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## Novel porous carbons derived from coal tar rejects

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1 Novel Porous Carbons derived from Coal Tar  
2 Rejects: Assessment of the Role of Pore Texture in  
3 CO<sub>2</sub> Capture under Realistic Post-combustion  
4 Operating Temperatures

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10

11 ABSTRACT

12 Activated carbons (ACs) are among the most commonly used sorbents for CO<sub>2</sub> capture because of  
13 their high surface areas and micropore volumes, which depend on precursor and activation  
14 methods. In this study, we evaluated different ACs obtained from a low-value fraction of liquid-  
15 derived coal pyrolysis, namely phenolic oil, which was used as gel precursor before carbonization  
16 and KOH activation. CO<sub>2</sub> capture performances were determined at temperatures between 25 and

1 120°C, with CO<sub>2</sub> concentrations ranging from 5 to 90 vol. %. The most efficient sample captured  
2 2.86 mmol of CO<sub>2</sub>/g AC at 25°C and 1 bar, which is a highly competitive capture capacity,  
3 comparable to previously reported values for ACs without any modification/functionalization.  
4 Finally, their thermal stability and cyclability (i.e., for a minimum of six adsorption-desorption  
5 cycles) were evaluated. CO<sub>2</sub> uptake was not affected by desorption temperature after six  
6 adsorption-desorption cycles. Based on the results obtained in this work, the role of the textural  
7 properties into the CO<sub>2</sub> capture at realistic postcombustion temperatures and partial pressures was  
8 elucidated. In particular, we concluded that CO<sub>2</sub> adsorption performance was more related to the  
9 volume of the narrowest pores and to the average pore size than to the surface area.

10 KEYWORDS: Coal tar; Xerogels; Cryogels; Activated carbon; Pore Texture; Post-combustion  
11 CO<sub>2</sub> capture.

12

### 13 **1. Introduction**

14 Atmospheric CO<sub>2</sub> concentration is continuously increasing, reaching values higher than 414 ppm  
15 in June 2019 <sup>1</sup>. To reduce this concentration, one of the key actions agreed is the application of  
16 Carbon Capture and Storage technologies (CCS) according to the report of the  
17 Intergovernmental Panel on Climate Change (IPCC) <sup>2</sup>.

18 Among the various carbon capture technologies, the use of solid adsorbents is becoming more  
19 relevant because of several advantages, such as lower energy requirements during regeneration  
20 and increased stability under corrosive atmospheres, compared to absorption-related processes <sup>3-</sup>  
21 <sup>5</sup>. However, these solids need to meet specific requirements to be considered for adsorption-  
22 based carbon capture processes including: 1) low heat capacity, 2) fast kinetics, 3) high CO<sub>2</sub>

1 capture capacity, 4) thermal and chemical stability, 5) high CO<sub>2</sub> selectivity, 6) long service life,  
2 and 7) low-cost raw materials <sup>6,7</sup>.

3 Various activated carbons (ACs), zeolites, ordered mesoporous silica, metal-organic frameworks  
4 (MOFs) and porous organic polymers (POPs), have been already evaluated for CO<sub>2</sub> physical  
5 adsorption <sup>5,8</sup>, as well as amine-based solids for CO<sub>2</sub> chemical adsorption <sup>7</sup>.

6 Even though amine-based solids present lower heat capacity than liquid absorbents, chemical  
7 adsorption is associated with high costs and low CO<sub>2</sub> capture capacities compared to physical  
8 adsorption <sup>7</sup>. For this reason, an increasing number of studies have focused on using porous  
9 solids for physical adsorption-based processes. Among them, CO<sub>2</sub> adsorption with ACs offers  
10 one the most promising alternatives due to their low cost, high stability after a large number of  
11 cycles, easy production, high surface area, and cheap regeneration after CO<sub>2</sub> capture <sup>9,10</sup>.

12 ACs are produced by physical or chemical activation of carbon precursors, which can be coals <sup>11-</sup>  
13 <sup>13</sup>, various pyrolyzed materials <sup>14-16</sup>, or biomass <sup>17-20</sup>. In any activation process, the ultimate goal is  
14 to increase the textural properties of the material (i.e., surface area and pore volume). Physical  
15 activation requires CO<sub>2</sub> or steam at high temperatures ( $\geq 800^{\circ}\text{C}$ ), while chemical activation  
16 requires impregnation or blending of the precursor with an activating agent (i.e., H<sub>3</sub>PO<sub>4</sub> or KOH,  
17 among others) and heated to lower temperatures than those used for physical activation <sup>5,15</sup>.

18 Wang et al. proved that CO<sub>2</sub> capture capacity is directly proportional to the micropore volume  
19 for ACs having similar BET surface areas, and demonstrated that both high surface area and high  
20 porosity are needed to increase the CO<sub>2</sub> capture on ACs <sup>21</sup>. Lee et al. <sup>8</sup> and Sevilla et al. <sup>22</sup> showed  
21 that the CO<sub>2</sub> capture capacity is directly related to the presence of ultramicropores (pore diameter  
22  $< 0.7$  nm) and supermicropores (pore diameter 0.7-2 nm). Furthermore, Lee et al. also concluded

1 that the pore size distribution (PSD) of micropores narrower than 0.7 nm has a high influence on  
2 the CO<sub>2</sub> capture capacity <sup>8</sup>, in agreement with Marco-Lozar et al. who showed that the CO<sub>2</sub>  
3 capture takes place in the ultramicropores at low partial pressures and at 25°C <sup>23</sup>.

4 Carbon gels are known as materials with a highly developed porous texture <sup>24</sup>, and are usually  
5 produced by the pyrolysis of organic and dried resorcinol-formaldehyde (RF) <sup>24</sup> or phenol-  
6 furfural <sup>25</sup> gels. Once the pyrolysis of the gel is controlled, it is possible to obtain highly  
7 microporous carbons, essentially comprising pores narrower than 1.5 nm. Robertson and  
8 Mokaya thus obtained ACs from RF carbon gels with micropores of size mainly between 0.8 and  
9 1.2 nm, and measured CO<sub>2</sub> adsorption capacities of 2.7 to 3 mmol/g at 25°C <sup>26</sup>. However,  
10 resorcinol and phenol are expensive and this has a direct impact on the final cost of carbon gels.  
11 Hence, new low-cost precursors should be targeted and studied to obtain highly microporous  
12 activated carbons for CO<sub>2</sub> capture applications. Furthermore, no assessment of the role of the  
13 ACs pore texture on the CO<sub>2</sub> adsorption process under more realistic operational capture  
14 conditions has been reported and could provide very helpful insights for future developments  
15 targeting improved AC materials.

16 In this study, we evaluated the CO<sub>2</sub> capture performance, at realistic operating temperatures, of  
17 carbon xerogels and cryogels based on low-value phenolic oil derived from coal pyrolysis.  
18 Furthermore, CO<sub>2</sub> adsorption studies were conducted at CO<sub>2</sub> concentrations (5 – 30 vol. %)   
19 representative of different flue gas streams from power plants or industries <sup>27,28</sup>. Selected ACs  
20 were submitted to a cyclic study to evaluate the effect of the regeneration temperature on the  
21 carbon stability and on their CO<sub>2</sub> uptake over several adsorption/desorption cycles. Finally, CO<sub>2</sub>  
22 capture capacities at different temperatures were correlated with the pore texture, and clear  
23 relationships were obtained.

## 1 **2. Experimental**

### 2 **2.1 Activated carbons**

#### 3 *2.1.1 Synthesis*

4 Three activated carbon (AC) series: XiPPO, XPPO and CWPO were prepared as indicated in  
5 Table 1. The first letter of the materials label stands for the type of gel (i.e., X for xerogel and C  
6 for cryogel). The organic gels used as AC precursors were prepared by dissolving phenolic oil  
7 (PO) and formaldehyde either in isopropanol (i) for XiPPO, in n-propanol (-) for XPPO, or in  
8 water (W) for CWPO series of gels. Acidic catalysis, using para-toluenesulphonic acid, was used  
9 in the synthesis of the XiPPO series, and basic catalysis, using NaOH, was used in the synthesis  
10 of the XPPO and CWPO ones.

11 After gelation in their respective solvent, the resultant wet hydrogels or alcogels were dried by  
12 convective heat exchange (85°C, 12h) in the case of XiPPO and XPPO materials, and by freeze-  
13 drying in the case of the CWPO series. Prior to the freeze-drying process of the CWPO  
14 hydrogels, water was exchanged thoroughly by tert-butanol (35°C, one exchange per day for 3  
15 days).

16 **Table 1.** Preparation methodology of the samples.

Series of samples	XiPPO	XPPO	CWPO
Type of gel	Xerogel	Xerogel	Cryogel
Organic precursor	Phenolic oil	Phenolic oil	Phenolic oil
Solvent used	isopropanol	n-propanol	Water
Type of Catalysis	Acidic	Basic	Basic
Activation agent	KOH	KOH	KOH

17

1 The dried gels were then ground and mixed with KOH, using KOH/dried gel mass ratios of 3, 4  
2 and 5 for XiPPO, of 1, 2, 3, 4 and 5 for XPPO, and of 1, 2, 3 and 4 for the CWPO series.  
3 Chemical activation of the dried gel was next performed by heating the KOH/dried gel mixture  
4 up to 750°C, and maintaining the final temperature for 1h in nitrogen flow (100 mL/min). Thus,  
5 pyrolysis and chemical activation were carried out in one single step. The obtained ACs were  
6 finally washed with 1 mol/L HCl, subsequently washed with distilled water in a Soxhlet  
7 extractor for 5 days, and dried in a ventilated oven (105°C, 12h). The ACs were labelled by  
8 adding the KOH/gel mass ratio (i.e., from 1 to 5) to the name of their gel precursor. Thus, for  
9 instance, XiPPO\_3 is an activated carbon prepared from a xerogel synthesized with isopropanol  
10 as solvent, dried by convection, ground and activated with a KOH/gel mass ratio equal to 3.  
11 For the sake of comparison, two well-known commercial ACs from Kansai Coke and Chemicals  
12 Co. Ltd (i.e., MSP-20X and MSC-30) were also characterized and tested as CO<sub>2</sub> adsorbents.

### 13 *2.1.2 Textural characterisation*

14 Textural characterization was performed by nitrogen and carbon dioxide adsorption at -196°C  
15 and 0°C, respectively, using an automatic adsorption apparatus (ASAP 2020, Micromeritics).  
16 Adsorption data were treated using the Microactive® software from Micromeritics. Prior to gas  
17 adsorption, all samples were degassed under secondary vacuum at 110°C until the pressure  
18 stabilized at about 0.2-0.4 mPa for more than 48h. Further degassing was carried out at the  
19 measuring port for at least 6h. Cool and warm volumes were determined after nitrogen or carbon  
20 dioxide adsorption to avoid helium entrapment in the narrowest pores.  
21 The BET area calculated by the Brunauer-Emmett-Teller (BET) method<sup>29</sup>,  $A_{\text{BET}}$ , was obtained  
22 by applying the BET equation in the appropriate range of relative pressures<sup>30</sup>.  $A_{\text{BET}}$  was only

1 determined for comparing our results with those reported in the open literature, and not used here  
2 for further calculation because of the well-known overestimation of surface area when applying  
3 the BET equation to materials having highly developed supermicroporosity. Micropore volumes  
4 were obtained using the Dubinin-Radushkevich (DR) equation <sup>31</sup>, and they are again only given  
5 here for comparison purposes with the literature <sup>32,33</sup>. The DR method was applied both to N<sub>2</sub> (-  
6 196°C) and to CO<sub>2</sub> (0°C) adsorption isotherms to obtain  $V_{DR,N_2}$  and  $V_{DR,CO_2}$ , respectively. The  
7 pore size distributions (PSDs) were obtained by using the non-local density functional theory  
8 (NLDFT) from the Solution of Adsorption Integral Equation Using Splines (SAIEUS®) routine.  
9 This method has the advantage of combining both CO<sub>2</sub> and N<sub>2</sub> adsorption data to get more  
10 accurate PSDs <sup>34</sup>. Moreover, it allows fitting the PSDs with a spline model, avoiding the usual  
11 singularities of the classical DFT model. The average micropore diameter was calculated using  
12 this PSD,  $L_{0,NLDFT}$ , and also the by applying the DR method together with the Stoeckli equation  
13 <sup>35</sup>,  $L_{0,DR}$ . The mesopore volume was calculated by subtracting the micropore volume obtained  
14 from the NLDFT method,  $V_{mic,NLDFT}$ , to the total pore volume directly measured by N<sub>2</sub> adsorption  
15 at a relative pressure of 0.99. The NLDFT method was also used to determine the surface area,  
16  $S_{NLDFT}$ , by integrating the PSDs over the whole range of pore sizes <sup>36</sup>. Moreover, the pore  
17 volumes corresponding to pore widths below 0.5 nm ( $V_{L<0.5}$ ), below 0.7 nm ( $V_{L<0.7}$ ), between 0.7  
18 and 2 nm ( $V_{0.7<L<2}$ ), below 2 nm ( $V_{L<2}$ ) and between 2 and 50 nm ( $V_{2<L<50}$ ), were also determined  
19 by integrating the PSD over the relevant pore diameters.

## 20 **2.2 CO<sub>2</sub> capture evaluation**

21 The CO<sub>2</sub> capture capacities were determined using a TA Q500 thermogravimetric analyzer (TA  
22 Instruments). In all experiments, a platinum pan was filled with approximately 8 mg of the AC to



1 be tested. The pan was heated up to 120°C and kept at this temperature for 30 minutes under N<sub>2</sub>  
2 flow (100 mL/min) to eliminate pre-adsorbed gases or water from the AC surface. After drying,  
3 the desired temperature (25, 50, 75, 100, or 120°C) was reached and the sample was kept under  
4 nitrogen flow until constant weight. Once the steady state was reached, the N<sub>2</sub> flow was switched  
5 to a total of 100 mL/min flow with a 90 vol. % of CO<sub>2</sub> in N<sub>2</sub>, and the temperature was maintained  
6 for 30 minutes to ensure that the total CO<sub>2</sub> capture capacity was achieved. CO<sub>2</sub> adsorption at  
7 25°C was repeated at least 3 times to evaluate the deviation and repeatability of the capture  
8 capacity for each AC, and the materials presenting the highest CO<sub>2</sub> capacity were selected for  
9 further studies.

10 For the most efficient ACs, the capture capacity at 25°C and at different concentrations of CO<sub>2</sub>,  
11 from 5 to 90 vol. % in N<sub>2</sub>, was evaluated. Low values such as 5, 15, 18 and 25 vol. % are  
12 particularly interesting to mimic the behavior of ACs in the presence of common concentrations  
13 of CO<sub>2</sub> from the combustion of natural gas and pulverized coal <sup>27</sup>. Furthermore, we used the best  
14 sample of the XiPPO series to evaluate the ageing of the AC after six adsorption-desorption  
15 cycles. For this purpose, we carried out adsorption at 25°C using a pure CO<sub>2</sub> flow of 100 mL/min  
16 and, after desorption, the AC was regenerated at different temperatures (i.e., 125, 150, 175 or  
17 200°C). Moreover, a thermal stability study was carried out for each sample for evaluating its  
18 behavior from 25 to 220°C with a heating ramp of 10°C/min under a 100 mL/min flow of inert  
19 atmosphere. Finally, six cycles of adsorption-desorption were done for the best sample selected  
20 out of each family of AC, using 200°C as regeneration temperature.

21

22

### 1 3. Results and discussion

#### 2 3.1 Porous texture of the ACs

3 Table 2 shows the main textural parameters of the ACs considered in this study. All were  
 4 essentially microporous, with micropore fractions ranging from 60 to 95 %, and with a well-  
 5 developed  $A_{\text{BET}}$ , from 1356 to 3305  $\text{m}^2/\text{g}$ .  $S_{\text{NLDFT}}$  gives a more realistic determination of the  
 6 surface area (having in mind that the maximum surface area of an AC is 2630  $\text{m}^2/\text{g}$  <sup>37</sup>), and it  
 7 indeed varied from 1436 to 2216  $\text{m}^2/\text{g}$ . Average micropore size,  $L_{0,\text{NLDFT}}$ , ranged from 0.7 to 1.3  
 8 nm. The two commercial ACs from Kansai, labelled according to their commercial  
 9 denomination, MSC-30 and MSP-20X, had porous textures that compared very well with those  
 10 of the present experimental activated carbon gels, whether surface areas or pore volumes are  
 11 considered. This is an important result, since it should be recalled that the present materials were  
 12 derived from a poorly valorized industrial waste: phenolic oil.

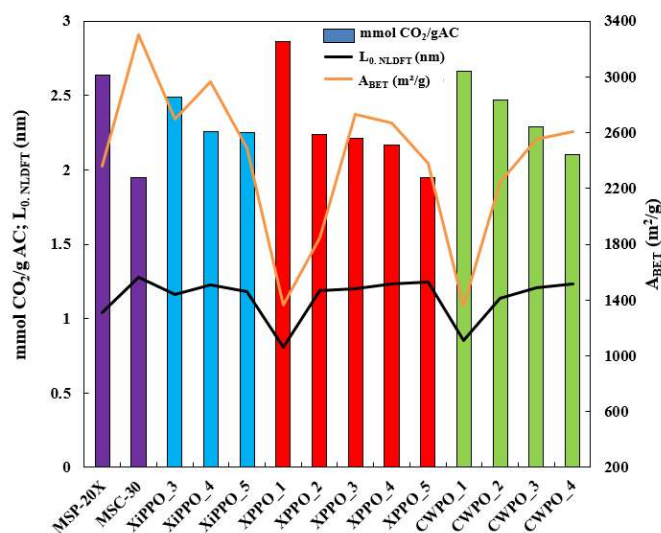
13 **Table 2.** Textural properties of all activated carbons.

Sample	$A_{\text{BET}}$	$S_{\text{NLDFT}}$	$V_{\text{tot}}$	$V_{L<0.5}$	$V_{0.5<L<0.7}$	$V_{L<0.7}$	$V_{0.7<L<2}$	$V_{2<L<50}$	$V_{\text{DR, N}_2/\text{CO}_2}$	$L_{0,\text{NLDFT}}$	$L_{0,\text{DR}} (\text{N}_2)$
	$\text{m}^2/\text{g}$	$\text{m}^2/\text{g}$	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$	$\text{cm}^3/\text{g}$	nm	nm
MSP-20X	2363	2007	0.93	0.02	0.17	0.19	0.69	0.05	0.83/0.42	1.04	0.96
MSC-30	3305	2216	1.60	0.00	0.04	0.04	0.91	0.64	1.02/0.37	1.28	1.29
XiPPO_3	2694	2086	1.15	0.01	0.14	0.15	0.80	0.19	0.90/0.44	1.16	1.21
XiPPO_4	2967	2133	1.34	0.01	0.10	0.11	0.85	0.38	0.94/0.41	1.23	1.25
XiPPO_5	2494	1913	1.11	0.02	0.08	0.10	0.76	0.25	0.83/0.47	1.18	1.24
XPPO_1	1364	1494	0.56	0.03	0.25	0.28	0.25	0.03	0.52/0.53	0.81	0.72
XPPO_2	1848	1943	1.10	0.02	0.13	0.15	0.73	0.22	0.82/0.39	1.19	1.25
XPPO_3	2729	2036	1.23	0.02	0.09	0.10	0.81	0.32	0.90/0.46	1.20	1.27
XPPO_4	2673	1964	1.27	0.02	0.07	0.10	0.75	0.42	0.85/0.36	1.23	1.30
XPPO_5	2383	1713	1.14	0.01	0.06	0.08	0.67	0.39	0.76/0.39	1.25	1.33
CWPO_1	1356	1436	0.56	0.03	0.22	0.25	0.27	0.04	0.51/0.41	0.85	0.80
CWPO_2	2245	1907	0.99	0.02	0.15	0.17	0.69	0.13	0.79/0.43	1.14	1.15
CWPO_3	2551	2039	1.21	0.02	0.11	0.13	0.79	0.28	0.87/0.42	1.21	1.20
CWPO_4	2607	2027	1.30	0.02	0.09	0.11	0.77	0.42	0.87/0.39	1.24	1.24

## 1 3.2 CO<sub>2</sub> capture capacities at 25°C

### 2 3.2.1 General trends

3 Figure 1 shows the CO<sub>2</sub> capture capacity, in mmol of CO<sub>2</sub> per gram of adsorbent, of each AC  
4 measured at 25°C. The best samples of each series were XPPO\_1 > CWPO\_1 > MSP-20X >  
5 XiPPO\_3. Table S1 shows the average CO<sub>2</sub> capture capacity of all samples after three  
6 repetitions. The deviation in the CO<sub>2</sub> adsorption measurement was calculated for all samples, and  
7 the CO<sub>2</sub> capture capacities were very repeatable, with a relative error of less than 3%.  
8 XPPO\_1 had the highest CO<sub>2</sub> capture out of all samples, 2.86 mmol CO<sub>2</sub>/g, followed by  
9 CWPO\_1, 2.66 mmol CO<sub>2</sub>/g. In the XPPO series, the XPPO\_1 presented a lower A<sub>BET</sub> than the  
10 rest, but a much higher fraction of micropores (> 90 %) as well as a higher volume of narrow  
11 pores (V<sub>DR</sub>). These values are comparable with previous work evaluating the use of asphalt as  
12 precursor of activated carbons<sup>38</sup>.



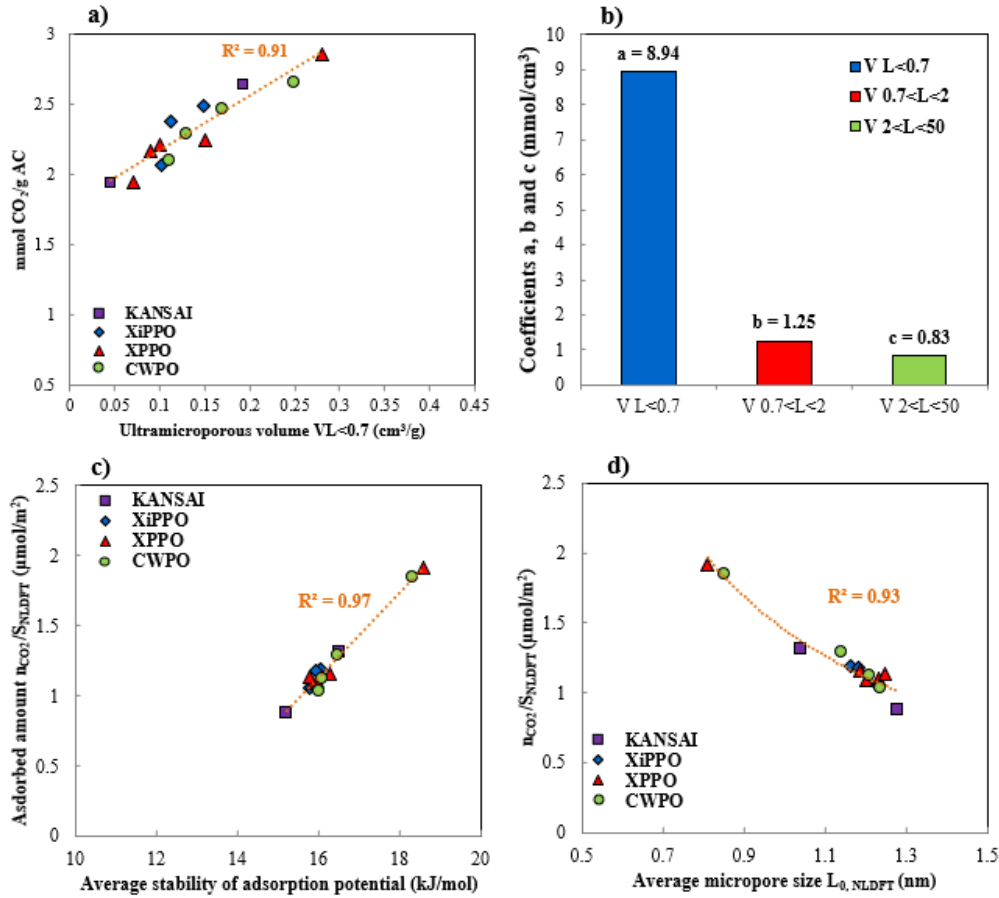
13  
14 **Figure 1.** Average micropore size L<sub>0,NLDFT</sub> (black line), A<sub>BET</sub> (yellow line) and CO<sub>2</sub> capture  
15 capacity (mmol/g AC) of each activated carbon. (Purple for KANSAI, blue for XiPPO, red for  
16 XPPO group and green for CWPO).

1 The CO<sub>2</sub> capture capacity of samples XPPO\_2, XPPO\_3 and XPPO\_4 slightly decreased as the  
2 xerogel/KOH mass ratio increased because the micropore volume fraction decreased, which  
3 implied a lower CO<sub>2</sub> capture capacity. The same trend was observed for the XiPPO samples,  
4 XiPPO\_3 presenting the highest CO<sub>2</sub> capture capacity and XiPPO\_4 and XiPPO\_5 having similar  
5 CO<sub>2</sub> capture capacities, with different textural characteristics. The latter clearly implies that CO<sub>2</sub>  
6 capture can be maintained even if the micropore volume decreases, as long as the total pore volume  
7 of the activated carbons increases sufficiently because CO<sub>2</sub> capture is due to both adsorption and  
8 pore filling.

9 Otherwise, for the CWPO and Kansai samples, a clear trend could be observed, as the decrease  
10 in CO<sub>2</sub> capture capacity appeared constant as the degree of activation increased (related to the  
11 cryogel/KOH ratio in the case of CWPO). In both families of materials, the samples that were  
12 more activated had an increase of surface area but that was not enough to compensate the  
13 decrease of CO<sub>2</sub> capture capacity, related to the correspondingly lower microporous fraction and  
14 micropore volume. MSP-20X and MSC-30 indeed had microporous fractions of 96.80% and  
15 59.83 %, respectively, and surface areas of 2363 m<sup>2</sup>/g and 3305 m<sup>2</sup>/g, respectively.

16 Finally, comparing in all cases the best samples from each family, it was observed that the  
17 samples with the highest  $V_{0.5 < L < 0.7}$  and the lowest  $L_{0, NLDFT}$  were the ones with the highest CO<sub>2</sub>  
18 capture capacity.

19 More generally, the adsorption of CO<sub>2</sub> near room temperature and atmospheric pressure is  
20 mainly due to the narrowest micropores. A quite good linear correlation between the  
21 ultramicroporous volume ( $V < 0.7$ ) and the amount adsorbed was indeed found ( $R^2 = 0.89$ ). It  
22 highlights the importance of such narrow pores when a good CO<sub>2</sub> capture under these conditions  
23 is sought (Figure 2a), which corroborates what has been previously reported<sup>14, 39, 40</sup>.



1  
2 **Figure 2.** a) Adsorbed CO<sub>2</sub> amount at 25°C as a function of the ultramicroporous volume. b)  
3 Coefficients of multiple linear regressions for CO<sub>2</sub> adsorption at 25°C. c) Amount adsorbed per  
4 unit of surface area as a function of the average adsorption potential stability (25°C and 1 bar). d)  
5 Same as c) but versus L<sub>0,NLDFT</sub>. The dotted lines are just guides for the eye.

### 6 3.2.2 Pore size effect: Multiple linear regression

7 In order to highlight the relative importance of pore size, some authors suggested to perform a  
8 multiple linear regression taking into account the pore volumes for each class of pores (V<sub><0.7</sub>,  
9 V<sub>0.7<L<2</sub> and V<sub>2<L<50</sub>) and the corresponding adsorbed amount of gas, n<sub>ads</sub>(T,P)<sup>41,42</sup>. The equation  
10 of this multiple linear regression takes the following form (eq. 1):

$$11 \quad n_{ads}(T,P) = a(T,P) \cdot V_{L<0.7} + b(T,P) \cdot V_{0.7<L<2} + c(T,P) \cdot V_{2<L<50} \quad (\text{eq. 1})$$

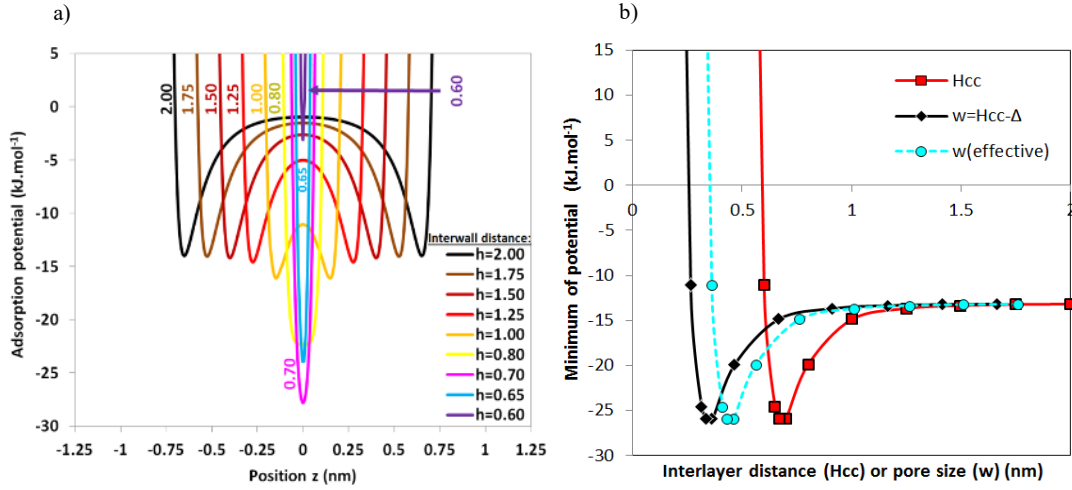
1  $V_{L<0.7}$ ,  $V_{0.7<L<2}$  and  $V_{2<L<50}$  refer to ultramicroporous, supermicroporous and mesoporous  
2 volumes, respectively, whereas a, b and c are real numbers and are the coefficients of the  
3 multiple linear regressions. The fitting algorithm (Levenberg-Marquardt) led to a good  
4 regression ( $R^2 = 0.87$ ), while the p-value was far below 0.05 (i.e.,  $\approx 0$ ). The high value of a  
5 compared to b and c, 8.94, 1.25 and 0.83 mmol/cm<sup>3</sup>, respectively, showed that the ultramicropore  
6 volume is of paramount importance for the adsorption of CO<sub>2</sub> at 25°C (Figure 2b).  
7 This conclusion is further confirmed by the evolution of such coefficients as a function of the  
8 pore size of the corresponding pore classes, which exhibits a dramatic decrease as the pore size  
9 increases. Figure S1 shows the same trend but when the ultramicroporous volume ( $V_{L<0.7}$ ) is  
10 subdivided into two other pore classes ( $V_{L<0.5}$  and  $V_{0.5<L<0.7}$ ). In this case, the coefficients of the  
11 multilinear regression show a dramatic and exponential-like decay as the pore size increases.

### 12 *3.2.3 Adsorption potential*

13 The adsorption potential decreases as the pore size increases due to less overlap of the interaction  
14 potentials exerted by the facing pore walls. Thus, pores having a size less than 0.7 nm and, to a  
15 higher extent, pores narrower than 0.5 nm have a paramount influence on the ability of materials  
16 to adsorb CO<sub>2</sub> at low pressure (1 bar) and at room temperature <sup>14</sup>.

17 These trends are also confirmed by the simple linear regression presented in Figure S2.

18 In order to verify this, the adsorption potential was modelled using the well-known Steele  
19 potential <sup>43</sup>. The parameters selected for the modelling were the same as those used by  
20 Kurniawan et al. for Grand Canonical Monte Carlo modelling of gas adsorption <sup>44</sup>.



1

2 **Figure 3.** Steele adsorption potential for the CO<sub>2</sub> – graphite system (slit pores model).

3 The adsorption potentials, as well as their related minima, are reported in Figure 3, where the  
 4 Steele adsorption potential and the minimum of Steele’s potential as a function of the distance  
 5 between median planes of the graphitic pore walls are represented.

6 This Steele potential <sup>43</sup> is described by the following expression (eq. 2):

$$7 \quad U_{sf}(z) = 2 \cdot \pi \cdot \rho_s \cdot \epsilon_{sf} \cdot \sigma_{sf} \cdot \Delta \cdot \left[ \frac{2}{5} \cdot \left( \frac{\sigma_{sf}}{z} \right)^{10} - \left( \frac{\sigma_{sf}}{z} \right)^4 - \frac{\sigma_{sf}^4}{3 \cdot \Delta (0.61 \Delta + z)^3} \right] \quad (\text{eq. 2})$$

8 where  $\rho_s$  is the number of atoms per unit volume of graphite (114 nm<sup>-3</sup>),  $\Delta$  is the interlayer spacing  
 9 of graphite (0.335 nm),  $z$  is the distance to the graphite wall,  $\epsilon_{sf}$  and  $\sigma_{sf}$  are the Lennard-Jones  
 10 parameters for the CO<sub>2</sub> molecule in interaction with graphite. The values of these parameters were  
 11 obtained using the classical Lorentz-Berthelot combination rules for pure fluid (CO<sub>2</sub>) and solid  
 12 (graphite). For the CO<sub>2</sub>-graphite system and in the case of one-center model, the parameters were  
 13 approximated to  $\epsilon_{sf} / k_b = 82.3165 \text{ K}$  and to  $\sigma_{sf} = 0.35075(\text{nm})$  <sup>44</sup>. Ravikovitch et al.  
 14 previously proposed a similar approximation for DFT modelling <sup>45</sup>. The total adsorption in a  
 15 medium, confined between two walls of a slit pore, reads (eq.3):

$$16 \quad U_{sf-total}(z) = U_{sf}(z) + U_{sf}(H_{cc} - z) \quad (\text{eq. 3})$$

1 where  $H_{cc}$  is the centre-to-centre distance, or distance between the median planes of the graphitic  
2 walls (Å). Then, the potential can be converted from K to kJ/mol using Avogadro and Boltzmann  
3 constants.

4 As used by some authors, an indicator of the strength of the potential is its stability, (s) <sup>46</sup>. The  
5 stability of a potential is defined by the opposite value of the minimum of the potential in a valid  
6 range of  $z$  (eq. 4).

$$7 \quad s(H_{cc}) = -\min(U_{sf-total}(z, H_{cc})) \quad (\text{eq. 4})$$

8 The adsorption potentials, as well as their related minima, are reported in Figures 3. It can be  
9 noticed that the adsorption potential follows a nonlinear evolution as a function of the distance  
10 between the two graphite walls. This adsorption potential decreases down to almost -28 kJ/mol for  
11  $H_{cc} = 0.7$  nm. Such distance corresponds to the space between the median planes of the wall. Given  
12 that the interlayer spacing in graphite is 0.335 nm, this distance corresponds to a real pore size of  
13 0.365 nm for this lowest minimum of potential <sup>46</sup>. Indeed, the effective pore size can be calculated  
14 from the interplanar ( $H_{cc}$ ) distance.

15 The interlayer distance of pure and defect-free graphite ( $\Delta$ ) is equal to 0.335 nm. Thus, the effective  
16 pore size can be calculated using the following formula. (eq. 5):

$$17 \quad w = H_{cc} - \Delta \quad (\text{eq. 5})$$

18 Some authors suggested that this calculation method leads to a poor estimation of the effective  
19 pore size <sup>47,48</sup>. Consequently, they proposed to use another estimation (eq. 6).

$$20 \quad w_{effective} = H_{cc} - (2 \cdot z_0 - \sigma_{ff}) \quad (\text{eq. 6})$$

21 where  $z_0$  has the following expression (eq. 7):

$$22 \quad z_0 = 0.8506 \cdot \sigma_{sf} \quad (\text{eq. 7})$$



1 Above  $H_{cc} \approx 1.00$  nm (i.e., for an effective pore size  $w_{effective}$  equal to 0.76 nm), the minimum  
2 of adsorption potential is almost constant and asymptotically converges to a value close to 13.95  
3 kJ/mol. Thus, in pores wider than ultramicropores, CO<sub>2</sub> is assumed to adsorb in the same way as  
4 that occurring on a flat graphitic surface. According to these observations, based on the  
5 minimum of adsorption potential, the ideal pore size for CO<sub>2</sub> adsorption would be close to 0.45  
6 nm ( $H_{cc} \approx 0.7$  nm). However, in practice, some authors have reported that cooperative  
7 adsorption, occurring in pores wider than 0.6 nm, promotes high densities of adsorbed CO<sub>2</sub> as the  
8 pressure increases <sup>46</sup>.

9 Representing the adsorbed amount per unit of surface area (using  $S_{NLDFT}$ ) as a function of the  
10 average potential stability (Figure 2c) makes the cloud of points much narrower compared to the  
11 case of using the average micropore size (Figure 2d), which is discussed in the next subsection.

#### 12 *3.2.4 Influence of adsorption potential and porous texture on CO<sub>2</sub> capture capacity*

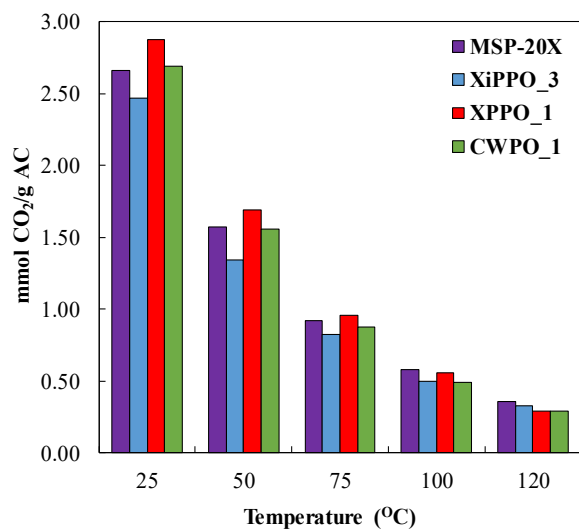
13 The amount of adsorbed CO<sub>2</sub> per surface area ( $\mu\text{mol.m}^{-2}$ ) is presented in Figure 2d versus the  
14 average micropore size. This methodology and representation have been already used by several  
15 authors <sup>49,50</sup>. Representing the adsorbed CO<sub>2</sub> per surface area versus  $A_{BET}$  and  $L_{0,DR,N_2}$ , a good fit  
16 was also obtained ( $R^2 = 0.86$ , Figure S3) but the quality of the fit was far better when using  
17  $S_{NLDFT}$  and  $L_{0,NLDFT}$  (i.e.,  $R^2 = 0.93$ ) (Figure 2d).

18 Likewise, the BET and DR methods overestimate the surface area and the micropore volume,  
19 respectively, of highly activated carbons. The linear dependence of the adsorbed amount of CO<sub>2</sub>  
20 per unit of surface area as a function of the average stability of the adsorption potential (Figure  
21 2c) induces a curvature when the same quantity is observed as a function of the average  
22 micropore size (Figure 2d). Indeed, the stability of the adsorption potential has a highly non-

1 linear dependence with the pore size (Figure 3b) which induces this curvature. With the  
2 exception of commercial activated carbons (MSC-30 and MSP-20X), all data points are located  
3 on one single trend line (Figure 2d). This suggests that the shapes of the pore size distributions of  
4 activated carbons derived from phenolic oil are similar or, at least, do not have, in this particular  
5 case, a significant influence on the adsorbed density. Moreover, Figure S4 confirms the  
6 similarity of the pore size distributions of activated carbons derived from phenolic oil. Indeed,  
7 the three families of synthesized materials follow the same trends: for each pore fraction, each  
8 class of pores depends on  $L_{0,NLDFT}$  in a similar way. The KANSAI family is the only one to  
9 present, here, some differences in the shape of the pore size distributions (Figure S4). Indeed, the  
10 MSP-20X has, given the average size of its micropores, a lower ultramicroporous volume than  
11 the rest of the materials. Hence, the advantage of using average adsorption potential stability  
12 (Figure 2b) instead of average micropore size (Figure 2c) is both to reduce scattering when  
13 comparing different families of materials and to linearize the trend.

### 14 **3.3 CO<sub>2</sub> capture capacity above room temperature (50-120°C)**

15 As it has been confirmed previously, the narrow micropore volume is the most important  
16 parameter for CO<sub>2</sub> capture at low temperatures, also concluded by Sevilla et al.<sup>51</sup>. However, in  
17 combustion processes, the most common flue gas temperatures range from 50 to 120°C<sup>3,52</sup>.  
18 Figure 4 shows the CO<sub>2</sub> uptake for the best samples previously identified (MSP-20X, XiPPO\_3,  
19 XPPO\_1 and CWPO\_1) for a representative range of temperatures from 25 to 120°C. As  
20 expected, the CO<sub>2</sub> capture capacities of all samples decreased as the adsorption temperature  
21 increased, because CO<sub>2</sub> physisorption is an exothermic process.



1

2 **Figure 4.** CO<sub>2</sub> capture capacity of the most efficient samples as a function of adsorption  
 3 temperature. (Purple for MSP-20X, blue for XiPPO\_3, red for XPPO\_1 and green for  
 4 CWPO\_1).

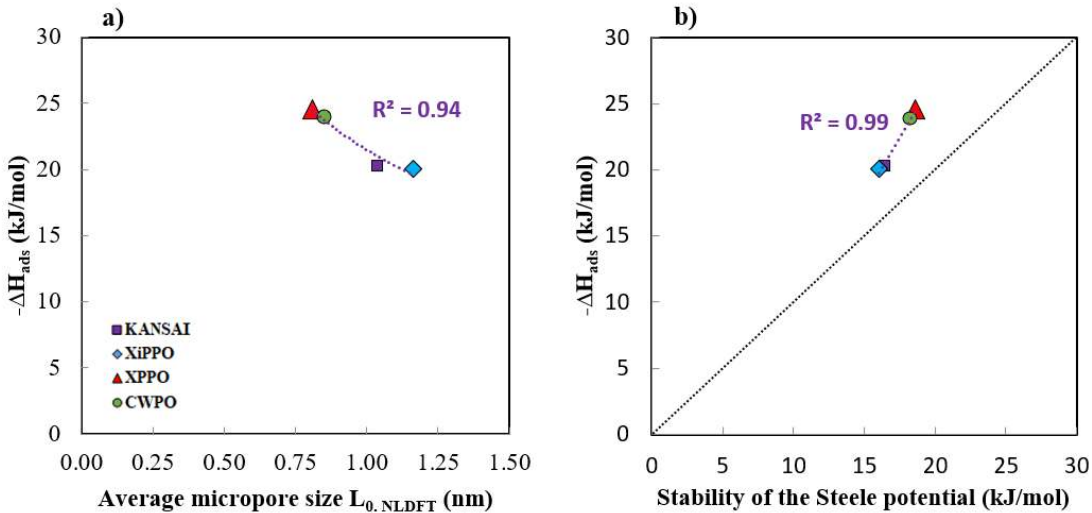
5 In agreement with Serafin et al. <sup>14</sup>, as the adsorption temperature increases, the range of pore size  
 6 in which the capture of CO<sub>2</sub> mostly takes place is considerably reduced and pores narrower than  
 7 0.5 nm become more important. However, it was observed that at 120°C, the CO<sub>2</sub> capture  
 8 capacity of all samples were very similar. Indeed, the CO<sub>2</sub> uptake of XPPO\_1 was the lowest,  
 9 even though it had the highest volume of narrow pores and the lowest L<sub>0,NLDFT</sub>. Hence, as the  
 10 capture temperature increases, the micropore volume of the samples becomes less relevant, as  
 11 opposed to the surface area and the total pore volume which become more important.

12 Indeed, the higher the specific area and total pore volume the higher the density (per mass unit of  
 13 carbon material) of possible defects on the surface of carbon structure (i.e. surface groups, edges,  
 14 corrugation and other topological defects). Under high temperature (i.e. 120 °C), such defects  
 15 should have a greater importance than under lower temperatures due to the polarization effect

1 they induce on the CO<sub>2</sub> molecules. This statement is justified by the study of adsorption  
 2 enthalpies as detailed below.

3 The calculation of adsorption enthalpies using Henry's law is detailed in the supplementary  
 4 information. The linear fits had a high R<sup>2</sup> (> 0.97). The enthalpies of CO<sub>2</sub> adsorption on the  
 5 materials MSP-20X, XiPPO\_3, XPPO\_1 and CWPO\_1 are respectively equal to 20.2, 20.1, 24.5  
 6 and 23.9 kJ/mol. These values are in the typical range of CO<sub>2</sub> adsorption on activated carbons <sup>53</sup>,  
 7 <sup>54</sup>. The decrease in heat of adsorption (opposite of the enthalpy of adsorption) as the average  
 8 micropore size increases (Figure 5a) is due to the decrease of the adsorption potential.

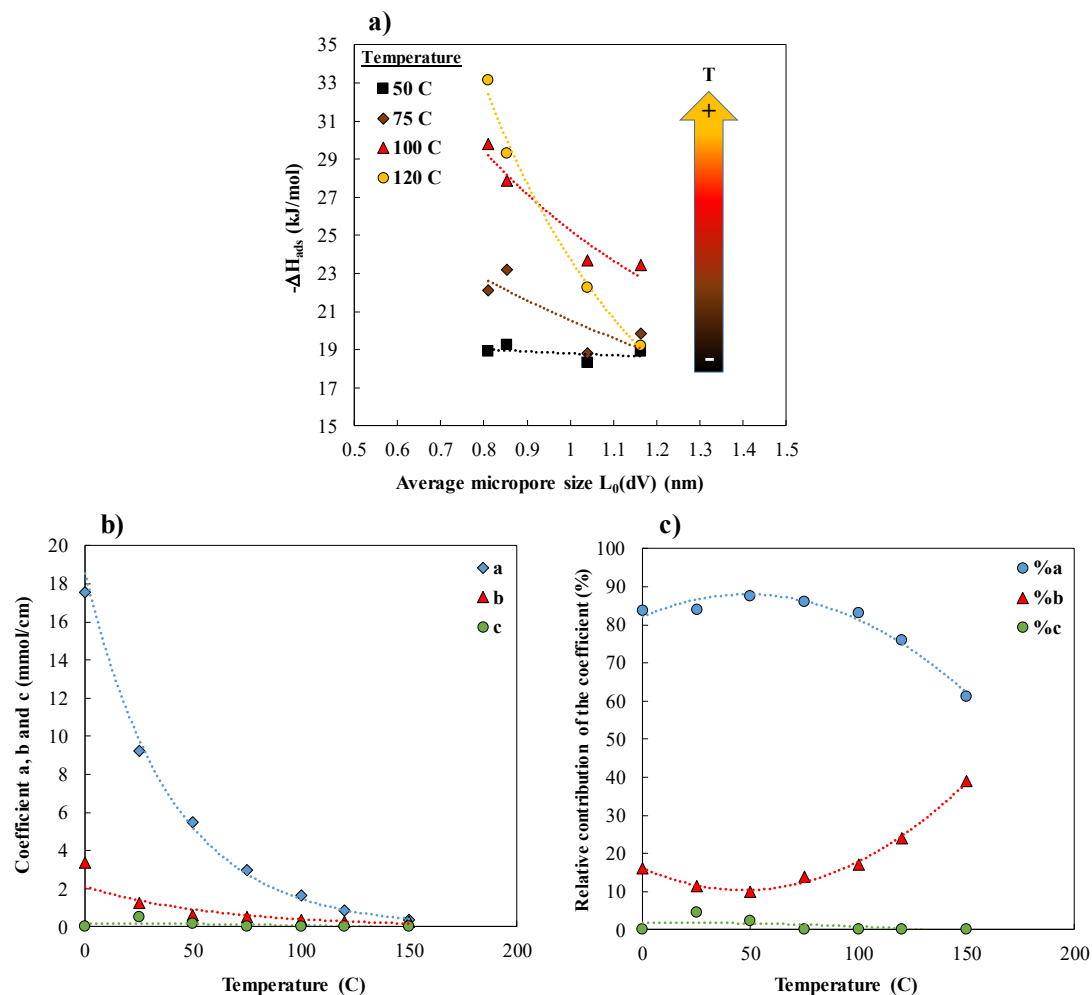
9 When the heat of adsorption is represented in relation to the average stability of the adsorption  
 10 potential calculated previously, instead of the average size of the micropores, the trend becomes  
 11 perfectly linear but does not correspond to the identity function (Figure 5b).



12  
 13 **Figure 5.** Heat of adsorption as a function of a) average micropore size according to NLDFT,  
 14 and b) stability of the adsorption potential.

1 This non-equality might be due to the fact that the potential of adsorption does not perfectly  
2 reflect the substrate-adsorbate interactions. Indeed, the adsorption potential does not account for  
3 intermolecular or lateral interactions of the adsorbate. These could increase the apparent heat of  
4 adsorption. In addition, the small amount of CO<sub>2</sub> possibly subjected to cooperative adsorption in  
5 the larger micropores could also affect the heat of adsorption and induce a higher heat of  
6 adsorption. Moreover, the adsorption potential has been calculated for an infinite flat graphitic  
7 surface, thus without edges or corrugation, and in the absence of specific surface group that  
8 might experimentally affect the adsorption heat and the adsorption process. Such characteristics  
9 of the carbon surface (corrugation, defects, edges and surface groups) could explain the higher  
10 values of adsorption heat obtained experimentally, compared to the average stability of  
11 adsorption potential.

12 Figure 6a shows the evolution of the heat of adsorption as a function of temperature and average  
13 micropore size. The heat of adsorption increases as the temperature of adsorption increases due  
14 to the preferential filling of the smallest pores at high temperature. Indeed, the high temperatures  
15 induce a greater decrease in the density of the adsorbed layer in the wide pores than in the  
16 narrow pores where the adsorption potential is very high <sup>14</sup>. In addition, the increase in  
17 temperature gives more importance to strong polarized adsorption on the surface of the sorbent  
18 compared to physisorption. In general, defects in carbon structure itself or surface groups such as  
19 hydroxyls can induce such strong polarized adsorption phenomena <sup>55,56</sup>.



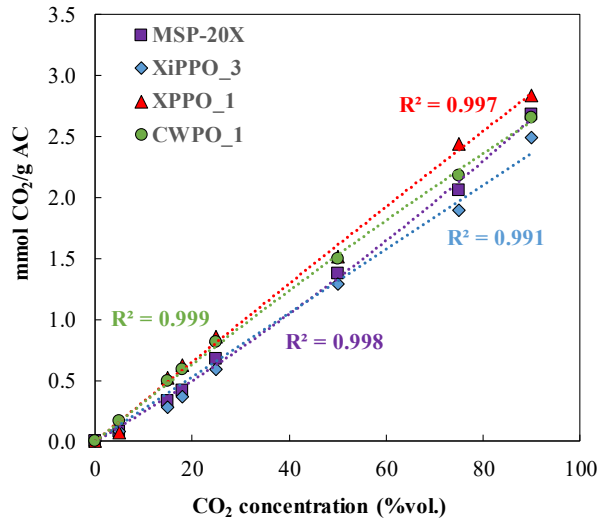
1  
2 **Figure 6.** a) Heat of adsorption as a function of the average micropore size for different  
3 temperatures, b) Coefficients  $a$ ,  $b$  and  $c$  of the multilinear regression (eq. 1), and c) their relative  
4 contribution as a function of temperature.  
5 By applying multiple linear regression (eq. 1) to each adsorption temperature, the coefficients  $a$ ,  
6  $b$  and  $c$ , corresponding to the contributions (in mmol/cm<sup>3</sup>) to CO<sub>2</sub> adsorption for each pore size,  
7 have been calculated. The variation of these coefficients as well as their relative contributions to  
8 capture capacities are shown in Figure 6b and 6c, respectively, as a function of temperature. The  
9 ultramicropores always constituted the most important volume fraction (Figure 6b), although  
10 their importance approached that of supermicropores at 120°C (Figure 6c).

1 Figure 6b exhibits an exponential decay of all coefficients related to the negative effect of  
2 temperature on the physisorption process. In addition, the relative contribution of each pore size  
3 (Figure 6c) shows that, in a range close to room temperature (i.e., 25-75°C), the contribution of  
4 ultramicropores increases (coefficient a) while that of supermicropores (coefficient b) decreases,  
5 which is due to the higher adsorption potential in ultramicropores. In contrast, above 75°C, the  
6 contribution of supermicropores (coefficient b) begins to increase. This indicates that the surface  
7 becomes, above a given temperature, more attractive for the adsorption of CO<sub>2</sub>.

### 8 **3.4 Effect of partial CO<sub>2</sub> pressure on the capture capacity**

9 When transforming fossil fuel energy in any combustion plant, the concentration of CO<sub>2</sub> released  
10 into the atmosphere is between 5 and 30 vol. %: the most common values from pulverized coal  
11 fired plants ranges from 8 to 15 vol. %<sup>28</sup>, whereas the concentration can reach 30 vol. % with  
12 cement plants<sup>27</sup>.

13 Figure 7 shows the CO<sub>2</sub> adsorption at 25°C for the most efficient samples of each family (MSP-  
14 20X, XiPPO\_3, XPPO\_1 and CWPO\_1) at different partial pressures of CO<sub>2</sub>. It was observed  
15 that at low concentrations, 5, 15 and 18 % by volume, the CO<sub>2</sub> capture capacities of MSP-20X  
16 and XiPPO\_3 were similar, with a higher CO<sub>2</sub> uptake of CWPO\_1.



1  
 2 **Figure 7.** CO<sub>2</sub> capture capacities at 25°C for the most efficient samples as function of the CO<sub>2</sub>  
 3 concentration. (Purple for MSP-20X KANSAI, blue for XiPPO\_3, red for XPPO\_1 and green for  
 4 the CWPO\_1).

5 The CO<sub>2</sub> capture of XPPO\_1 at 5 vol. % of CO<sub>2</sub> was the lowest among all samples. However, it  
 6 became the highest as the concentration increased, showing the largest differences for CO<sub>2</sub>  
 7 concentrations above 50 vol. %.

8 For any AC, at low CO<sub>2</sub> concentrations, the most important pores for adsorption are the  
 9 narrowest pores available, pores narrower than 0.6 nm are the most relevant when working at 15  
 10 % of CO<sub>2</sub> <sup>14</sup>. Samples MSP-20X and XiPPO\_3 have a similar V<sub>micro DR</sub> (CO<sub>2</sub>) and showed similar  
 11 CO<sub>2</sub> uptakes at low concentrations. XPPO\_1, at CO<sub>2</sub> concentrations higher than 15 vol. %,   
 12 became the best sample due not only first to the highest V<sub>micro DR</sub>, but also to its lowest L<sub>0,NLDFT</sub>,  
 13 (0.72 nm). However, at CO<sub>2</sub> concentrations lower than 15 vol. %, XPPO\_1 had the lowest capture  
 14 capacity and the lowest pore volume between 0.7 and 50 nm. Consequently, when the CO<sub>2</sub>  
 15 concentration increased, the contribution of pores less than or equal to 0.7 nm became important,



1 which means that all samples with a higher  $V_{L<0.7}$  would show a higher  $\text{CO}_2$  capture capacity, as  
2 indicated previously and as reported elsewhere <sup>14, 39, 40</sup>.

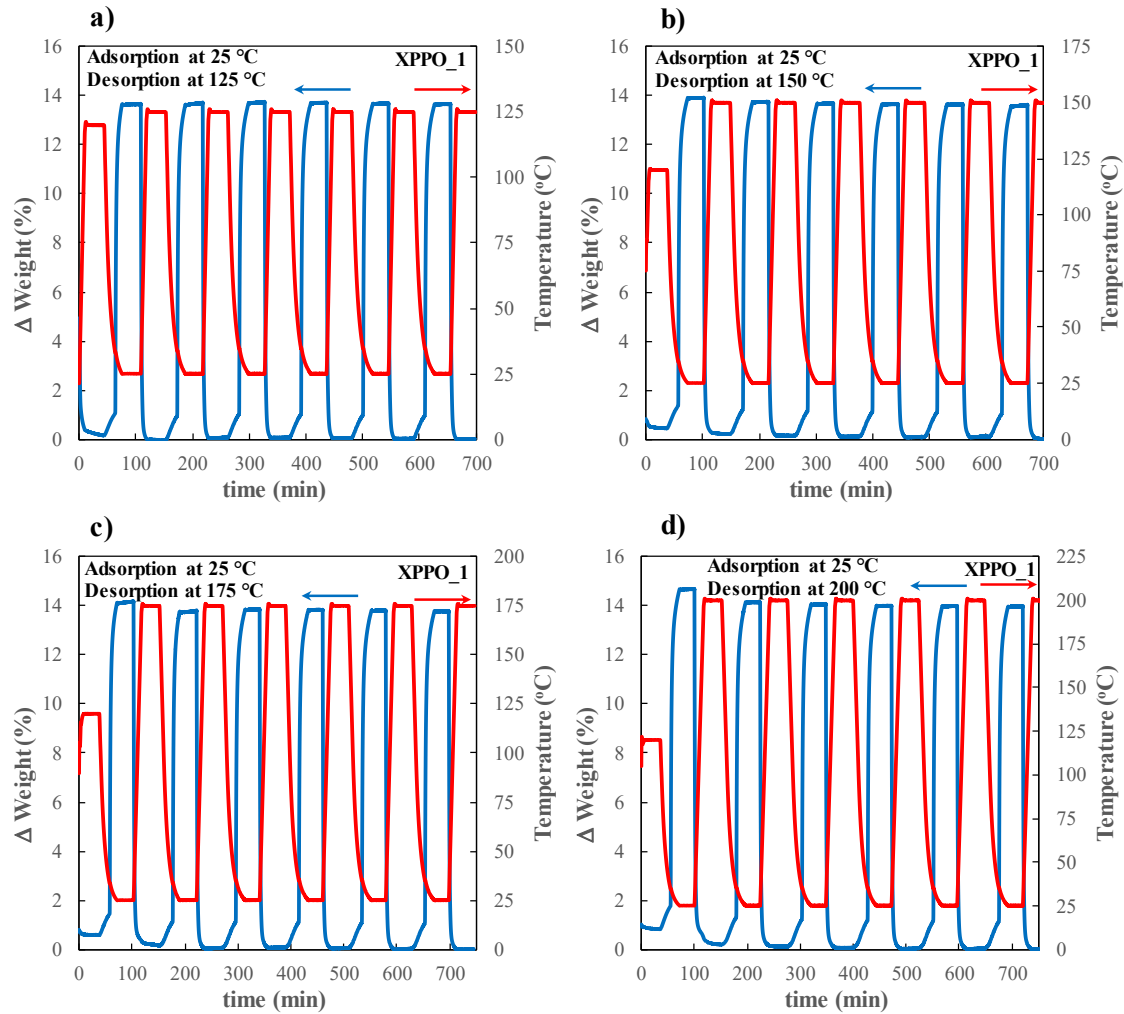
3 For common  $\text{CO}_2$  concentrations in combustion processes, both XPPO\_1 and CWPO\_1 had a  
4 similar behavior with respect to  $\text{CO}_2$  capture.

### 5 **3.5 $\text{CO}_2$ adsorption-desorption evaluation**

6 For any  $\text{CO}_2$  capture process, the ultimate practical objective is to determine the feasibility of the  
7 method over a large number of adsorption-desorption cycles. In the case of ACs for which  $\text{CO}_2$  is  
8 physically adsorbed on the material, the increase of the temperature favors the desorption of  $\text{CO}_2$   
9 from the surface of the adsorbent and can also affect the stability of the carbon materials. The  
10 thermal stability of the best ACs considered in this study is illustrated in Figure S6.

11 There is first a drop of sample weight associated to the presence of moisture in the AC, followed  
12 by a progressive but slight decrease in weight between 8 and 10 % for CWPO\_1 and XPPO\_1,  
13 respectively, until stabilization. Therefore, the regeneration temperature used might have a  
14 negative effect on the  $\text{CO}_2$  working capacity after the desorption step, as the structure and  
15 stability of the samples could be affected.

16 Figure 8 shows the variation of the weight according to the adsorption-desorption profiles for the  
17 sample XPPO\_1 using an adsorption temperature of  $25^\circ\text{C}$  and desorption temperatures of 125,  
18 150, 175 or  $200^\circ\text{C}$ . It was observed that after the first cycle, the initial weight of the AC before  
19  $\text{CO}_2$  adsorption at each cycle was smaller as the desorption temperature increased. However, the  
20  $\text{CO}_2$  working capacity ( $2.47 \text{ mmol CO}_2/\text{g AC}$ ) was the same in all cycles, regardless of the  
21 desorption temperature. The same behavior was observed for all other ACs.



1  
 2 **Figure 8.** Adsorption-desorption cycles of the activated carbon XPPO\_1, with adsorption at  
 3 25°C and 90% CO<sub>2</sub> concentration and desorption at: a) 125°C, b) 150°C, c) 175°C, and d)  
 4 200°C.

5 Table 3 shows the CO<sub>2</sub> working capacity of the most efficient samples through 6 adsorption-  
 6 desorption cycles at 200°C as a regeneration temperature chosen to evaluate the behavior of the  
 7 materials at the highest temperature considered and their degradation during cycles. In all cases,  
 8 the CO<sub>2</sub> working capacity remained constant, corroborating the stability of the samples upon  
 9 cycling, even using a high temperature for the regeneration step.

1 **Table 3.** CO<sub>2</sub> working capture capacity of the most efficient samples at adsorption and desorption  
 2 temperatures of 25°C and 200°C, respectively.

Number of cycle	MSP-20X mmol CO <sub>2</sub> / g AC	XiPPO_3 mmol CO <sub>2</sub> / g AC	XPPO_1 mmol CO <sub>2</sub> / g AC	CWPO_1 mmol CO <sub>2</sub> / g AC
1	2.68	2.51	2.86	2.73
2	2.68	2.48	2.88	2.66
3	2.68	2.46	2.88	2.65
4	2.61	2.46	2.88	2.68
5	2.68	2.48	2.88	2.69
6	2.66	2.42	2.89	2.72
Average	2.66 ± 0.02	2.47 ± 0.02	2.88 ± 0.003	2.69 ± 0.02

3  
 4 **4. Conclusion**  
 5 This work presents the development of different activated carbon xerogels and cryogels, all  
 6 derived from a low-value industrial product, phenolic oil, for the capture of CO<sub>2</sub> under different  
 7 conditions of adsorption temperature, CO<sub>2</sub> concentration, and regeneration temperature.  
 8 Some of these samples showed higher CO<sub>2</sub> capture capacities than commercial activated carbons,  
 9 with very good repeatability. The carbon xerogel produced with a basic catalyst and activated  
 10 with a carbon/KOH ratio equal to 1:1 had the best CO<sub>2</sub> uptake (2.86 mmol/g AC). The second  
 11 most efficient sample was the carbon cryogel activated under the same conditions. The obtained  
 12 values in this study are indeed comparable to previously reported values for ACs without  
 13 any modification/functionalization. Furthermore, the role of the textural properties of these  
 14 new ACs on the CO<sub>2</sub> capture under different postcombustion conditions has been elucidated.  
 15 Initially, it has been observed that two different samples with different surface areas and  
 16 microporous fractions could present the same CO<sub>2</sub> capture capacity. Nevertheless, the influence

1 of the presence of micropores and, more importantly, narrow pores in the structure of the  
2 samples has been demonstrated as the main CO<sub>2</sub> capture factor at 25 °C, with a clear trend as the  
3 partial pressure of CO<sub>2</sub> increased. Therefore, if the microporous fraction was reduced during  
4 activation, the surface area should be high enough to maintain a constant CO<sub>2</sub> capture  
5 capacity. It was observed that two samples with different textural characteristics have  
6 similar CO<sub>2</sub> capture capacities.

7 However, as the temperature increased, it was determined that the presence of narrow pores had  
8 a lesser influence on CO<sub>2</sub> adsorption, and a higher surface area, total pore volume and absolute  
9 micropore volume become more important. This was justified by a polarized physisorption  
10 phenomenon taking place on the surface defects of the carbon surface. Moreover, it has been  
11 determined that as the partial pressure of CO<sub>2</sub> increases, getting values higher than 25 vol. %, the  
12 narrow and micropores get more relevance.

13 The stability of the best samples of each family selected in this work was evaluated up to a  
14 temperature of 220°C. It was determined that, as the temperature increased, there was a slight  
15 variation in the weight of the AC. However, it was also determined that the desorption  
16 temperature has no effect on the CO<sub>2</sub> capture capacity during cycles.

17 Finally, six adsorption-desorption cycles were carried out for each of the best samples at a  
18 regeneration temperature of 200°C. The repeatability and feasibility of samples for CO<sub>2</sub> capture  
19 was demonstrated in all cases, and the materials with the highest capacity at 25°C were the ones  
20 showing the best behavior upon cycling. These results highlighted the possibility of using  
21 activated carbon gels produced using phenolic oil as a relevant precursor for CO<sub>2</sub> capture.

22

23

1 ASSOCIATED CONTENT

2 **Supporting Information**

3 Reproducibility of CO<sub>2</sub> capture capacity values at 25°C and 1 bar under a 90% CO<sub>2</sub> atmosphere,  
4 coefficients of multiple linear regressions for CO<sub>2</sub> adsorption at 25°C for four different pore  
5 classes, simple linear regression between adsorbed amounts of CO<sub>2</sub> at 25°C and pore volumes: a)  
6 VL<0.5, or b) V0.5<L<0.7, Steele, adsorption potential and effective pore size calculations, Steele  
7 adsorption potential for the CO<sub>2</sub> – graphite system (slit pores model), minimum of Steele’s  
8 potential as a function of the distance between the median planes of the graphitic pore walls,  
9 adsorbed amount of CO<sub>2</sub> per unit of BET surface area as a function of the average micropore size  
10 calculated by application of the Dubinin-Radushkevich method ( $L_{0,DR}$ ), ultramicropore fraction,  
11 supermicropore fraction and mesopore fraction, as a function of the average micropore size  
12 according to the NLDFT method, enthalpy of adsorption calculation for adsorbed CO<sub>2</sub>  
13 monolayer, Van’t Hoff plot for CO<sub>2</sub> adsorption at a pressure of 10<sup>5</sup> Pa, and thermal stability of  
14 ACs from room temperature to 220°C: a) MSP-20X, b) XiPPO\_3, c) XPPO\_1, and d) CWPO\_1.  
15 The following files are available free of charge via the Internet at <http://pubs.acs.org>.

16

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4

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## REFERENCES

- (1) “Recently Monthly Average Mauna Loa CO<sub>2</sub>”, NOAA, [Online]. Available: <https://www.esrl.noaa.gov/gmd/ccgg/trends/>.
- (2) IPCC, “Global Warming of 1.5°C. Summary for Policymakers.”, Intergovernmental Panel on Climate Change, Switzerland, **2018**.
- (3) Wang, Q.; Luo, J.; Zhong, Z.; Borgna, A.; CO<sub>2</sub> Capture by Solid Adsorbents and their Applications: Current Status and Trends. *Energy Environ. Sci.* **2011**, 4, 42-55.
- (4) Cuellar-Franca, R.; Azapagic, A. Carbon Capture, Storage and Utilisation Technologies: a Critical Analysis and Comparison of their Life Cycle Environmental Impacts. *J. CO<sub>2</sub> Util.* **2015**, 9, 82-102.
- (5) Rashidi, N.; Yusup, S. An Overview of Activated Carbons Utilization for the Post-Combustion Carbon Dioxide Capture. *J. CO<sub>2</sub> Util.* **2016**, 13, 1-16.
- (6) Plaza, M.; Garcia, S.; Rubiera, F.; Pis, J.; Pevida, C. Post-combustion CO<sub>2</sub> Capture with a Commercial Activated Carbon: Comparison of Different Regeneration Strategies. *Chem. Eng. J.* **2010**, 163, 41-47.
- (7) Yu, C. H.; Huang, C. H.; Tan, C. S. A Review of CO<sub>2</sub> Capture by Absorption and Adsorption. *Aerosol and Air Quality Res.* **2012**, 12, 745-769.
- (8) Lee, S. Y.; Park, S. J. Determination of the Optimal Pore Size for Improves CO<sub>2</sub> Adsorption in Activated Carbon Fibers. *J. Colloid Interface Sci.* **2013**, 389, 230-235.
- (9) Drage, T.;Kozynchenko, O.; Pevida, C.; Plaza, M.; Rubiera, F.; Pis, J.; Snape, C.; Tennison, S. Developing Activated Carbon Adsorbents for Pre-Combustion CO<sub>2</sub> Capture. *Energy Procedia.* **2009**, 1, 599-605.
- (10) Marsh, H.; Rodriguez-Reinoso, F. Activated Carbon, *Elsevier Sci.* **2006**.

- (11) Maroto-Valer, M.; Lu, Z.; Zhang, Y.; Tang, Z. Sorbents for CO<sub>2</sub> Capture from High Carbon Fly Ashes. *Waste Management*. **2008**, 28, 2320-2328.
- (12) Jimenez, V.; Sanchez, P.; Valverde, J.; Romero, A. Effect of the Nature the Carbon Precursor on the Physo-Chemical Characteristics of the Resulting Activated Carbon Materials. *Mater. Chem. Phys.* **2010**, 124, 223-233.
- (13) Zhao, W.; Fierro, V.; Zlotea, C.; Aylon, E.; Izquierdo, M.; Latroche, M.; Celzard, A. Optimzation of Activated Carbons for Hydrogen Storage. *Int. J. Hydrogen Energy*. **2011**, 18, 11746-11751.
- (14) Serafin, J.; Narkiewicz, U.; Morawski, A.; Wróbel, R.; Michalkiewicz, B. Highly Microporous Activated Carbons from Biomass for CO<sub>2</sub> Capture and Effective Micropores at Different Conditions. *J. CO<sub>2</sub> Util.* **2017**, 18, 73-79.
- (15) Yaumi, A.; Abu Bakar, M.; Hameed, B. Recent Advances in Functionalized Composite Solid Materials for Carbon Dioxide Capture. *Energy*. **2017**, 124, 461-480.
- (16) Nowrouzi, M.; Younesi, H.; Bahramifar, N. Superior CO<sub>2</sub> Capture Performance on Biomass-derived Carbon/Metal Oxides Nanocomposites from Persian Ironwood by H<sub>3</sub>PO<sub>4</sub> Activation. *Fuel*. **2018**, 223, 99-114.
- (17) Fadhil, A.; Ahmed, A.; Salih, H. Production of Liquid Fuels and Activated Carbons from Fish Wast. *Fuel*. **2017**, 187, 435-445.
- (18) Jeder, A.; Sanchez-Sanchez, A.; Gadonneix, P.; Masson, E.; Ouederni, A.; Celzard, A.; Fierro, V. The Severity Factor as Useful Tool for Producing Hydrochars and Derived Carbon Materials. *Environ. Sci. Pollut. Res. Int.* **2018**, 25(2) 1497-1507.
- (19) Taher, S.; Sanchez-Sanchez, A.; Gadonneix, P.; Jagiello, J.; Seffen, M.; Sammouda, H.; Celzard, A.; Fierro, V. Tetracycline Removal with Activated Carbons Produced by



Hydrothermal Carbonisation of Agave Americana Fibres and Mimosa Tannin. *Industrial Crops and products*. **2018**, 115, 146-157.

- (20) Schaefer, S.; Muñiz, G.; Izquierdo, M.; Mathieu, S.; Ballinas-Casarrubias, M.; Gonzalez-Sanchez, G.; Celzard, A.; Fierro, V. Rice Straw-based Activated Carbons Doped with SiC for Enhanced Hydrogen Adsorption. *Int. J. Hydrogen Energy*. **2017**, 42(16), 11534-11540.
- (21) Wang, J.; Heerwig, A.; Lohe, M.; Oschatz, M.; Borchardt, L.; Kaskel, S. Fungi-based Porous Carbons for CO<sub>2</sub> Adsorption and Separation. *J. Mater. Chem*. **2012**, 22, 13911-13913.
- (22) Sevilla, M.; Fuertes, A. Sustainable Porous Carbons with a Superior Performance for CO<sub>2</sub> Capture. *Energy Environ. Sci*. **2011**, 4, 1765-1771.
- (23) Marco-Lozar, J.; Kunowsky, M.; Suarez-Garcia, F.; Lianres-Solano, A. Sorbent Design for CO<sub>2</sub> Capture under Different Flue Gas Conditions. *Carbon*. **2014**, 72, 125-134.
- (24) Reynolds, G.; Fung, A.; Wang, Z.; Dresselhaus, M.; Pekala, R. The Effects of External Conditions on the Internal Structure of Carbon Aerogels. *J. Non-Cryst. Solids*. **1995**, 188, 27-33.
- (25) Pekala, R.; Alviso, C.; Lu, X.; Fricke, J. New Organic Aerogels Based upon a Phenolic-Furfal Reaction. *J. Non-Cryst. Solids*. **1995**, 188, 34-40.
- (26) Robertson, C.; Mokaya, R. Microporous Activated Carbon Aerogels via a simple Subcritical Drying Route for CO<sub>2</sub> Capture and Hydrogen Storage. *Microporous Mater*. **2013**, 179, 151-156.

- (27) Lee, K.; Sircar, S. Removal and Recovery of Compressed CO<sub>2</sub> from Flue Gas by a Novel Thermal Swing Chemisorption Process. *AIChE. J.* **2008**, 54, 2293-2302.
- (28) Choi, S.; Drese, J.; Jones, C. Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources. *Chem. SusChem.* **2009**, 2, 796-854.
- (29) Brunauer, S.; Emmet, P.; Teller, E. Adsorption in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, 60, 2, 309-319.
- (30) Thommes, M.; Kaneto, K.; Neimark, A.; Olivier, J.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure and Appl. Chem.* **2015**, 87, 1051-1069.
- (31) Dubinin, N. Fundamentals of the Theory of Adsorption in Micropores of Carbon Adsorbents: Characteristics of their Adsorption Properties and Microporous Structures. *Carbon.* **1989**, 27(3), 457-467.
- (32) Chen, S.; Yang, R. Theoretical Basis for the Potential-theory Adsorption Isotherms-The Dubinin-Radushkevich and Dubinin-Astakhov Equations. *Langmuir.* **1994**, 10(11), 4244-4249.
- (33) Hutson, N.; Yang, R. Theoretical Basis for the Dubinin-Radushkevitch (D-R) Adsorption Isotherm Equation. *Adsorption-J. of the Int. Adsorption Soc.* **1997**, 3(3), 189-195.
- (34) Jagiello, J.; Ania, C.; Parra, J.; Cook, C. Dual Gas Analysis of Microporous Carbons using 2D-NLDFT Heterogeneous Surface Model and Combined Adsorption Data of N<sub>2</sub> and CO<sub>2</sub>. *Carbon.* **2015**, 91, 330-337.

- (35) Stoeckli, F. *Porosity in carbon. Characterization and applications*. Eds. Patrick. Arnold, J. **1995**, London
- (36) Centeno, T.; Stoeckli, F. The Assessment of Surface Areas in Porous Carbons by two Model-independent Techniques, the DR equation and DFT. *Carbon*. **2010**, 48(9), 2478-2486.
- (37) Fierro, V.; Szczurek, A.; Zlotea, C.; Mareche, J.; Izquierdo, M.; Albiniak, A.; Latroche, M.; Furdin, G.; Celzard, A. Experimental Evidence of an Upper Limit for Hydrogen Storage at 77 K on Activated Carbons. *Carbon*. **2010**, 48, 1902-1911.
- (38) Jalilov, A.S.; Ruan, G.; Hwang, C.-C.; Schipper, D.E.; Tour, J.J.; Li, Y.; Fei, H.; Samuel, E.; Tour, J.M. Asphalt-Derived High Surface Area Activated Porous Carbons for Carbon Dioxide Capture. *ACS Appl. Mater. & Interfaces*. **2015**, 7(2), 1376-1382.
- (39) Martin, C.; Plaza, M.; Pis, J.; Rubiera, F.; Pevida, C.; Centeno, T. On the Limits of CO<sub>2</sub> Capture Capacity of Carbons. *Separation and purification Techn.* **2010**, 74, 225-229.
- (40) Casco, M.; Martinez-Escandell, M.; Silvestre-Albero, J.; Rodriguez-Reinoso, F. Effect of the Porous Structure in Carbon Materials for CO<sub>2</sub> Capture at Atmospheric and High-Pressure. *Carbon*. **2014**, 67, 230-235.
- (41) Zhao, W.; Fierro, V.; Zlotea, C.; Aylon, E.; Izquierdo, M.; Latroche, M.; Celzard, A. Activated Carbons with Appropriate Micropore Size Distribution for Hydrogen Adsorption. *Int. J. Hydrogen Energy*. **2011**, 36(9), 5431-5434.
- (42) Schaefer S.; Fierro, V.; Izquierdo, M.; Celzard, A. Assessment of Hydrogen Storage in Activated Carbons produced from Hydrothermally Treated Organic Materials. *Int. J. Hydrogen Energy*. **2016**, 41(28), 12146-12156.

- (43) Steele, W. Physical interaction of gases with crystalline solids. 1. Gas solid Energies and Properties of Isolated Adsorbed Atoms. *Surface Sci.* **1973**, 36(1), 317-352.
- (44) Kurniawan, Y.; Bhatia, S.; Rudolph, V. Simulation of Binary Mixture Adsorption of Methane and CO<sub>2</sub> at Supercritical Conditions in Carbons. *Aiche J.* **2006**, 52(3), 957-967.
- (45) Ravikovitch, P.; Vishnyakov, A.; Russo, R.; Neimark, A. Unified Approach to Pore Size Characterization of Microporous Carbonaceous Materials from N<sub>2</sub>, Ar and CO<sub>2</sub> Adsorption Isotherms. *Langmuir.* **2000**, 16(5), 2311-2320.
- (46) Chen, L.; Watanabe, T.; Kanoh, H.; Hata, K.; Ohba, T. Cooperative CO<sub>2</sub> Adsorption Promotes high CO<sub>2</sub> Adsorption Density over wide Optimal Nanopore Range. *Adsorption Sci. & Techn.* **2018**, 36 (1-2), 625-639.
- (47) Kaneko, K.; Cracknell, R.; Nicholson, D. Nitrogen Adsorption in Slit Pores at Ambient Temperatures-comparison of Simulation and Experiment. *Langmuir.* **1994**, 10(12), 4606-4609.
- (48) Kaneko, K. Specific Intermolecular Structures of Gases Confined in Carbon Nanospace. *Carbon.* **2000**, 38(2), 287-303.
- (49) Sevilla, M.; Mokaya, R. Energy Storage Applications of Activated Carbons: Supercapacitors and Hydrogen Storage. *Energy & Environ. Sci.* **2014**, 7(4), 1250-1280.
- (50) Schaefer, S.; Muñiz, G.; Izquierdo, M.; Mathieu, S.; Ballinas-Casarrubias, M.; Gonzalez-Snachez, S.; Celzard, A.; Fierro, V. Rice Straw-based Activated Carbons Doped with SiC for Enhanced Hydrogen Adsorption. *Int. J. Hydrogen Energy.* **2017**, 42(16), 11534-11540.

- (51) Sevilla, M.; Parra, J.B.; Fuertes, B. Assessment of the Role of Micropore Size and N-Doping in CO<sub>2</sub> Capture by Porous Carbons. *ACS Appl. Mater. & Interfaces*. **2013**, *5*, 6360-6368.
- (52) Arenillas, A.; Smith, K.; Drage, T.; Snape, C. CO<sub>2</sub> Capture Using some Fly Ash-Derived Carbon Materials. *Fuel*. **2005**, *84*, 2204-2210.
- (53) Trinh, T.; van Erp, T.; Bedeaux, D.; Kjelstrup, S.; Grande, C. A Procedure to find Thermodynamic Equilibrium Constants for CO<sub>2</sub> and CH<sub>4</sub> Adsorption on Activated Carbon. *Physical Chem. Chem. Physics*. **2015**, *17*(12), 8223-8230.
- (54) Himeno, S.; Komatsu, T.; Fujita, S. High-pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons. *J. Chem. and Eng. Data*. **2005**, *50*(2), 369-376.
- (55) Radovic, L. The Mechanism of CO<sub>2</sub> Chemisorption on Zigzag Carbon Activate Sites: A Computational Chemistry Study. *Carbon*. **2005**, *43*(5), 907-915.
- (56) Liu, Y.; Wilcox, J. Effects of Surface Heterogeneity on Adsorption of CO<sub>2</sub> in Microporous Carbons. *Environ. Sci. & Technol.* **2012**, *46*(3), 1940-1947.

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