

Effect of the porous structure in carbon materials for CO₂ capture at atmospheric and high-pressure

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ABSTRACT

Activated carbons prepared from petroleum pitch and using KOH as activating agent exhibit an excellent behavior in CO₂ capture both at atmospheric (~168 mg CO₂/g at 298 K) and high pressure (~1500 mg CO₂/g at 298 K and 4.5 MPa). However, an exhaustive evaluation of the adsorption process shows that the optimum carbon structure, in terms of adsorption capacity, depends on the final application. Whereas narrow micropores (pores below 0.6 nm) govern the sorption behavior at 0.1 MPa, large micropores/small mesopores (pores below 2.0-3.0 nm) govern the sorption behavior at high pressure (4.5 MPa). Consequently, an optimum sorbent exhibiting a high working capacity for high pressure applications, e.g., pressure-swing adsorption units, will require a poorly-developed narrow microporous structure together with a highly-developed wide microporous and small mesoporous network. The appropriate design of

the preparation conditions gives rise to carbon materials with an extremely high delivery capacity ~ 1388 mg CO₂/g between 4.5 MPa and 0.1 MPa. Consequently, this study provides guidelines for the design of carbon materials with an improved ability to remove carbon dioxide from the environment at atmospheric and high pressure.

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1. Introduction

Anthropogenic CO₂ emissions coming from the combustion of fossil fuels have become an environmental concern due to the continuous increase in the energy demand worldwide as a result of the increase population and the standards of life. European strategic energy technology plan (SET-PLAN) targets for 2020 to reduce greenhouse gas emissions by 20% and a greater ambition of reducing by 50% by 2050. Among the different technologies to mitigate CO₂ emissions, adsorption processes based on porous solids (e.g., carbon materials) are becoming an excellent alternative in economical and environmental terms compared to actual technology based on absorption processes using basic solutions [1-10]. In order to be industrially attractive, a porous sorbent must combine a high adsorption capacity, a high selectivity towards CO₂, an easy regeneration and last but not least, a high working capacity. Upon concentration in a porous solid, CO₂ can be injected into deep subsurface rock formation for long-term storage (geological sequestration) or it can be used as an energy source as recently described [11].

Many industrial adsorption processes are based on pressure-swing-adsorption (PSA) units using porous sorbents where adsorption and desorption/release takes place by pressure changes in parallel vessels. Under high pressure CO₂ is adsorbed on the solid surface, whereas when the pressure is reduced, the gas is released [12,13]. In order for a sorbent to be efficient in a PSA unit, the difference between the amount adsorbed at the highest and the lowest pressure must be as large as possible, i.e., a high working capacity under these conditions is required. Recent studies by Yong and coworkers have shown that pressure-swing adsorption (PSA) units using porous solids constitute a competitive technology even with the low cost amine scrubbing technology [14]. An optimization of the working capacity for CO₂ capture using porous solids requires a perfectly designed porous structure and, consequently, a perfect knowledge of the role

of the porous structure in the adsorption process at low and high pressures. Previous studies described in the literature on structure-adsorption relationships using carbide-derived carbons have anticipated that the microporous structure on carbon materials is critical for defining the adsorption capacity both at sub-atmospheric (0.01 MPa) and atmospheric pressure (0.1 MPa) [5]. Taking into account that PSA units work at high pressure, herein we extend these analyses to high pressure CO₂ adsorption processes in order to give a clear image of the critical porous structure under these conditions.

Petroleum residue based activated carbons have been recently proposed in the literature as excellent sorbents for CO₂ capture both at atmospheric (0.1 MPa) and high pressure (4.5 MPa) [6,7]. Petroleum residues go through a liquid-crystal phase state (mesophase) when heat treated and they may become graphite after a high temperature treatment (above 2273 K). However, if the pyrolysis treatment is carried out at a lower temperature (~673-773 K), mesophase pitches with particular characteristics can be obtained [15]. Furthermore, if the activation conditions are well-defined (activating agent, activating agent/carbon precursor ratio, activation temperature and so on), activated carbons with a wide range of porosity can be obtained [6,7]. These materials combine a highly developed micro- and mesoporous structure which provides them with a high adsorption capacity, a high selectivity towards CO₂ and an easy regeneration under mild conditions. Consequently, these materials can be envisaged as excellent candidates for the aforementioned evaluation.

2. Experimental Section

2.1 Mesophase pitch preparation

Two different mesophase pitches were prepared using an aliphatic petroleum residue, vacuum residue (VR), as a raw material. Pyrolysis conditions were selected to achieve (a) a pitch with low mesophase content (5%) and (b) a pitch with high mesophase content (93%). Sample VR5 was obtained by carbonization of the petroleum residue at 693 K for 3h. Sample VR93 was obtained at a higher carbonization temperature, 733 K, using a soak time of 1.5 h. The pyrolysis was carried out in a laboratory-scale pilot plant using 350 g of residue. The resultant mesophase pitch was milled in a ball mill until a particle size diameter lower than 500 μm is reached.

2.2 Activated carbons preparation

Two series of activated carbons, as a powder, have been prepared starting from the VR mesophase pitches and using KOH as activating agent. The KOH/mesophase pitch ratio has been modified from 1:1 to 4:1 (wt.%/wt.%). After a physical mixing in a ball milling, samples were heat treated in a horizontal furnace at 1073 K for 2h under nitrogen atmosphere (100 ml/min), using a heating rate of 5 K/min. The final materials were washed first with a 10% HCl solution to remove potassium and secondly with distilled water using a Soxhlet apparatus until pH= 7 and absence of chloride ions. The absence of chloride ions in the final solution was checked using silver nitrate. Finally, samples were dried overnight at 283 K. Samples were labeled including the nature of the petroleum residue, the mesophase content and the hydroxide/precursor ratio (e.g., VR5-1:1 indicates petroleum residue VR with 5 % mesophase, activated with a KOH: precursor ratio 1:1).

2.3 Samples characterization

The textural properties of the synthesized activated carbons were analyzed using gas adsorption, i.e., nitrogen at 77.4 K and carbon dioxide at 273 K. Gas adsorption measurements were performed in a home-made fully automated manometric equipment designed and constructed by the Advanced Materials Group (LMA), now commercialized as N₂Gsorb-6 (Gas to Materials Technologies; www.g2mtech.com). Before any adsorption experiment, samples were degassed under UHV conditions (10^{-3} Pa) for 4h at 523 K. N₂ adsorption data at 77.4 K were used to determine the total pore volume (V_t) at a relative pressure around 0.95, the specific surface area, after application of the BET equation, and the total micropore volume (V_0), after application of the Dubinin-Radushkevich (DR) equation. The difference between the V_t and V_0 is considered the mesopores volume (V_{meso}). CO₂ adsorption data at 273 K were used to determine the narrow micropore volume (V_n), after application of the DR equation. Pore size distribution was calculating by applying Quenched Solid Density Functional Theory (QSDFT) analysis to the nitrogen adsorption data. QSDFT analysis applied to the N₂ and NLDFT applied to CO₂ adsorption data were also used to estimate the volume of specific pores (NLDFT_{CO₂} for pores below 1 nm and QSDFT_{N₂} for pores below 3 nm).

2.4 High-pressure adsorption measurements

The CO₂ adsorption capacity was measured at 298 K and up to a final pressure of 4.5 MPa. Before any adsorption experiment, samples were degassed at 523 K for 4h. High-pressure analyses were performed in a home-made fully automated manometric equipment designed and constructed by the Advanced Materials group (LMA), now commercialized as iSorbHP by Quantachrome Instruments.

3. Results and discussion

Figure 1 shows the nitrogen adsorption/desorption isotherms at 77.4 K for VR-5 samples prepared using a KOH/precursor ratio ranging from 1:1 to 4:1.

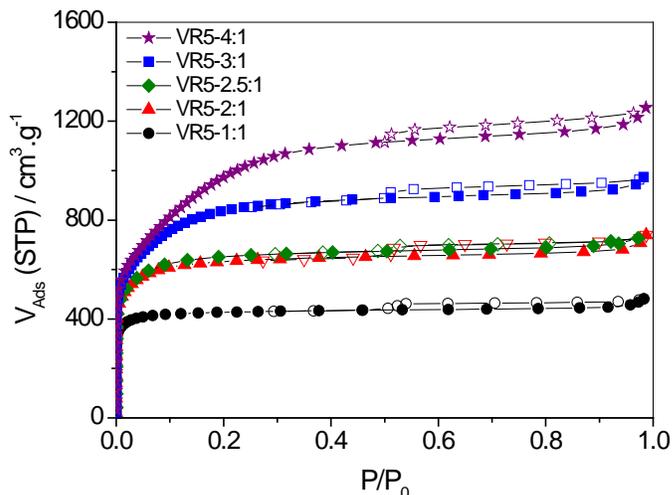


Figure 1. N₂ adsorption/desorption isotherms for samples VR-5 at 77.4 K.

N₂ isotherms shown in Figure 1 clearly reflect the important effect of the KOH/mesophase pitch ratio in the development of the porosity. Samples with a low ratio (e.g., 1:1) exhibit a type I isotherm with a narrow knee at low relative pressures, thus reflecting the presence of a narrow micropore size distribution. An increase in the amount of activating agent gives rise to the development of new micropores, i.e., an increase in the amount of nitrogen adsorbed at low relative pressures, together with the widening of the existing ones, i.e., larger micropores and mesopores are created. A similar development of porosity has been observed for sample VR-93 (see figure S1 in the supplementary content). The pore size distribution calculated after application of the QSDFT method (Figure S2, slit-shape pore; equilibrium model) clearly confirms the presence of narrow micropores (< 1 nm) on samples with a low activation degree whereas large micropores (> 1.5 nm) and small mesopores (2.0-3.0 nm) are developed for

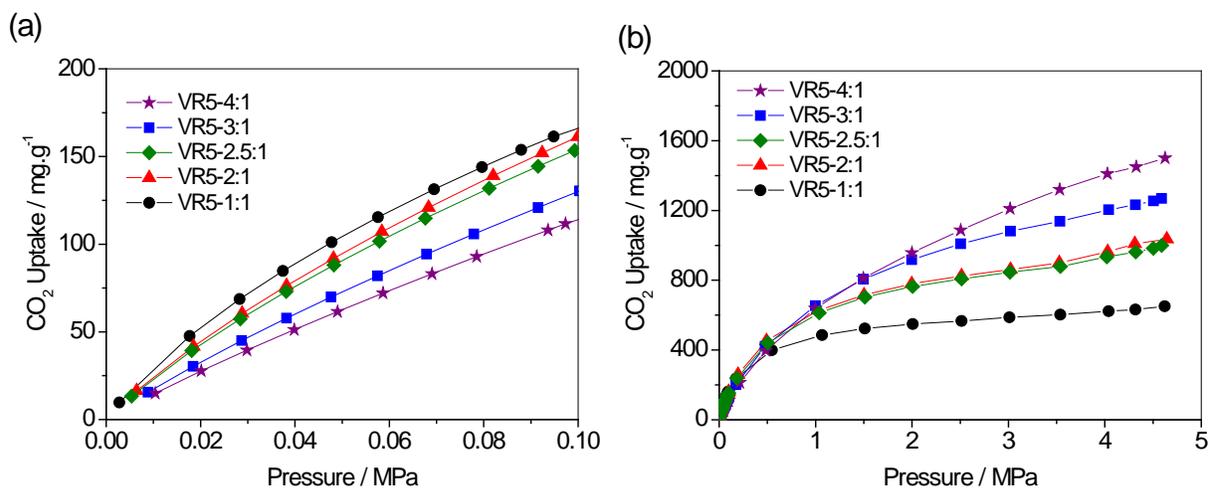
samples prepared using a larger KOH/precursor ratio. Table 1 contains a compilation of the textural parameters obtained from the N₂ and CO₂ physisorption measurements at atmospheric pressure and 77.4 K and 273 K, respectively. The “apparent” BET surface area of the synthesized carbons range from 1500 to 3600 m²/g, depending on the mesophase content and the activation degree achieved. A comparison of the total micropore volume (V₀) and the volume of narrow micropores (V_{CO2}), obtained after application of the Dubinin-Radushkevich equation, shows that synthesized carbons range from pure carbon molecular sieves (V_n ≥ V₀) , with a narrow pore size distribution, to samples with a broad pore size distribution (V_n < V₀) [16]. Interestingly, large activation degrees (above 2.5) gives rise to a widening of the porous structure, i.e., the development of wide micropores (an increase in V₀) and small mesopores (an increase in V_{meso}) together with the disappearance of narrow micropores/constrictions (a decrease in V_n).

Table 1. Textural characteristics for samples VR-5 and VR-93 activated using different KOH: precursor ratios.

Sample	S _{BET} m ² ·g ⁻¹	V _t cm ³ ·g ⁻¹	V ₀ cm ³ ·g ⁻¹	V _{meso} cm ³ ·g ⁻¹	V _n cm ³ ·g ⁻¹	Yield* wt%
VR5-1:1	1770	0.73	0.70	0.03	0.67	57
VR5-2:1	2430	1.05	0.91	0.15	0.80	57
VR5-2.5:1	2455	1.09	0.96	0.13	0.84	45
VR5-3:1	3125	1.45	1.05	0.40	0.73	49
VR5-4:1	3575	1.83	1.22	0.61	0.76	42
VR93-1:1	1550	0.64	0.61	0.03	0.64	64
VR93-2:1	2140	0.90	0.80	0.10	0.78	56
VR93-2.5:1	2770	1.22	0.99	0.23	0.84	55
VR93-3:1	3165	1.60	1.03	0.58	0.77	37
VR93-4:1	3410	1.77	1.06	0.71	0.75	44

*Yiel (wt%)= (dry carbon mass/ precursor mass)*100

In summary, the presence of a wide variety of samples covering a wide range of well-defined pores, from samples exhibiting exclusively narrow micropores to samples containing both micropores and small mesopores, will ensure an accurate analysis of the effect of the porous structure in CO₂ capture both at atmospheric (0.1 MPa) and high pressure (4.5 MPa).



capacity at atmospheric pressure, larger micropores and also small mesopores seem to govern the adsorption at high pressure. This observation is in coherence with the fundamentals of the Dubinin's micropore filling theory. At atmospheric pressure mainly narrow micropores, exhibiting a high adsorption potential, adsorb CO_2 whereas higher pressures, i.e., higher fugacities, are required for pore filling in wide micropores [17]. In this sense, the absence of these wide micropores/small mesopores in sample VR5-1:1 will explain the near saturation achieved at pressures above 1.0 MPa, i.e., the porosity present on this sample (mainly narrow micropores) is already filled with CO_2 at 1.0 MPa (see Figure 2b).

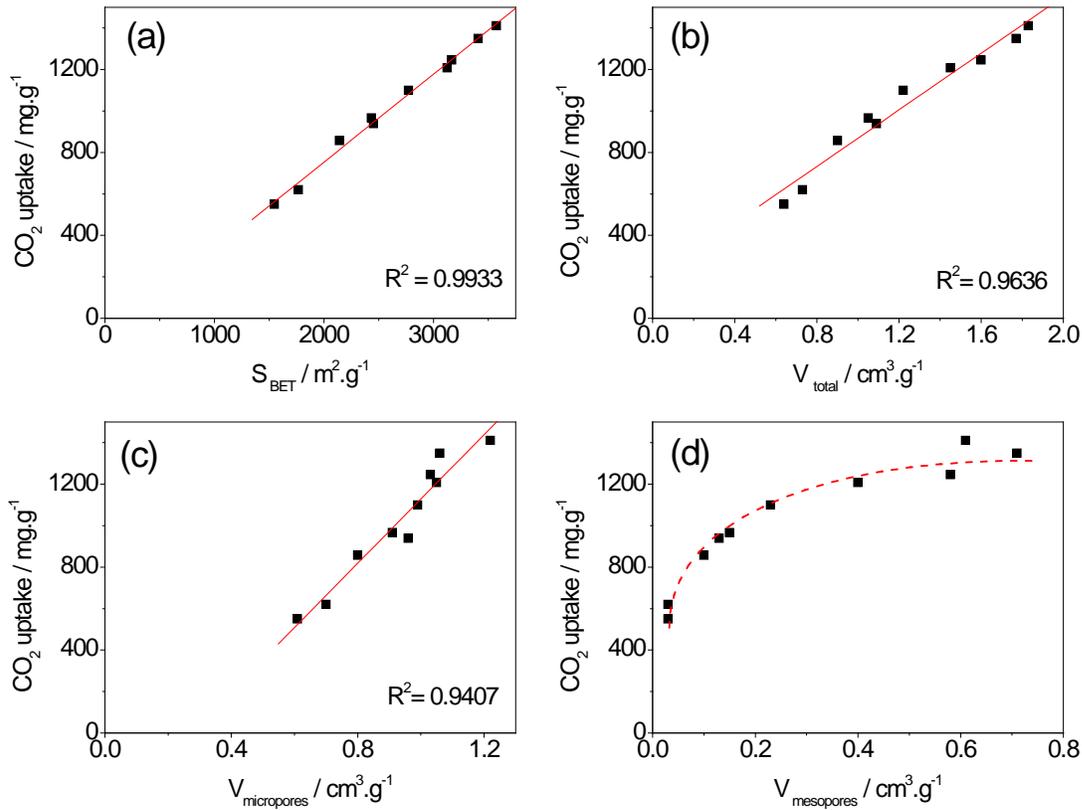


Figure 3. CO_2 uptake at 4.5 MPa (298 K) as a function of (a) BET surface area, (b) total pore volume, (c) total volume of micropores and (d) mesopore volume.

To get a better understanding of the textural parameters defining the sorption behavior at high pressure, Figure 3 shows the evolution of the gravimetric adsorption capacity (mg/g) at 298 K and 4.5 MPa (relative pressure $p/p_0 = 0.73$) for both series of samples as a function of the different textural parameters. As it can be observed, there is a certain correlation between the adsorption capacity under these conditions and the total pore volume (see Figure 3b), although with a poor coefficient of determination ($R^2=0.9636$). A better correlation is observed with the “apparent” surface area ($R^2= 0.9933$), whereas any correlation with the mesopore volume fails. Interestingly, the presence of a plateau in the amount adsorbed for samples with a large mesopore volume (samples activated above a KOH/precursor ratio ≥ 2.5 in Figure 3d) demonstrate that mesopores (mainly those above 3.0 nm, according to the QSDFT data) do not govern the adsorption behavior at high pressure (4.5 MPa). This observation suggest that 4.5 MPa is still not enough to fill mesopores above 3.0 nm, i.e., the adsorption potential within these pores is not enough to favor capillary condensation. Interestingly, for the higher coefficient of determination (Figure 3a), the linear function has an y-axis intersect of approximately zero as corresponds to a CO₂ adsorption capacity of 0 mg/g when there is no surface area.

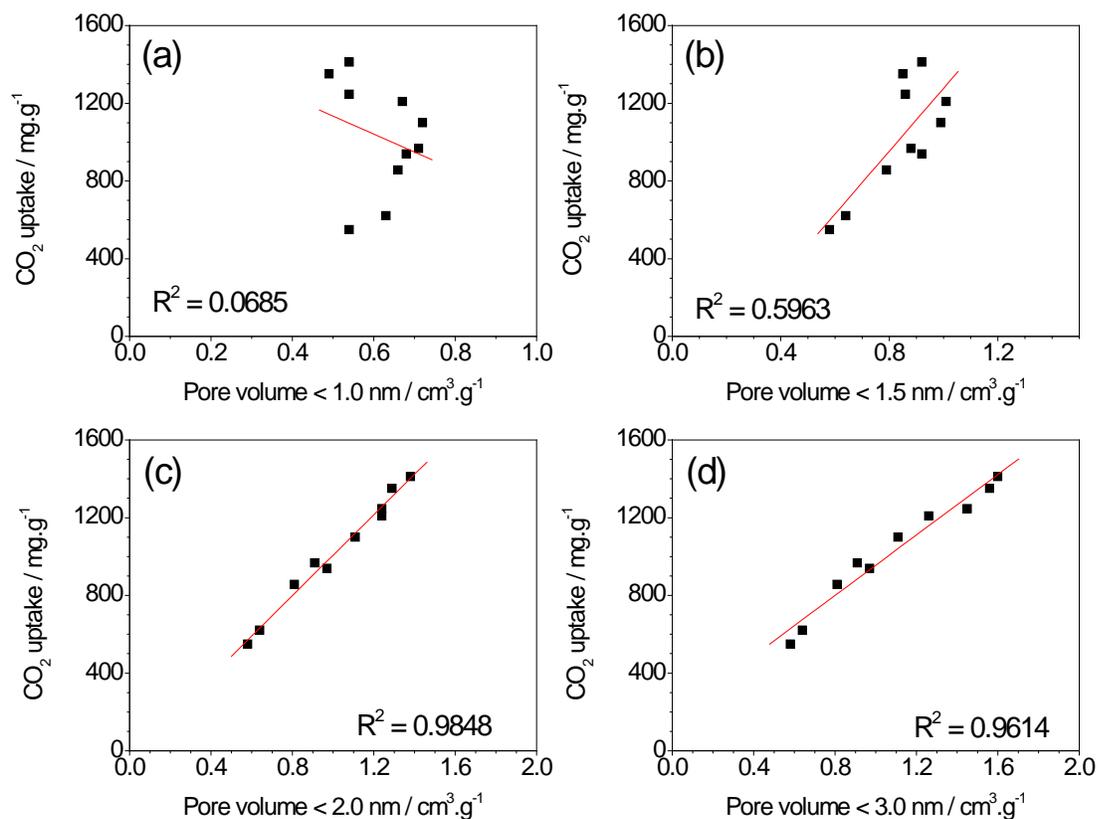


Figure 4. CO₂ uptake at 4.5 MPa (298 K) as a function of the volume of pores below (a) 1.0 nm, (b) 1.5 nm, (c) 2.0 nm and (d) 3.0 nm.

A more accurate analysis of the effect of the porous structure can be obtained by comparison of the total CO₂ uptake at high pressure with the volume of specific pores smaller than a certain size. In this sense, Figure 4 shows the correlation between the adsorption capacity (mg/g) and the volume of pores smaller than 3.0 nm, 2.0 nm, 1.5 nm and 1.0 nm, as determined by the QSDFIT method. According to Figure 4, no clear correlation can be achieved between the amount of CO₂ adsorbed and the volume of pores smaller than 1.0 nm. As expected, larger coefficients of determination are obtained when considering the volume of pores below 2.0 nm, the correlation slightly worsening for larger pores (< 3.0 nm). Furthermore, the correlation with the volume of

pores smaller than 2.0 nm has an y-axis intersection of approximately zero which is physically meaningful.

Consequently, these values demonstrate that the CO₂ uptake at high pressures (4.5 MPa) using carbon materials is mainly governed by the total volume of micropores (pores smaller than 2.0 nm) although a certain contribution from small mesopores (pores below 3.0 nm) cannot be ruled out. Interestingly, the same data analysis applied to the atmospheric pressure (0.1 MPa) CO₂ adsorption measurements (Figure S3) reflect a better correlation with the volume of pores smaller than 0.6 nm, in close agreement with previous analysis described in the literature [5-7, 18].

Figure 5 plots the coefficient of determination between the CO₂ uptake at a certain pressure (between 1.0 MPa and 4.5 MPa) and the cumulative pore volume of pores smaller or equal to a certain pore diameter (between 1.0 nm and 4.0 nm). High correlation coefficients indicate a strong correlation between the adsorption capacity of CO₂ at a certain pressure and the pore volume of pores equal or smaller than a certain diameter that contributes the most. In agreement with previous data from Figure 4, at low pressures (1.0 MPa) wide micropores *ca.* 1.5 nm contribute the most to the total CO₂ uptake while larger pores 2.0-3.0 nm are required for high-pressure applications (4.0-4.5 MPa).

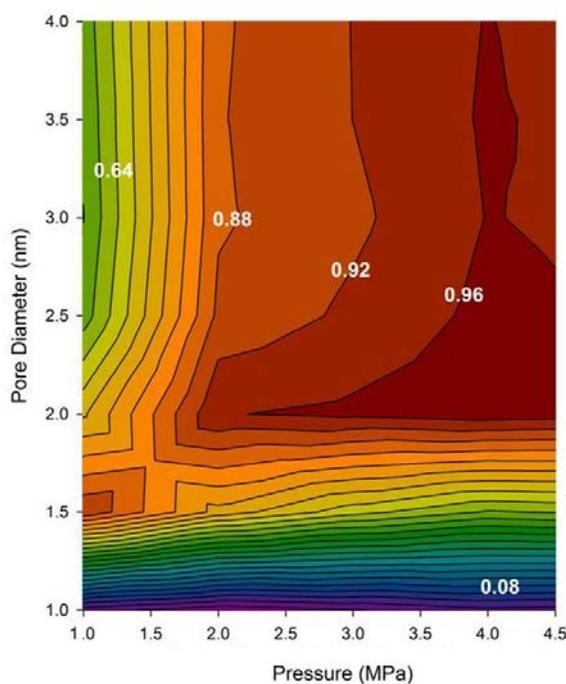


Figure 5. Coefficient of determination for CO₂ uptake between 1 MPa and 45 MPa (x-axis) and the volume of pores smaller to threshold size (y-axis).

4. Conclusion

In summary, these results show that the textural properties required for CO₂ capture highly depend on the final pressure used, i.e., depending on the final emission point source and the sorption technology used (pressure-swing adsorption-PSA, vacuum-swing adsorption-VSA, and so on). A large volume of narrow micropores (below 0.6 nm) is required for applications concerning atmospheric pressure whereas larger pores (below 2.0-3.0 nm) govern the adsorption capacity for high pressure applications. Considering a final application of the porous sorbent on a pressure-swing adsorption unit at high pressure (~4.5 MPa), an optimum design of the carbon material for CO₂ capture will require a high volume of large micropores/small mesopores,

whereas the narrow micropore volume must be kept to a minimum, i.e., V_0/V_n ratio must be maximum. In this sense, sample VR-5 with a 4:1 KOH/precursor ratio could be a good candidate for this application due to the large V_0/V_n ratio ~ 2.4 and, consequently, the large working capacity (~ 1388 mg/g delivery between 4.5 MPa and 0.1 MPa) when using pure CO_2 . Last but not least, it is important to highlight that this study constitutes a guideline for the design of porous carbons materials to remove CO_2 at atmospheric and high pressure, although the final design will also be defined by i) the selected sorption technology, ii) the selected sorption temperature [19], iii) the CO_2 composition in the effluent stream and iv) the final CO_2 pressure achieved, in case of PSA units.

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