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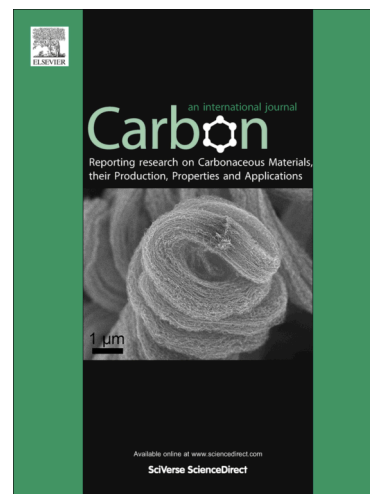
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Gas Storage Scale-up at Room Temperature on High Density Carbon Materials

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Abstract

In relation to the current interest on gas storage demand for environmental applications (e.g., gas transportation, and carbon dioxide capture) and for energy purposes (e.g., methane and hydrogen), high pressure adsorption (physisorption) on highly porous sorbents has become an attractive option. Considering that for high pressure adsorption, the sorbent requires both, high porosity and high density, the present paper investigates gas storage enhancement on selected carbon adsorbents, both on a gravimetric and on a volumetric basis. Results on carbon dioxide, methane, and hydrogen adsorption at room temperature (i.e., supercritical and subcritical gases) are reported. From the obtained results, the importance of both parameters (porosity and density) of the adsorbents is confirmed. Hence, the densest of the different carbon materials used is selected to study a scale-up gas storage system, with a 2.5 l cylinder tank containing 2.64 kg of adsorbent. The scale-up results are in agreement with the laboratory scale ones and highlight the importance of the adsorbent density for volumetric storage performances, reaching, at 20 bar and at RT, 376 g l^{-1}, 104 g l^{-1}, and 2.4 g l^{-1} for CO_2, CH_4, and H_2, respectively.

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1. Introduction

In the last decade, there has been a special interest in developing gas storage systems for applications such as H_2 storage for automotive applications, or CO_2 capture to palliate greenhouse gas emissions, or volatile organic compound (VOC) for transportation, etc. Among the different alternatives, high-pressure adsorption on highly porous adsorbents appears to be an interesting approach to store gases [1-14]. In these storage applications, based on physisorption adsorption processes on sorbent materials, the adsorbate gas molecules are bonded by attractive forces (Van der Waals forces) to the adsorbent surface. Although interactions between gas molecules and the adsorbent are weak, they are enough to enhance the amount of stored gas. Hence, the adsorbent requires a high porosity development [6,15]. However, to maximize the gas storage per unit of volume (volumetric gas storage) the adsorbent demands, in addition to a high adsorption capacity, a high density [13,14,16].

Regarding the sorbent materials, a wide variety of porous materials with different properties is available, such as zeolites, highly activated carbons, activated carbon fibers, carbon nanotubes, zeolite template carbons, carbide-derived carbons, metal organic frameworks (MOFs) or covalent organic frameworks (COFs) [1,5-7,9,14,16-21]. For all of them, porosity, morphology, size, and shape can be controlled and, hence, further improvements can be expected. In this sense, the number of publications reporting their subsequent performance improvements for gas storage is increasing considerably.

The suitability of an adsorbent for a gas storage application can be evaluated from two different points of view: (i) its adsorption capacity expressed per grams of material, or (ii) based on its capacity per liter of adsorbent. For the former, textural properties (i.e.,

adsorption capacity (surface area, and micropore volume) or the micropore size distribution) are the main factors responsible for the gas uptake [6,13-14,16,21-24]. However, if the adsorption capacity is expressed on a volumetric basis (i.e., per unit of volume of the adsorbent), not only does the porosity play a fundamental role, but also the density of the adsorbent. This parameter is crucial, because it determines the final gas uptake, especially in those cases where the adsorbent has to be confined in a given volume, as it is the case for gas storage applications.

There are not many papers analyzing, and revealing, the importance that both parameters (porosity and density) have on the results related to gas storage applications [6,14,16,21,25-29]. Additionally, most of these papers use to deal with small amounts of samples (laboratory scale, usually with << 1 g obtained). Therefore, to strength gas storage application on highly porous sorbents, further investigations are welcome to confirm: a) the importance of the density for enhancing storage in a given tank volume, and b) to scale gas storage results using much higher amount of sorbent than the one used for most published results. This paper deals with the two above mentioned items (a and b). Thus, it analyzes, on a gravimetric and on a volumetric basis, the effects that the sample porosity and density have on the storage of carbon dioxide, methane, and hydrogen at room temperature. To reach such objective different carbon materials are selected from our published results, because they all have different porosity developments and densities. Item b) has been evaluated using 2.6 kg of a carbon monolith, filling a tank of 2.5 liters. Such monolith has the highest density among all the selected samples studied. Additionally, the paper presents a comparative study of results obtained under the same experimental conditions, but using different amount of samples; small amount (laboratory scale) and large ones (scale-up).

2. Experimental

2.1. Adsorbent Materials

To analyze the importance that both variables (textural properties and density) have on the gas storage capacity, a wide number of carbon materials which come from different raw materials (i.e., coals, carbon fibers, etc.), activation methods and activation conditions (different activating agents, activating agent/precursor ratios, etc.), were selected, including commercially available samples (Maxsorb3000 supplied by Kansai Coke & Chemical Co. and a carbon monolith provided by ATMI Co.), as well as samples prepared previously in our laboratory. The reason for focusing the analysis on these samples, and not on samples reported by other researchers, is that density measurements are preformed using exactly the same conditions. This aspect is essential for our comparison purposes. Additionally, with these selected samples, a wide range of properties and morphologies (powders, fibers, monolith material, etc.) is covered which allows to compare their gas storage in terms of gravimetric and volumetric capacities. In the special case of the scale-up studies, these experiments were carried out with the densest carbon material; ATMI carbon monoliths.

2.2. Textural characterization and densities

Textural properties of all the carbon materials were assessed by physical gas adsorption of nitrogen and carbon dioxide at -196 and 0ºC, respectively, in a Quantachrome instrument (Autosorb 6). Samples were degassed at 250ºC under vacuum for 4 hours. The micropore volumes were calculated from N_2 adsorption data and the micropore volumes of narrow pores (< 0.7 nm) were obtained from CO_2 adsorption isotherms at 0ºC, both using the Dubinin-Radushkevich equation [30-32]. Likewise, densities (packing density in the case of powders and fibers, as well as piece density for monolith

materials) were measured. The packing densities were obtained by pressing a given amount of sample in a mould at a pressure of 415 kg cm^{-2} [33]. Piece densities were measured at room temperature, using the weight and the geometric volume of the carbon monoliths [13].

2.3. High pressure gas adsorption

For high pressure CO_2 and CH_4 adsorption a gravimetric apparatus, Sartorius 4406-DMT high-pressure microbalance, and for H_2 adsorption a fully automated volumetric Quantachrome device (iSorbHP1) were used. In both devices, about 300 mg of sample were used. In the particular case of the gravimetric instrument, the experimental results were corrected for buoyancy effects related to the displacement of gas by the sample, sample holder, and pan [6,24]. In both devices, samples were degassed "in situ" at 150ºC under vacuum for 4 h. With these different devices excess adsorption isotherms at room temperature of carbon dioxide, methane and hydrogen were obtained.

2.4. Scale-up experiments

In the case of scale-up storage, the amount of carbon adsorbent was increased from mg to 2.64 kg. Based on the lab-scale results, a carbon monolith with the highest density (ρ: 1.07 g cm^{-1}) and with a moderate porosity development ($V_{DR}(N_2)$: 0.43 cm g^{-1} and $V_{DR}(CO_2)$: 0.44 cm g^{-1}) was used for this purpose. For comparison, two tanks with the same volume (2.5 l), one remaining empty and the other one being filled with 2.64 kg of sample, were used to analyze the gas storage. The pictures of Figure 1 show the cylinder used for this investigation and a demo unit in which the disposition of the carbon monoliths can be seen. It can be observed that the filled cylinder is based on stacked monoliths which perfectly fit inside the cylinder and completely fill its volume. In the
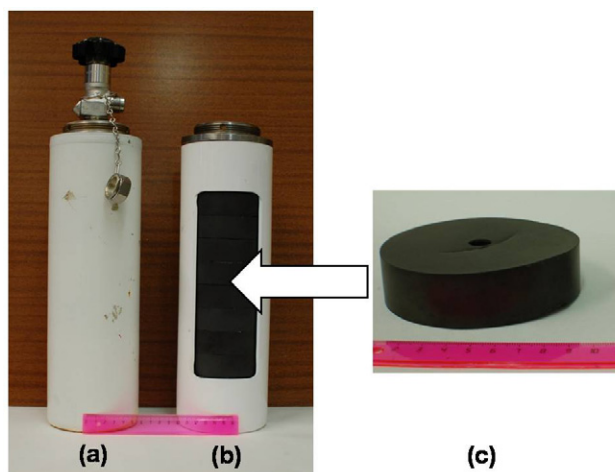
Figure 1. Photographs showing (a) the cylinder used for the gas scale-up storage study, (b) a demonstration unit in which the distribution of the (c) monoliths is disclosed.

scope of its manufacture, the open shell structure of the cylinder was filled with the monolith stack previous to welding the upper plate, which features the in- and outlet valve, on its top [34]. Gas storage capacity was studied for CO_2, CH_4, and H_2. In all the cases, measurements were carried out at room temperature (21±1ºC) and at a maximum working pressure of 20 bar, due to the constructional limitations of the tanks and for safety reasons. The amount of stored gas was obtained by the increment of weight before and after storage.

3. Results and Discussion

3.1. Adsorbent characterization

Figure 2(a) presents the porous texture results (micropore volume $V_{DR}(N_2)$, measured by N_2, and narrow micropore volume $V_{DR}(CO_2)$, measured by CO_2) of the different carbon materials used. It can be observed that the selected carbons cover a considerable wide range of textural properties which will allow to analyze the porosity development contributing to the adsorption capacity. Thus, these samples vary widely in adsorption capacity (for example their total micropore volume values range from 0.2 cm g^{-1} to

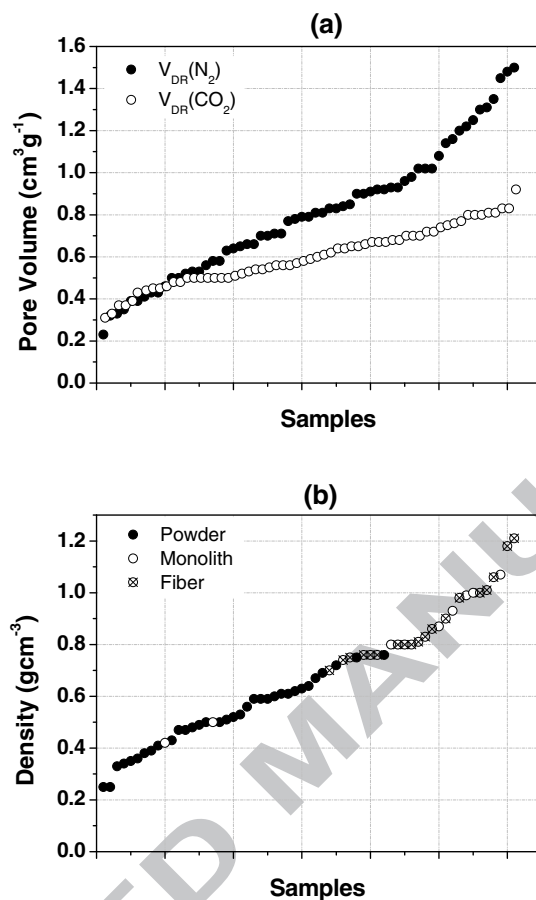**Figure 2.** (a) Textural properties and (b) density values of the selected samples studied.

more than 1.5 cm g^{-1}). Interestingly, the combination of the carbon precursors used and the activation processes carried out generate samples with interesting attributes, e.g., a very high adsorption capacity (pore volume) maintaining also a very high narrow micropore volume, the highest one reaching an outstanding value above 0.9 cm g^{-1}.

The packing densities of the selected adsorbents, that include powders, fibers, and monolith materials, are summarized in Figure 2(b). They vary considerably, and this will allow to analyze later on the effect that the density has on the adsorption uptake in volumetric terms. It should be noted that materials with the highest densities are carbon fibers and monoliths. In the former case, it is well known that this kind of carbon

material presents a high compressibility which could make them interesting candidates for gas storage applications. However, it is also known that they have an important resiliency behavior (tendency to recover its original state when the applied pressure is released). This last observation is a technical issue from an application point of view. Possible solutions for avoiding resiliency behavior and to increase the effective packing density values are: (i) to maintain the packing pressure during the carbon fibers tank filling process, which can have technological difficulties, and (ii) to prepare carbon monoliths with these materials. For this reason, among these two samples, carbon monoliths stand out, due to their easy handling and also their high density values (from 0.8 g cm^{-1} to more than 1 g cm^{-1}).

3.2. High pressure gas adsorption at room temperature

3.2.1. CO_2 adsorption

Depending on the adsorbate and on the experimental conditions in which the adsorption process takes place, different textural parameters control the adsorption capacity on a gravimetric basis. In other words, the correlation between adsorption capacity per grams of adsorbent and porosity varies, depending on the nature of the gas and on the conditions of the storage system (i.e., temperature and pressure). From previous investigations, it is known that, in the case of room temperature CO_2 adsorption at 30 bar, there exists a linear correlation between adsorption capacity and the micropore volume [13,14,35-37]. Thus, higher total micropore volumes ($V_{DR}(N_2)$) lead to higher adsorption capacities. Based on our previous results [13,14,35-37], Figure 3(a) summarizes the gravimetric adsorption capacities (mmol of adsorbate per gram of sample) at 30 bar versus the micropore volume of the selected samples. Regardless of the different raw materials and activation methods used in these samples, the results confirm the existence of a linear tendency between the total micropore volume and the CO_2 adsorption capacity on a gravimetric basis for a pressure of 30 bar.
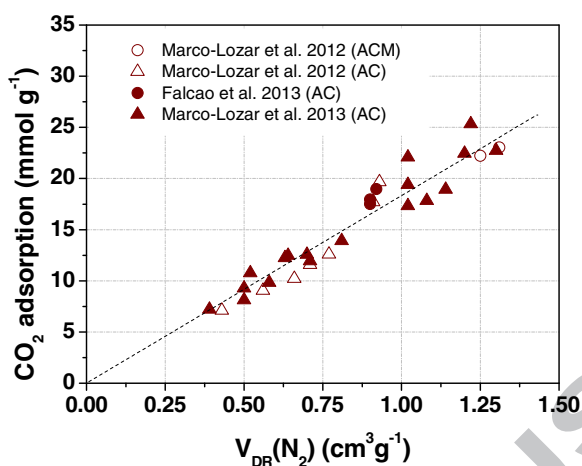
(a)
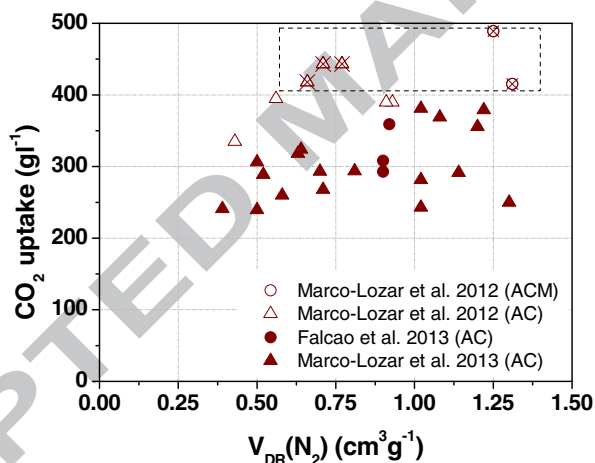
(b)

Figure 3. CO_2 adsorption capacity at 25ºC and up to 30 bar versus micropore volume on (a) gravimetric, and (b) volumetric basis for a selection of carbon samples [13,14,36,37].

From an application point of view, the amount of gas that can be adsorbed per unit volume is more important than the gravimetric amount. Figure 3(b) shows the CO_2 adsorption capacity per volume of adsorbent, which was calculated using the density of each sample. It can be seen that the relatively good linear correlation observed in Figure

3(a) disappears in Figure 3(b). This indicates that when the results are expressed on a volumetric basis, besides the influence of the sample porosity, the density of the adsorbent strongly affects the volumetric CO_2 uptake. Among the samples of Figure 3(b) two types of samples stand out: (i) samples with the highest porosity development (X empty circles), and (ii) adsorbents with a moderate porosity development but high densities (X empty triangles). For the former, their high CO_2 uptakes can be explained only by their high micropore volumes (> 1.2 cm g^{-1}). In the latter case, the high CO_2 capacity is due to a combination of both, porosity and density, where their high densities have the main influence. In fact, all the samples indicated by filled circles correspond to carbon monoliths which have densities between 0.8 and 1.07 g cm^{-1}. In summary, in the case of CO_2 storage by adsorption at room temperature and 30 bar, the adsorbent requires a combination of high adsorption capacity, high material density, and suitable micropore size distribution.

3.2.2. CH_4 adsorption

In the particular case of methane storage at room temperature and pressures up to 30 bar, it is well known that adsorption on porous materials takes place in micropores with a pore size around 1.1 nm [26,33,38-41]. This dependence implies that the amount of the total micropore volume can provide an idea of the adsorption capacity of a selected porous adsorbent. In this sense, Figure 4(a) shows CH_4 adsorption capacity expressed on a gravimetric basis versus the micropore volume of the selected samples that cover a wide range of micropore volumes (up to 1.5 cm g^{-1}). The results confirm the well known trend, existing between CH_4 uptake and the $V_{DR}(N_2)$. Again, as in the case of the gravimetric CO_2 adsorption, those samples with the highest micropore volumes present the highest gravimetric CH_4 adsorption capacity values, as expected.
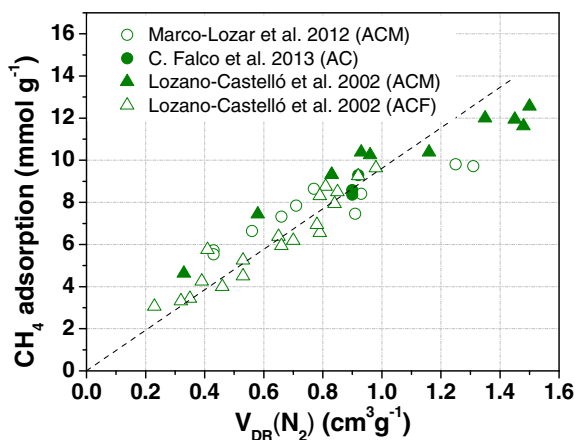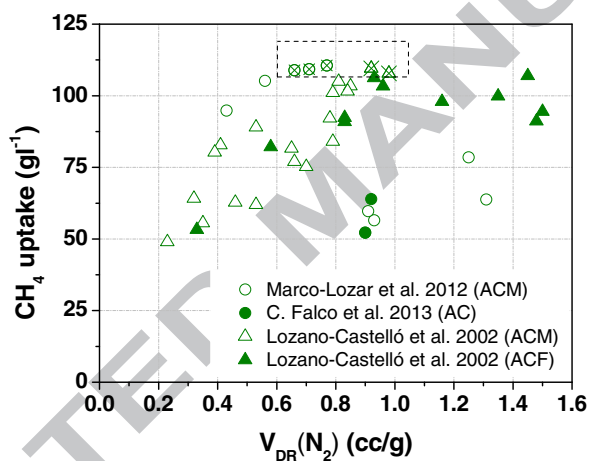
(a)

(b)

Figure 4. CH$_4$ adsorption capacity at 25ºC and up to 30 bar versus total micropore volume on (a) gravimetric, and (b) volumetric basis for a selection of carbon samples [13,33,36,38].

As indicated before, the amount of gas adsorbed per unit volume is the key parameter from an application point of view. Figure 4(b) shows the CH$_4$ adsorption capacity expressed per gram of adsorbent and obtained at room temperature and 30 bar. Similarly to the case of volumetric CO$_2$ adsorption, the correlation observed in Figure 4(a) disappears in Figure 4(b), due to the importance of the material density. Thus, the five

samples of Figure 4(b) having the highest CH_4 uptakes (~110 g l^{-1}) also have the highest densities: Three of them correspond to carbon monoliths (X empty circles), and two (X empty triangles) correspond to adsorbents which combine high densities with suitable micropore size distributions. Similar to what was observed for CO_2, a suitable adsorbent for CH_4 storage at room temperature and 30 bar has to combine high adsorption capacity, high material density, and suitable micropore size distribution.

3.2.3. H_2 adsorption

Hydrogen adsorption capacities, measured at 25ºC and 200 bar and expressed on a gravimetric basis, are shown in Figure 5(a). In difference to CO_2 and CH_4, if the gravimetric adsorption capacity is represented versus the total micropore volume $(V_{DR}(N_2))$ no correlation is observed. From previous results it is known that under the same investigated conditions (i.e., room temperature and pressures below 200 bar), H_2 uptake per gram of adsorbent is controlled by the narrow micropore (< 0.7 nm) volume $(V_{DR}(CO_2))$ [6,13,24,42,43] as it is shown in Figure 5(a). In other words, for this wide variety of samples, there is no dependence between the adsorption capacity and the nature of the raw material, nor the activation method used, nor their sample morphology. This indicates that the only factor that controls the adsorption process of H_2 at room temperature and 200 bar is the control and development of the narrow micropore volume (< 0.7 nm).

In Figure 5(b), the adsorption capacity is expressed on a volumetric basis and plotted against the narrow micropore volume. In contrast to Figure 5(a) no tendency is observed, since, once again, the density of the adsorbent material plays a key role. In the case of hydrogen adsorption, only samples with very high densities reach the highest volumetric values. Thus, the five samples (X empty circles) having the highest densities

(a)

(b)

Figure 5. H_2 adsorption capacity at 25ºC and up to 200 bar versus narrow micropore volume on (a) gravimetric, and (b) volumetric basis for a selection of carbon samples [13,14,24,42].
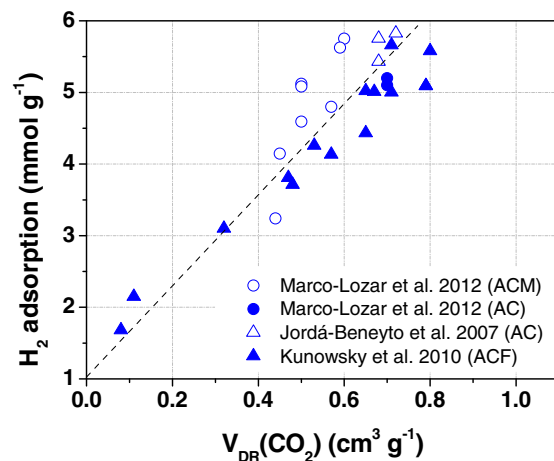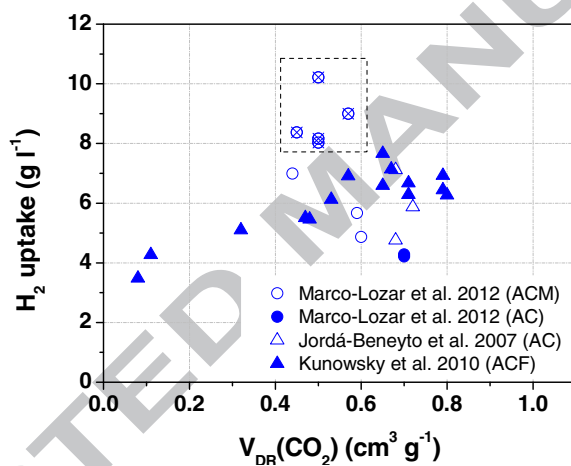
(monolith materials) stand out from the rest of samples. This highlights the particular importance of the density for hydrogen adsorption at room temperature and high pressures, when the results are expressed per liter of sample.

3.3. Scale-up storage

Until now, only the gravimetric and the volumetric excess adsorption of the different adsorbates have been analyzed in the present work. However, from an application point

of view, the amount of gas that can be stored inside a given tank volume is essential [6,13,16,24,44]. If the volume of the tank is filled with the adsorbent, then gas molecules can be stored (i) on the surface of the adsorbent (adsorption process), or (ii) in the void space in-between the adsorbent particles (compression). Because adsorbents always contain a certain amount of void spaces, the contribution of the compression has to be taken into account for a proper estimation of the total storage [44,45]. Thus, the total storage capacity can be calculated by Equation 1.

$$x_{stor} = x_{ads} + \rho_{adsorbate} \cdot C_{void}$$

(1)

With x_{stor} and x_{ads} being the total storage amount and the adsorbed excess amount on volumetric basis, respectively, $\rho_{adsorbate}$ being the thermophysical adsorbate density (weight of gas molecules per volume), and C_{void} being the dimensionless void space contribution that can be estimated by means of the following formula (Equation 2) [33,38]:

$$C_{void} = 1 - \left(\rho_{pack} / \rho_{skel} \right)$$

(2)

where

ρ_{pack} is the packing density (for powder and fiber samples) or the piece density (for monoliths) and ρ_{skel} is the real (skeletal) density (He density).

In order to prove also the influence that both parameters (porosity and density) have on the storage capacity of the different adsorbates used for this study, two commercially available carbon materials were selected for this study, one carbon monolith (CM) from ATMI Co. which has a exceptionally high density ($\rho = 1.07$ g cm^{-1}) and a moderate porosity development ($V_{DR}(N_2) = 0.43$ cm g^{-1}) and one powdered activated carbon (AC) -Maxsorb3000- with a moderate density ($\rho = 0.36$ g cm^{-1}), but a high porosity

development ($V_{DR}(N_2) = 1.31$ cm g^{-1}). Figures 6(a,c,e) show the excess adsorption on a gravimetric basis for the three adsorbates and Figures 6(b,d,f) present the corresponding total storage capacities on a volumetric basis. As was concluded above, when the adsorption capacity is expressed per gram of adsorbent, important differences can be observed between the two carbon adsorbents. Thus, even though the differences vary depending on the gas, the sample with the highest porosity development (AC) always shows a higher adsorption capacity than the carbon monolith ($CO_2 > CH_4 > H_2$). However, when the total storage capacities are plotted the behavior is completely different, and the better results correspond to the carbon monoliths due to their higher densities. This will allow that a greater amount of monolith adsorbent than powdered activated carbons can be loaded into the tank. In summary, all these results highlight the importance of both parameters and their influence for the total storage capacity.

Furthermore, the amount of gas that can be stored only by compression has also been represented in Figures 6(b,d,f). Clearly, the presence of an adsorbent is extremely beneficial (especially for CO_2 and CH_4), since the amount of stored gas is much higher than in the case of the gas which is stored only by compression.

The number of papers in which the total storage capacity is analyzed, has increased during the last few years. However, as far as we know, none has verified experimentally this total storage capacity of an adsorbent on a large scale. With the aim to verify the theoretical results obtained for the total storage capacity on a large scale, two cylinders with the same volume (2.5 l), one empty and the other one filled with 2.64 kg of a carbon monolith were used. Storage measurements for the three gases were performed at room temperature (21±1°C). Because of the constructional limitations of the tanks, the maximum pressure used was 20 bar. The amount of stored gas was obtained by the
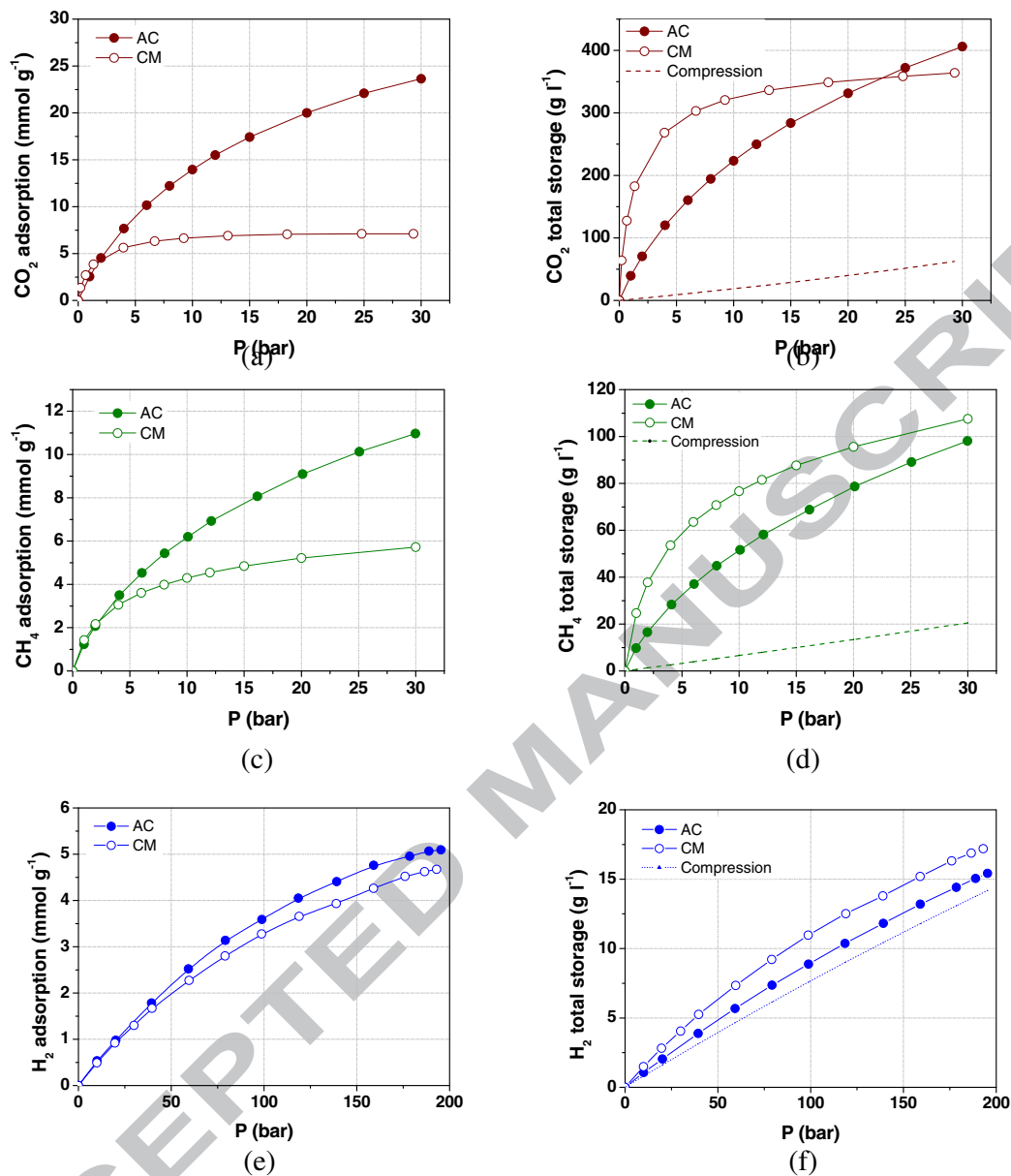
Figure 6. Isotherms of (a,b) CO_2, (c,d) CH_4, and (e,f) H_2. Excess adsorption isotherms at 25ºC for AC and CM materials are shown (a,c,e) on a gravimetric basis, and (b,d,f) as total storage capacities on a volumetric basis, including the thermophysical gas densities due to compression.

increment of weight before and after storage. In Figure 7, data obtained from both tanks and for CO_2, CH_4 and H_2, respectively, are plotted. In all these graphs and for the three gases studied the Figures 7(a,c,e) show the weight of the tank before (degassed tank) and after the storage step (at 20 bar) for the empty tank and for the carbon filled tank.
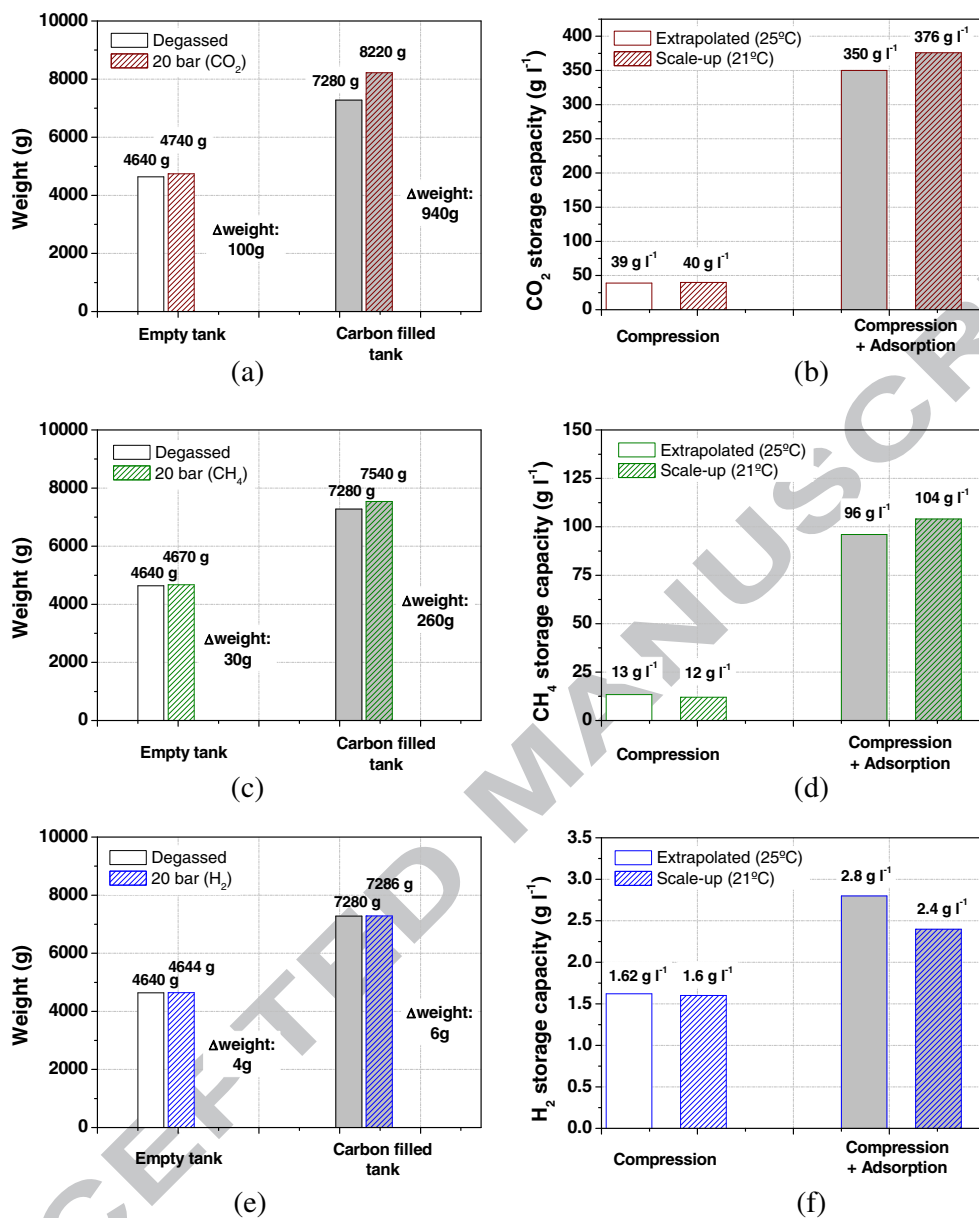
Figure 7. (a,c,e) Comparison between the increase in weight of the gas storage by compression (empty tank) and by adsorption (carbon filled tank) and (b,d,f) comparison between the extrapolated and real gas storage capacities. Results are given for (a,b) CO_2, (c,d) CH_4, and (e,f) H_2.

Likewise, Figures 7(b,d,f) present the comparison of the total storage obtained by compression (empty tank) and by compression + adsorption (carbon filled tank). In both cases, the extrapolated value, obtained from Equation (1) (taking into account the

density of the gas and the adsorption isotherm at 25ºC), and the capacity obtained from the scale-up measurements at 21ºC are represented.

From these results, different aspects are worthy of mention. Firstly, comparing the amount of gas storage by compression and by adsorption, it can be clearly observed that the presence of an adsorbent with suitable properties has important advantages over the empty tank. Thereby, in all the cases, the amount of gas stored in a tank which contains the carbon adsorbent is higher than the amount of gas stored by compression in an empty tank, in both, gravimetric and in volumetric terms. Even in the case of H_2 storage, where much higher pressures are needed for reaching viable storage amounts, the results obtained with the adsorbent are higher when compared with the compression process. At 20 bar, the carbon filled tank can store 376 g l^{-1}, 104 g l^{-1} and 2.4 g l^{-1} of CO_2, CH_4 and H_2, respectively, while the amounts stored by compression are only 40 g l^{-1}, 12 g l^{-1} and 1.6 g l^{-1}, respectively. Therefore, in the cases of CO_2 and CH_4 almost 10 times more gas can be stored by adsorption, in comparison with the amount obtained by compression. In the particular case of H_2, adsorption allows to store 1.5 times more, as compared to compression, even when unfavourable conditions are used (only 20 bar at room temperature).

Finally, the results obtained from the excess adsorption isotherms using small amount of sample (laboratory scale) are compared with the results obtained using large amount of sample (scale-up experiments) in the following. Table 1 compiles the adsorption capacity and the total storage capacity obtained from the excess adsorption isotherms and the scale-up storage, corresponding to the monoliths filling the tank. Both sets of results are in perfect agreement, from this it can be concluded that: (i) the adsorption process presents important advantages over the simple compression for gas storage

Table 1. Comparison of the gas storage obtained from the excess adsorption isotherms and by adsorption on carbon material under practical conditions in the tank cylinders.

Adsorbate	Adsorption capacity from isotherm (mmol/g)[a]	Storage obtained from isotherm (g/l)[a]	Scale-up storage (g/l)[b]
CO_2	6.98	355	376
CH_4	5.22	96	104
H_2	0.92	2.8	2.4

[a] Temperature 25ºC; [b] Temperature 21ºC

applications, and (ii) Equation (1) is suitable for calculating reliable total storage capacities from lab experiments which are in agreement with the results obtained from scale-up measurements.

4. Conclusion

The carbon materials used in this study present a wide range of properties, such as morphology (powdered samples, fibers, and monoliths), pore volume (micropore volumes ranging from 0.2 cm g^{-1} to more than 1.5 cm g^{-1}), narrow micropore volume (ranging from 0.3 to 0.9 cm g^{-1}), and densities (ranging from 0.25 g cm^{-1} to 1.2 g cm^{-1}). This sample selection has allowed to investigate (on a gravimetric and on a volumetric basis) their storage capacities for carbon dioxide, methane, and hydrogen at room temperature and at 30 bar.

On a gravimetric basis, the storage of CO_2, CH_4 and H_2 by adsorption at 30 bar is controlled by the textural properties of the used adsorbent. The correlation between gas excess adsorption and porosity depends on the nature of the adsorbate and on the experimental conditions of the adsorption process. At 25ºC and 30 bar, CO_2 and CH_4 adsorption amounts can be related with the total micropore volumes of the adsorbents. In the case of H_2 adsorption at 25ºC and 200 bar, the adsorption amounts reveal a linear

correlation with the narrow micropore volumes (< 0.7 nm). On a volumetric basis, not only the porosity is important, in fact the density of the adsorbent has the highest impact on the gas uptake.

The scale-up adsorption measurements conducted for CO_2, CH_4, and H_2 in two cylinders with 2.5 l volume (one empty, and the other one filled with 2.6 kg of carbon monolith adsorbent), have shown that at room temperature and for pressures up to 20 bar, the carbon filled tank can store 376 g l^{-1}, 104 g l^{-1} and 2.4 g l^{-1} of CO_2, CH_4 and H_2, respectively. These results are in agreement with results obtained from the adsorption isotherms on laboratory scale and confirm the importance of the sample density when the storage is expressed on a volumetric basis. Also, the scale-up results confirm that gas storage based on physisorption has important advantages over gas compression, when an adsorbent with suitable properties is used. Thus, under similar conditions, CO_2 and CH_4 storage can be increased 10 times when compared to compression.

Acknowledgements

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