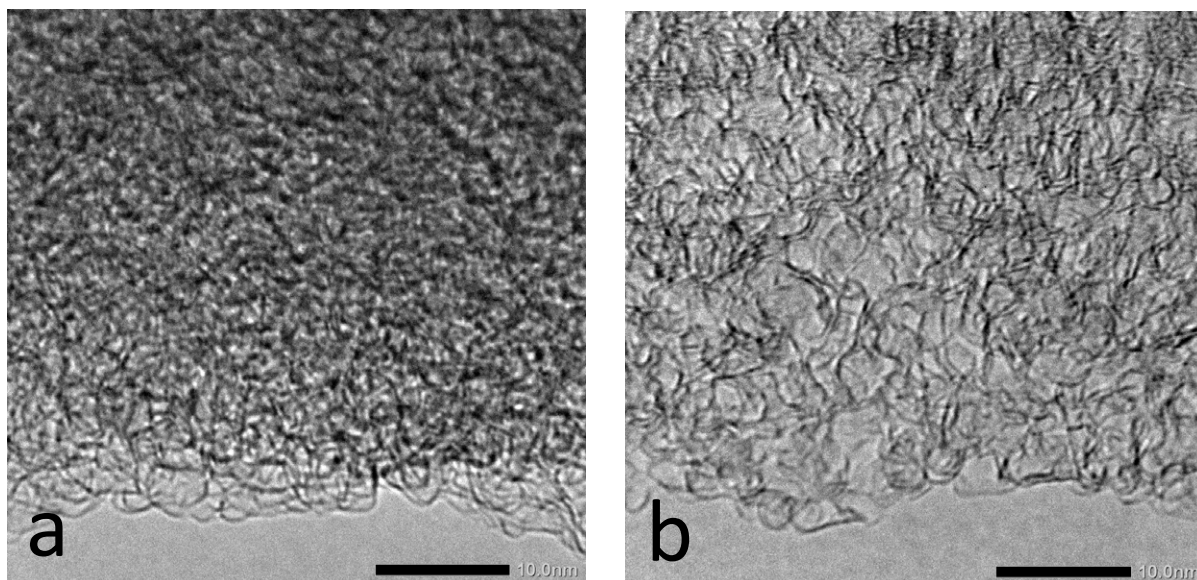
Figure 4. TEM images for activated carbons from mesophase pitch with a high and low content of mesophase a) DO100-3:1_800 ºC and b) DO10-3:1_800 ºC.

Thus, it seems that it has been possible to minimize the volume of carbon skeleton and maximize the microporous volume using the precursors with high mesophase content. The second step of this work is to control the volume and size of mesopores. For this reason DO100 and PY100 pitches were selected to prepare another series of activated carbons changing the activation temperature.

3.3 Effect of activation temperature

For this part of the research, the activation process was performed at 600, 700 and 800 ºC for 2 h using a 3:1 KOH ratio. N_2 adsorption isotherms at -196 ºC for the series DO100-3:1 and PY100-3:1 are presented in Fig 5 a and b, respectively, all of them normalized at the relative pressure of 0.5. These isotherms clearly shows that the higher the activation temperature, the wider the knee of the isotherm. Hence, a decrease in the activation temperature brings a narrowing of the pore size distribution. Table 3

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includes the textural characteristics calculated from the nitrogen adsorption data. The values show that by reducing the temperature of the activation process by two hundred degrees, it was possible to minimize the mesoporosity drastically by 54-60%, without compromising largely the microporosity (reduce 13-17%). In terms of methane storage, the density of methane is lower in the mesopores than inside the micropores; nonetheless a minimum amount of mesoporosity is necessary to facilitate the connection between the inner porous structure and the exterior of the carbon particle in order to maximize the adsorption/desorption kinetics during the charge/discharge process under real conditions. It is noteworthy to mention that even at the lowest temperature (600 ºC) it was possible to prepare highly activated carbon materials with a simultaneous enhancement of the packing density (more than 20%).
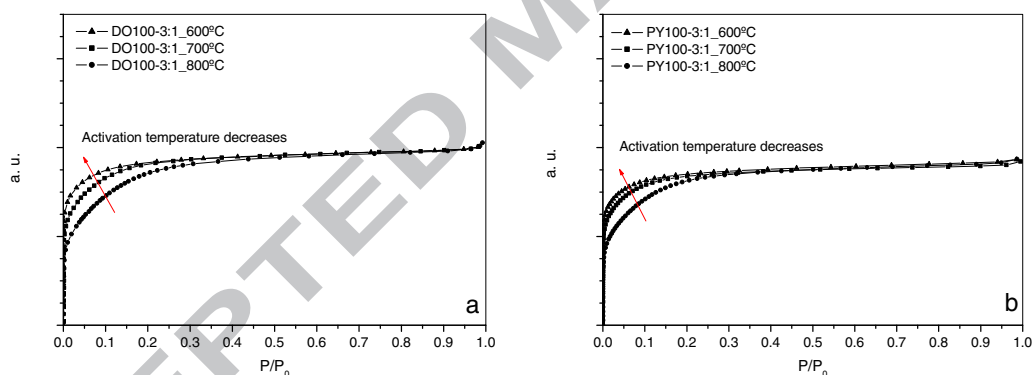

Figure 5. Normalized nitrogen adsorption isotherm at -196 ºC up to 1 bar for the precursor with high content of mesophase a) DO100, b) PY100, activated at different temperature.

Table 3. Textural characteristic and excess methane uptake (cm^3/g and $cm^3(STP)/cm^3$) at 25ºC and 3.5 MPa for samples activated at different temperature.

Sample	S_{BET} m^2/g	V_{total} cm^3/g	$V_{N2,DR}$ cm^3/g	V_{meso} cm^3/g	Density g/cm^3	3.5 MPa, 25ºC	
						CH_4 uptake $cm^3(STP)/g$	CH_4 uptake $cm^3(STP)/cm^3$
PY100-3:1_800	2800	1.31	0.94	0.37	0.55	260	145
PY100-3:1_700	2465	1.12	0.89	0.22	0.60	250	150
PY100-3:1_600	2225	0.99	0.82	0.17	0.65	220	140
DO100-3:1_800	3005	1.43	1.07	0.36	0.54	260	140
DO100-3:1_700	2700	1.23	0.93	0.30	0.62	255	160
DO100-3:1_600	2300	1.05	0.89	0.16	0.70	220	155

To sum up, in a first step, the precursors with higher mesophase content were selected for the final activated carbons due to presence of an optimum density together with a great development of microporosity. In a second step these precursors were activated at a lower temperature in order to eliminate most of the mesoporosity. In the following section the performance of these materials on methane adsorption will be discussed.

3.4 Application: methane adsorption

One of the requirements for an adsorbent to exhibit an optimum behavior in methane storage below 3.4 MPa is to have a large micropore volume, where methane molecules can be strongly adsorbed, together with a certain mesopore volume to increase the adsorption/desorption kinetics. In addition, the adsorbent must exhibit a narrow pore size distribution, centered at around 0.8-1.2 nm [17], which is the size required to accommodate two or three methane molecules. Under these circumstances, the packing density of the adsorbed phase achieves a maximum.

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The amount of excess methane adsorbed at 3.5 MPa (cm^3(STP)/g and cm^3 (STP)/cm^3, taking into account packing density for the calculation) into the carbons has been deduced from the adsorption isotherm at 25 ºC. A clear relationship between the excess amount of methane adsorbed at 3.5 MPa and the volume of micropores was found (Figure 6), in agreement with previous results described in the literature [18-20]. In this sense, the largest amount adsorbed in a gravimetric basis (expressed as wt.%) was 19.5 wt.% for sample DO100-4:1-800 ºC, the sample with the highest micropore volume ($V_{N2,DR}$=1.1 cm^3/g). Interestingly, this methane uptake exceeds previous values reported in the literature at ambient temperature and 3.5 MPa [21-22].

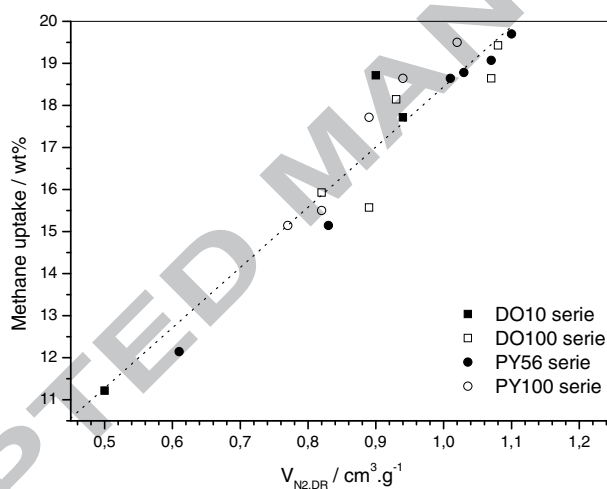***Figure 6***. Relationship between volume of micropores ($V_{N2,DR}$) and methane excess adsorption capacity (expressed as wt%) at 25 ºC and 3.5 MPa for all of series.

The methane excess adsorption isothems calculated on a gravimetric basis for sample DO100-3:1 activated at three different temperatures (800, 700 and 600 ºC) is presented in Figure 7, a. The shape of the isotherms is similar to that described for other types of activated carbons [23]. Moreover, these materials show a considerable enhancement of methane adsorption with pressure in the pressure range studied, superior to that expected by the compression of the gas. Activated carbon DO100-

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3:1_800 ℃ shows the highest storage capacity (close to 19 wt.% at 3.5 MPa) due to the highest microporosity development compared to its homologous one activated at a lower temperature. The activated carbons obtained using PY100 pitch shows an identical trend and methane adsorption values expressed on a gravimetric basis are quite similar.

Choosing the appropriate density is an important factor when volumetric capacity is evaluated (expressed as cm^3 (STP)/cm^3) [24]. The packing density calculated by compressing the powder is a useful approach because it represents the bulk density. Indeed, for samples with similar nature than the published in this paper it was demonstrated that a mechanical compression does not affect the adsorption behavior, i.e. a change in the micro/mesopores structure is not expected [25]. Thus, taking into account the methane excess adsorption results (cm^3 (STP)/g) and the packing density of the activated carbon, it is possible to estimate the volumetric adsorption capacity (cm^3 (STP)/cm^3) (Figure 7, b). A change in the trend is observed, since now the activated carbon DO100-3:1_800 ℃ is the sample which presents the lowest amount of methane adsorbed due to its lower packing density. Samples activated at 700 ℃ and 600 ℃ exhibit values larger than 150 cm^3 (STP)/cm^3 (old DOE target). Table 3 includes the gravimetric and volumetric methane uptake for the activated carbons described and for the PY100-3:1 series. The highest value (160 cm^3 (STP)/cm^3) was obtained for sample DO100-3:1_700 ℃, where a compromise between packing density (0.62 g/cm^3) and micropore ($V_{N2,DR}$=0.93 cm^3/g) volume was reached. Furthermore, this sample exhibits a certain amount of mesopores which guarantees a good adsorption/desorption kinetics.
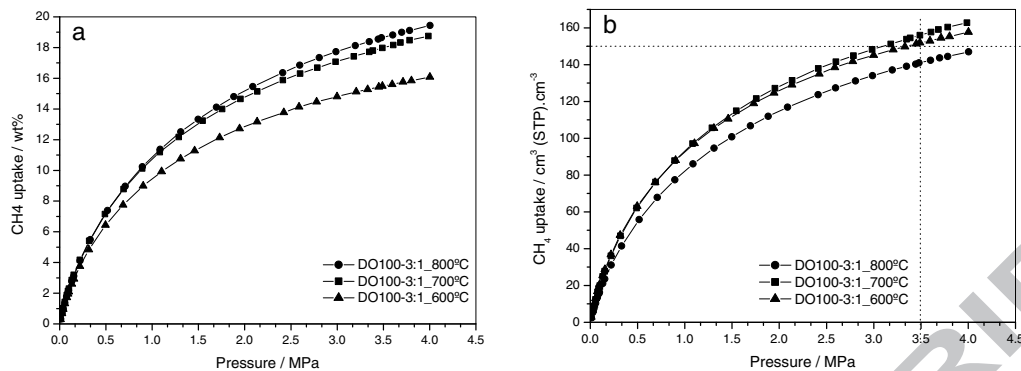
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Figure 7. Methane excess adsorption isotherm at 25 ºC up to 4 MPa for the samples DO100-3:1 activated at different temperature, a) gravimetric basis and b) volumetric basis. Discontinue line, old DOE target.

In the case of the activated carbons obtained using PY100 pitch a similar trend is observed. However, as packing density of the activated carbons becomes lower, storage capacity values decrease, Table 3. As the porosity achieved within these carbons is rather similar and the methane adsorbed values, expressed on a gravimetric basis, are also similar, the reduction on the methane adsorption capacity, in $cm^3 (STP)/cm^3$, can be explained in terms of a lower density of the carbon skeleton. It seems that the more ordered mesophase produced by DO residue (flow domains) can be the responsible for this improvement.

The first section of this work was mainly focused in finding a balance between porosity and density of the carbon, trying to maximize microporosity and reduce mesoporosity. However, some of the evaluated carbons, especially those presenting high micro- and mesopore volumes, presented excess methane adsorption isotherms at 25ºC and 3.5 MPa that show significant enhancement at this pressure. Motivated for this issue, isotherms up to higher pressures (10 MPa) have been obtained for samples PY56-1:1_800°C (essentially microporous), DO100-3:1_700°C (with higher microporosity

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and some mesoporosity, exhibiting at 3.5 MPa the best methane excess adsorption values), sample PY56-8:1_800°C (showing the largest development of microporosity and mesoporosity) and commercial MaxSorb MSC-30 (for the sake of comparison). The characterization of porosity of the activated carbons, obtained by nitrogen adsorption isotherms at -196ºC is presented in Table 4. When values of methane uptake are expressed on a gravimetric basis (Figure 8 a) it can be observed that the isotherm of the sample with only microporosity saturates at pressures below 3.5 MPa, showing a maximum value of 13.8 wt%. On the other hand, samples DO100-3:1_700°C and MSC-30 have similar curves, although they do not reach saturation at 3.5 MPa but rather at higher values (above 7.5 MPa), giving maximum uptake values of 22.7 and 21.6 wt.%, respectively. Moreover, in case of the sample PY56-8:1_800°C, with more mesoporosity, saturation is not appreciated at 10.0 MPa, reaching values of methane uptake as high as 26.0 wt.%, see Table 4. Figure 8b shows the methane adsorption capacity at 10 MPa on a volumetric basis. The behavior found is very similar, although in this case sample DO100-3:1_700°C presents a higher methane uptake than sample MSC-30 due to the higher packing density of the former. Interestingly, the samples DO100-3:1_700°C and PY56-8:1_800°C present methane uptakes near 165 and 175 cm^3/cm^3, respectively, very close to the 2002 DOE target by only increasing pressure from 3.5 to 5 MPa. Furthermore, with sample PY56-8:1_800°C the amount of methane uptake increases continuously with the adsorption pressure up to 10 MPa, reaching values close to 200 cm^3 (STP)/cm^3. It is important to highlight that the DOE target refers to storage capacity while these values are referred to excess adsorption capacity. To compare the values it is necessary to convert excess to storage values, as described recently by Casco et al. [4].

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The results obtained indicate the importance of mesoporosity in the adsorption of methane at high pressures. These values are in the range of those found in the literature for methane storage on wet carbons, which were at lower temperature, 2ºC and similar pressure [26, 27]. Thus, the storage capacity for methane of carbon sample PY56-8:1 800ºC is similar than the one reached for CNG at 20 MPa, but using half of the pressure.

Table 4. Textural characteristic and volumetric methane uptake at 25ºC and different pressure for different samples.

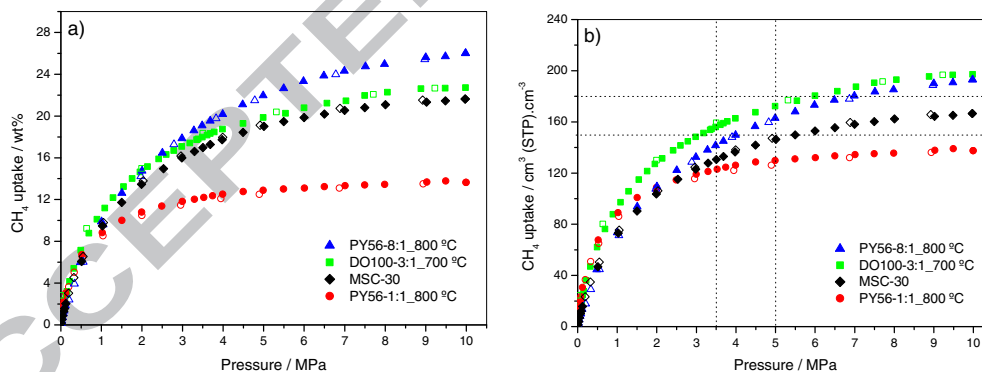| Sample	S_{BET}	V_{total}	$V_{N2,DR}$	V_{meso}	CH_4 uptake cm^3 (STP)/cm^3	
	m^2/g	cm^3/g	cm^3/g	cm^3/g	5.0 MPa	10.0 MPa
PY56-1:1_800	1470	0.63	0.61	0.02	130	140
PY56-8:1_800	3290	2.20	1.10	1.10	165	195
DO100-3:1_700	2700	1.23	0.93	0.30	170	200
MSC-30	2970	1.53	0.90	0.63	150	165

Figure 8. Methane excess adsorption isotherm at 25 ºC up to 10 MPa for the samples PY56-1:1_800ºC, PY56-8:1_800ºC, MSC-30 and DO100-3:1_700ºC, a) gravimetric basis and b) volumetric basis.

Last but not least, to determine the behavior of these activated carbons during cycles of charge/discharge, the methane uptake isotherms were performed for multiple

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cycles of adsorption/desorption of methane, at 25°C and 5 MPa without degassing between cycles, using two of the activated carbons with large differences in porous distributions, PY56-1:1_800°C (essentially microporous) and PY56-8 1_800°C (with increased mesoporosity), Figure 9. Both materials have a very homogeneous behavior during the cycles.
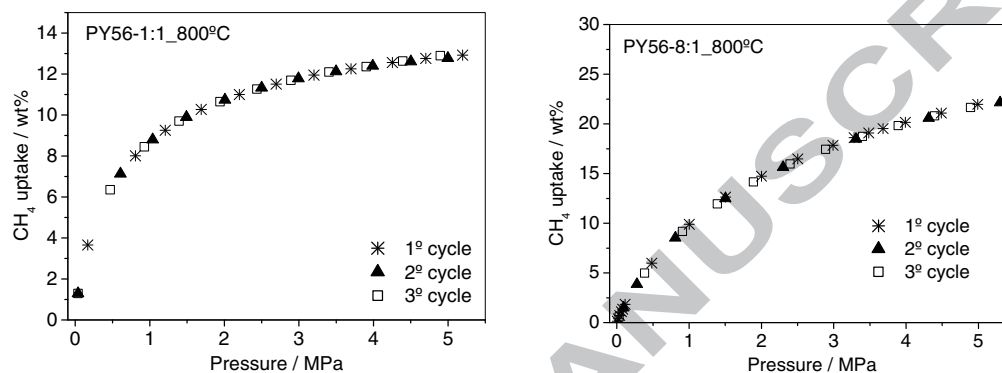

Figure 9. Cycles of excess methane adsorption isotherms on a gravimetric basis at 25 ºC up to 5 MPa for: a) PY56-1:1_800 ºC and b) PY56-8:1_800 ºC .

3.5 Average methane density in pores

From the excess methane adsorption isotherms at 25°C of all the studied activated carbons and the volume of narrow micropores (V_{CO2}) and the volume of micropores (V_{N2}) determined using CO_2 and nitrogen isotherms, the density of methane in narrow micropores and in wide micropores can be estimated using the method suggested by Rodriguez-Reinoso et al. [28]. As highly concentrated clusters of methane molecules easily form in micropores regardless the application of small pressure of 2-3 MPa [29], in that work the method was applied in a pressure range of 5.0 MPa, assuming that of all the methane was adsorbed preferentially in narrow micropores and wide micropores. In addition, the activated carbons used were essentially microporous. In the present work it has been observed that in some carbons methane storage at

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pressures above 5.0 MPa has to be considered, as it seems that there can be a contribution not only of narrow micropores but also wide micropores and even narrow mesopores for the adsorption above that pressure.

To improve the previous results, all the adsorption data obtained in this study have been used to calculate the average density of the methane storage in pores of different range of sizes. The method only allows calculating the density of methane adsorbed in two ranges of pore size. Thus, nine different situations have been analyzed. The analysis was carried out using the pore volumes obtained for a size range of pores determined by NLDFT and QSDFT cumulative plots from CO_2 and N_2 adsorption isotherms, respectively (slit pore assumption). Table 5 summarizes the different ranges of pore size studied.

Table 5. Different range of pores studied for the determination of methane density

Pores < 0.8 nm	Pores < 0.8 nm	Pores < 0.8 nm
Pores 0.8-1.5 nm	Pores 0.8-2.0 nm	Pores 0.8-2.5 nm
Pores < 1.0 nm	Pores < 1.0 nm	Pores < 1.0 nm
Pores 1.0-1.5 nm	Pores 1.0-2.0 nm	Pores 1.0-2.5 nm
Pores < 1.2 nm	Pores < 1.2 nm	Pores < 1.2 nm
Pores 1.2-1.5 nm	Pores 1.2-2.0 nm	Pores 1.2-2.5 nm

Figure 10 (a-c) presents the evaluation of average methane density in pores < 1.0 nm and 1.0-1.5 nm (a), < 1.0 nm and 1.0-2.0 nm (b) and < 1.0 nm and 1.0-2.5 nm, as examples of all the situations analyzed. When all the methane is forced to be stored in pores ranges <1nm and 1.0-1.5 nm (Figure 10 a), the density of methane in the largest pores have to reach values superior to the methane stored in narrower pores, as high as 0.45 g/cc, to fulfill the methane uptake values reached at high pressure, which seems to be rather improbable. When the possibility of using larger pores (1.0-2.0 nm) is allowed there is an increase in the density of methane in the narrower pores and a reduction of the density in the wider pores, but at pressures higher than 6 MPa the density of

methane in the wider pores slightly surpasses that of the narrower pores, which is difficult to understand. However, if the adsorption occurs in the pores below 1.0 nm and the pores between 1.0 and 2.5 nm a more reasonable situation occurs as the density in the narrower pores is always larger than in the wider pores in all the ranges of pressure studies. In fact, for pores below 1 nm it seems that density increases fast with pressure for pressures below 4 MPa, reaching values close to 0.24-0.25 g/cm^3 [28]. In the cases of wider pores the filling is faster below 6 MPa and similar to the free gas at higher pressures, reaching values close to 0.16-0.17 g/cm^3. Average correlation coefficients for the plots of Figure 10 a are 0.89, 0.93 for Figure 10 b and 0.95 for Figure 9 c. In fact, the latter presents the best correlation coefficient of all the sceneries studied, the results of this conditions showing the best approach (see supporting information, figure S1). Thus, these results indicate that it is necessary the contribution of pores as large as 2.5 nm to explain the high methane uptake measured at 10 MPa in micro-mesoporous carbons.
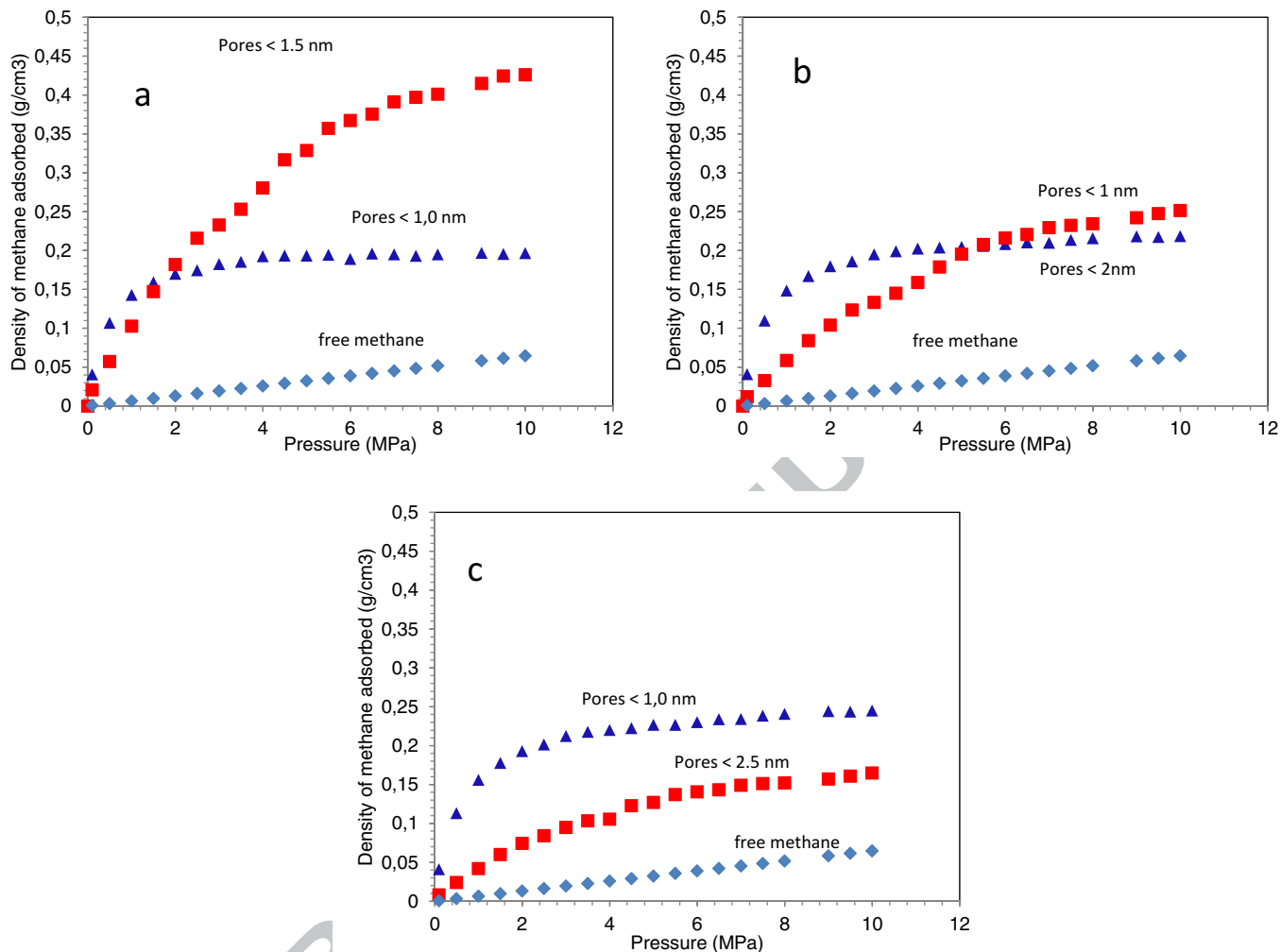
Figure 10. Density of methane calculated from methane excess adsorption isotherms (at 25 ºC up to 10 MPa) and CO_2 (0ºC) and N_2 (196ºC) DFT pore size distribution curves: a) in pores smaller than 1 nm and in pores between 1.5-1 nm; b) in pores smaller than 1 nm and in pores between 2-1 nm; c) in pores smaller than 1 nm and in pores between 2.5-1 nm.

4. Conclusions

Activation conditions of mesophase pitches have been optimized in terms of developing a very high methane adsorption capacity together with a high packing

density. In general, when carbon precursors with high content of highly oriented mesophase are activated with KOH, high packing density and high micropores volume can be obtained. The KOH/pitch ratio of 3:1 is the optimum to obtain a most favorable porosity development with a narrow pore size distribution. Temperatures of activation of 700 ºC it seems to be appropriate to minimize the mesopores content but at the same time to guarantees a small content required to improve the adsorption kinetics. All this parameters were evaluated by a systematic study that derived in a good volumetric capacity of methane adsorption at 25ºC and 3.5 MPa, higher than the target of 150 cm^3 (STP)/cm^3. Interestingly, the activated carbons presenting a large volume of microporosity and narrow mesoporosity exhibit large excess methane adsorption at high pressure, giving values of 175 cm^3 (STP)/cm^3 at 5 MPa and 200 cm^3 (STP)/cm^3 at 10 MPa (the same amount as in a cylinder with no adsorbent but at half of the pressure). To understand these results, the density of methane in narrow micropores and in micro-mesopores up to 10 MPa has been calculated using methane adsorption isotherms at 25ºC and pore size distributions obtained by DFT. Results indicate a contribution of pores below 1-2.5 nm in methane uptake at high pressures.

Acknowledgements

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