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# Preparing a Suitable Material Designed for Methane Storage: A Comprehensive Report

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The preparation of a suitable material designed for methane storage is addressed in the present paper. The main features of methane as an energy source are first recalled, and adsorption is recognized as one of the most efficient ways of storing it. The ideal adsorbent is described next, and it is argued that the best candidates are among microporous carbonaceous materials. Preparation of the most relevant carbon requires appropriate choice of both the precursor and its mode of activation. A discussion leads to the conclusion that anthracites chemically activated with alkaline hydroxides are especially adapted for the intended application, because the highest intrinsic molar capacities ever found so far in the open literature are obtained. However, because of their low density, only low-volume storage capacities are attained with such materials. It is then shown that simple processing allows a significant densification, and, therefore, the formerly accepted target for a viable application of methane as an alternative fuel—150 V/V delivered at 25 °C—is finally met and even exceeded. Thus, the present work is a comprehensive report explaining how a recent problem was solved through a systematical approach.

## Introduction

Air quality is actually a major public health concern, especially in urban areas. Thus, the use of clean fuels for vehicular applications is strongly encouraged, hence the numerous researches made on hydrogen, which is the only fuel that can produce zero emission through fuel cells. However, the storage of such a very light and highly combustible gas has not been completely solved, and hydrogen is not expected to become a common commercial fuel for many years.<sup>1</sup> Therefore, natural gas, which primarily consists of methane, is a valuable alternative fuel with two major advantages, in comparison with gasoline, namely, low cost and clean-burning characteristics. Indeed, methane is inexpensive, because it is very abundant worldwide, which is a highly valuable feature, because of the last two petroleum shocks and the projected lack of crude oil. Also, low emission levels of ozone, unburned hydrocarbon, and oxides of sulfur and nitrogen are observed using natural gas.<sup>2,3</sup> In addition, the greenhouse effect is much less than that of classical liquid hydrocarbon fuels.<sup>4</sup> Finally,

methane has the highest hydrogen-to-carbon (H/C) ratio and, consequently, the greatest energy per unit mass of all the other hydrocarbons.<sup>5</sup>

However, methane is supercritical at room temperature (it has a critical point of  $T_c = 190.6$  K and a critical pressure of  $P_c = 45.8$  atm) and, therefore, cannot be liquefied by compression above  $T_c$ . In other words, it cannot be stored at the same density as the more classical fuels. Thus, storage of the greatest amounts of methane in a given limited volume is a real challenge for its application to both gas transportation and gas-powered vehicles. The latter indeed require, as much as possible, light, small, and diversely shaped tanks.<sup>6</sup> Compressed natural gas should use thick and heavy vessels, generally spherical or cylindrical; hence, it is unpractical for automotive applications. In addition, compressing the gas to 200 bar is a costly process. The liquefaction of methane increases its specific weight and, hence, its energy density, but requires very low temperatures, because its boiling point is 111.2 K. On the other hand, the production of methane hydrates is difficult and still requires low temperatures (close to 0 °C) and high pressures (higher than 35–40 bar), and the preservation of such metastable compounds is an unsolved problem.<sup>7,8</sup>

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Consequently, storing methane via adsorption in porous materials quickly seemed to be one of the best issues, because it combines much lower pressures than those required for compressed natural gas and may be achieved at room temperature, unlike liquefaction. For at least a decade, much effort has been made to produce materials that could adsorb the greatest volume of gas (measured under standard temperature and pressure (STP) conditions) per volume of storage vessel (V/V) at moderate pressures.<sup>2,9</sup> Some time ago, the Atlanta Gas Light Adsorbent Research Group (AGLARG) suggested a target of 150 V/V delivered at 3.5 MPa and room temperature for a viable application of natural gas vehicles.<sup>9,10</sup> In the following discussion in the present article, it will be shown how such a requirement can be met through the discerning choice of adapted materials and preparative routes and final processing of the resulting adsorbent. The target was later revised to 180 V/V;<sup>11</sup> however, it is not clear if such a value corresponds to stored or delivered amounts, which is very different, given that the release of 100% of the stored methane is not obvious at atmospheric pressure. If 180 V/V is a stored quantity, such a target is still met with our materials; otherwise, efforts must be made, because, to the best of our knowledge, so far, no material is able to release 180 L STP (1 atm, 25 °C) of gas per liter of storage vessel.

### Principles of Methane Storage by Adsorption

**Adsorption Basics.** Methane, like any other gas, may be densified by the adsorption phenomenon, for which several molecules formerly in the gaseous phase (i.e., the adsorbate) are retained at the surface of a solid (i.e., the adsorbent). In the case of physical adsorption (which is also called physisorption), the interactions between the adsorbate and the adsorbent are dispersive, of the van der Waals type, and, hence, are very weak. The fixation of methane molecules is then fully reversible and is strongly dependent on both pressure ( $P$ ) and temperature ( $T$ ). Increasing  $T$  considerably hinders adsorption; thus, studying the equilibrium between gaseous and adsorbed phases as a function of pressure is conducted at fixed temperatures: the corresponding experimental data are called adsorption isotherms.

The greater the available surface of the adsorbent, the higher the number of adsorbed molecules at fixed  $P$  and  $T$ . Thus, efficient materials for gas storage are those that have the highest specific surface areas; therefore, porous solids are the best candidates. Among these, active carbons, porous polymers, and amorphous (e.g., silica xerogels) or crystalline (e.g., zeolites) porous ceramics were proposed.<sup>12</sup> However, simple area considerations are not enough to obtain an efficient material: the sizes of the pores are of considerable impor-

tance, especially as far as adsorption of a supercritical gas is concerned. Indeed, the latter does not lead to a condensed phase, but rather only adsorbs in the form of low-density monolayers, in which the molecules are in permanent agitation. Therefore, adsorption predominantly occurs within the pores that are able to create a sufficiently high attractive potential. Such a situation is met as soon as the pore walls are so close to each other that their own potential fields overlap.<sup>13</sup> Thus, the corresponding pores are very narrow, having widths that are typically less than four times the molecular diameter of the considered adsorbate.

In regard to methane, numerical simulations have shown that the maximum density of the adsorbed phase is attained within slit pores 1.12–1.14 nm wide.<sup>13–15</sup> With such an optimal width, two facing CH<sub>4</sub> monolayers may be inserted between pore walls. It should be emphasized that, because of the thermal agitation within the supercritical adsorbed phase, the thickness of a monolayer at 298 K is greater than the van der Waals diameter of methane. Indeed, if CH<sub>4</sub> is assumed to behave similar to a spherical molecule, its diameter is 0.381 nm.<sup>16</sup> Hence, pores that have widths  $W$  of less than  $\sim 1$  nm can accommodate only one monolayer, whereas those narrower than  $\sim 0.4$  nm cannot store methane at all. The existence of an optimal value of  $W$  is also easily understood if wider pores are considered. Indeed, the attractive potential created by the facing pore walls decreases very rapidly with  $W$ , in such a way that it becomes almost that of a simple isolated surface for  $W > 3\text{--}4$  nm.<sup>13</sup> Consequently, in such “wide” pores, methane is poorly adsorbed, and its density is similar to that of the gas phase in equilibrium with it.

Metal-organic frameworks<sup>17,18</sup> were developed recently and were shown to present attractive sorption properties. Very high storage capacities were reported; however, two serious problems were not detailed by the corresponding authors. First, no deliverable amounts were given, whereas such quantities are fundamental for the application of methane as a fuel. Now, methane seems to be strongly entrapped in such structures and heating (up to at least 100 °C)<sup>17</sup> is necessary for the desorption (complete or not). Next, the volume capacity (expressed in terms of V/V) was only estimated from the bulk density of the materials, which are not monolithic. Given that a powder always comprises a large amount of voids, the real volume deliveries are expected to be much lower.

**Why Active Carbons are Better.** Given the previously mentioned considerations, it is clear that the highest adsorption capacities are reached with materials for which the volume of pores that have the relevant width is the highest. In addition, slit-shaped pores were shown, from numerical simulations, to lead to higher volumetric methane storage than any other geometry.<sup>19,20</sup> For these reasons, active carbons (having such slit-shaped pores, the widths of which can be tailored)

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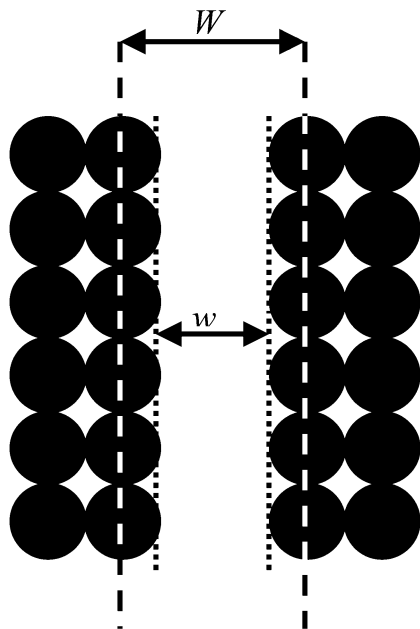
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**Figure 1.** Schematic definition of the pore size ( $W$ ), which is the physical interlayer spacing measured between the centers of C atoms of a slit-shaped pore, and the inner, effective, pore width ( $w$ ), which is the actual available space of a slit-shaped pore.

show greater performance than zeolites, for example. Moreover, zeolites present much more hydrophilic surfaces than carbons and, hence, have a tendency to adsorb water preferentially. Active carbons may be seen as comprising crumpled graphene sheets and ribbons,<sup>21,22</sup> the loose stacking of which is responsible for the high porosity present in these materials. Depending on the spacing between the carbon surfaces, various types of pores are encountered. According to the IUPAC classification,<sup>23</sup> micropores correspond to voids such that the inner pore-wall spacing ( $w$ ) is  $<2$  nm. In active carbons, micropores are slit-shaped, as shown in Figure 1, wherein the definitions of both the physical pore width  $W$  and the really accessible inner space  $w$  are specified. The parameter  $w$  is usually measured through the adsorption of various probe molecules (such as  $\text{CO}_2$  near room temperature or  $\text{N}_2$  at 77 K) and is given by the relation  $w = W - 2r_{\text{C}}$ ,<sup>24</sup> where the radius of a C atom ( $r_{\text{C}}$ ) is assumed to be the half of the normal separation of planes of graphite, i.e., 0.17 nm. Hence, the optimal pore width that has been discussed previously ( $W \approx 1.14$  nm) corresponds to an ideal inner pore size of  $w \approx 0.8$  nm. With such an ideal value of  $w$ , the sorbed phase indeed has the highest density at 3.5 MPa.<sup>25</sup> Coming back to the IUPAC classification of pores, mesopores are the voids with an inner space dimension of  $2 < w < 50$  nm, and macropores are those

with inner widths of  $>50$  nm.<sup>23</sup> The two last types of voids have rather cylindrical shapes or, at least, may be modeled as such, especially when porosimetry techniques such as intrusion of mercury are used. Although micropores of suitable widths are required to obtain the highest methane uptakes, a small fraction of wider pores are nevertheless necessary for heat and mass transfer throughout the adsorbent bed; average widths of 1.5 and 2.5 nm were proposed for optimized charge and discharge steps, respectively.<sup>26</sup>

Among the possible materials that can be used for methane storage, active carbons are those which have the highest micropore volumes. Thus, the most microporous carbons are clearly required to obtain the highest adsorption capacities; however, the role of the other pores should not be minimized. Although, indeed, useless for storage, their presence is necessary for the transport of methane throughout the material. It was calculated that a hypothetical monolithic adsorbent, only consisting of parallel carbon layers that form micropores with the optimal width, would be able to store a theoretical maximum of 28 mol of methane per kilogram of material at 3.5 MPa and room temperature.<sup>14</sup> However, because such an unphysical adsorbent is free of voids, allowing the diffusion of the gas toward the microporosity, and that an ideal affinity between the adsorbed phase and the carbon surface was assumed in the calculation, real storage capacities are expected to be much lower.

### Preparation of the Relevant Active Carbon

**Possible Precursors.** Active carbons may be prepared from a large number of precursors, possibly having a vegetal origin, such as wood and other lignocellulosic matters, or may be mineral carbons forms, such as lignite and anthracite, or may be purely synthetic, such as organic gels and polymers in general. Choosing the best precursor requires considering several criteria, such as coke yield, pore texture, density, and purity of the resultant carbon, as well as cost. Carbons derived from vegetal matter are inexpensive and, hence, are widely used for many purposes; they may contain high levels of mineral impurities, and the maximum expected coke yields are  $\sim 50\%$ . In addition, because of their particular pore texture, which retains that of the former vegetal cells, low-density materials ( $<1$  g/cm<sup>3</sup>) are obtained, within which large pores (which are useless for methane storage) are present. Mineral carbons do not require a preliminary pyrolysis, because they are already, more or less, evolved coals. Anthracites are usually rather pure, whereas lignites may have high ash contents. Such materials possess high densities ( $\sim 2$  g/cm<sup>3</sup>) and are rather inexpensive. Finally, carbons prepared from polymers may have very different characteristics,<sup>27</sup> especially various tailored pore textures, depending on both the precursor and the thermal treatment. The major drawback of such adsorbents is that they are very expensive and are, hence, reserved for specialized applications, such as molecular sieving.

Whether it is pyrolyzed or not, the precursor or its resultant char is not directly suitable for adsorption

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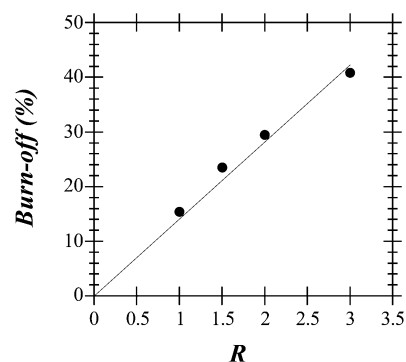
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purposes, since its microporosity is low. New pores must be created and/or former pores (open or closed) must be widened and made accessible through a necessary activation process.

**Possible Activation Processes.** Activation is a controlled oxidation of the carbon that leaves a more-or-less developed porosity. Two possible separate activation processes, termed physical and chemical, are usually applied. Physical activation is a two-step process: the precursor is first pyrolyzed in an inert atmosphere at temperatures close to 700 °C, so that most of the volatile matters are removed. The resultant char is next gasified by formation of carbon monoxide (CO) through the oxidative action of either steam or carbon dioxide (CO<sub>2</sub>) at high temperatures. The weight loss of the char, expressed as a percentage, is called burnoff. Depending on the level of burnoff, which is usually fixed by the duration of the activation, the final amount of porosity and the type of pores that prevails, and also their average widths, may be adjusted approximately. However, increasing the burnoff unavoidably induces a widening of all the families of pores; hence, high micropore volumes can never be obtained alone, but are always accompanied by non-negligible amounts of mesopores and macropores. In contrast, chemical activation is a single-step process. The raw precursor is mixed with an activating agent, and such a mixture is directly pyrolyzed in an inert atmosphere at temperatures usually less than those required for physical activation. The activating agents are strong dehydrating reagents and sometimes also are able to oxidize carbon at the considered heat-treatment temperature; these are, for example, concentrated orthophosphoric and perchloric acids, anhydrous salts of transition metals, and metallic hydroxides. Depending on both the activating agent and the precursor, very different pore textures may be obtained, from almost only microporous to highly mesoporous. Moreover, the carbon yield is usually high, because the activating agents minimize the production of volatile tars, because of an effective cross-linking action. It is then clear that, because it allows the preparation of almost purely microporous materials, chemical activation should be preferred.

Among the classical reagents that can be used for chemical activation, alkaline hydroxides seem to be those for which the microporosity of the as-prepared materials is the most developed. Such a statement is of first importance, because it was argued previously that the materials that have the greatest micropore volumes are those for which the highest methane storage capacities are expected. Potassium hydroxide (KOH) is the most classical hydroxide that is used as an activating agent, usually according to the following protocol. A very concentrated aqueous KOH solution is prepared, with which the precursor is impregnated; the resultant paste is then dried and next pyrolyzed. Brunauer–Emmett–Teller (BET) surface areas as high as 3200 m<sup>2</sup>/g were reached with anthracite precursors,<sup>28,29</sup> which obviously led to very interesting methane storage capacities (~12.5 mol/kg at 3.5 MPa and 25 °C).<sup>2,29</sup> However, sodium hydroxide (NaOH) was recently shown to be



**Figure 2.** Evidence of a linear relationship between the burnoff and the NaOH/carbon mass ratio ( $R$ ).

particularly advantageous, because of its lower cost, simpler handling, and lower corrosive action than KOH.<sup>30,31</sup> Indeed, materials that present unexpectedly high surface areas and micropore volumes, of the same order of magnitude of those already found with KOH, were obtained by a simple physical mixing of NaOH beads with anthracites and subsequent pyrolysis.<sup>30–32</sup> Even if NaOH and KOH are related compounds, the direct transfer of the results from KOH activation to NaOH activation is not straightforward at all. Indeed, the reaction mechanisms of these two hydroxides are known to be different. Indeed, KOH intercalates between carbon layers,<sup>33,34</sup> whereas NaOH reacts with the most energetic sites of the surface, thus presenting a reactivity that is strongly dependent on both the rank and crystallinity of the carbonaceous precursor.<sup>31,35,36</sup> Given the aforementioned remarks, the effect of NaOH activation on the pore texture and the corresponding methane storage capacities is worthy of further detailed study. It seems that NaOH is a good activating agent of high-rank coals, but is rather poor for biomass, for which KOH should be used. Finally, unlike what is classically encountered with chemical activation, namely, a lack of adequate control over porosity development,<sup>37</sup> using definite amounts of NaOH advantageously leads to definite burnoffs, as evidenced by Figure 2, which involves the anthracite that will be discussed below.

Given the aforementioned results, the method of preparing a highly efficient active carbon for methane storage can be identified.

**Choice of Both Precursor and Activation Process, and Evaluation of Methane Storage Capacities.** Because of their low reactivity toward steam or CO<sub>2</sub> activation (up to several days at 800 °C to reach a burnoff level of 50%), anthracites are not often used as precursors of active carbons.<sup>38</sup> However, these materials have a well-developed but narrow pore structure (and,

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hence, may be activated, because activation requires the presence of an initial porosity), are abundant in the world, and have a high carbon content and, usually, high densities. Some authors have shown that these materials could be interesting precursors and that their reactivity could be increased after specific pretreatment (such as preoxidation<sup>39–41</sup>) or after impregnation with  $\text{HClO}_4$ , followed by a thermal shock treatment,<sup>42</sup> or, more drastically, after exfoliation.<sup>43</sup> In addition, raw anthracites that have a very low ash content are easy to find and, when activated with alkaline hydroxides, no cumbersome reaction products are produced. Rinsing the resultant active carbon with an acidic solution allows us to eliminate completely the possible unreacted hydroxide and the carbonates formed during the activation<sup>44</sup> and further reduces the level of mineral matters initially present. Thus, a very pure material can be prepared.

Because NaOH was determined to lead very easily to high micropore volumes, which are associated with a very slightly developed mesoporosity, it was preferred to KOH. Precursor and activation parameters were modified to reach higher methane storage capacities than those which, although yet very interesting, were obtained previously.<sup>2,29</sup> For that purpose, a German anthracite, from the Sophia mine, was chosen; it was first ground and sieved to collect the grains whose average size is in the range of 100–200  $\mu\text{m}$ . With such small grains, the activation was indeed expected to be homogeneous and efficient at any point of the material. The anthracite powder was then simply physically mixed with NaOH beads according to various mass ratios of  $R = \text{NaOH/anthracite}$  (in the range of  $R = 1$ –3). The mixture next was introduced into a nickel crucible, closed by a circular nickel sheet of the same diameter, and finally heat-treated in a vertical furnace under a stream of nitrogen with a flow rate of 400 mL/min. A heating rate of 5 K/min was applied up to the final activation temperature  $T_a$ , which was maintained for 1 h; several  $T_a$  values were tested, in the range of 600–830  $^\circ\text{C}$ . The crucible was then allowed to cool to room temperature under a nitrogen flow.

The methane uptakes were measured at 20  $^\circ\text{C}$  and up to 3.5 MPa in a vessel that was full of the adsorbents prepared using various activation parameters. The classical volumetric method was applied, using a Honeywell 0–40 MPa pressure transducer with an accuracy of  $\pm 0.1\%$ . The powdery adsorbents were poured (i.e., first uncompacted) into a stainless-steel sample holder that had a volume of  $\sim 1.6 \text{ cm}^3$  and were outgassed overnight at 250  $^\circ\text{C}$  under secondary vacuum. After such a complete evacuation, the storage vessel, which was full of adsorbent under vacuum, was accurately weighed.

The entire volumetric apparatus was immersed into a thermostatic bath that was maintained at a temperature of  $20 \pm 0.1 \text{ }^\circ\text{C}$ . The methane uptake was measured point to point by discontinuous introduction of the adsorbate (commercial cylinder, with a purity of  $>99.5\%$ ) into the sample holder; all the measurements were corrected from the compression of gaseous methane outside of the vessel, i.e., in the parts of the device free of adsorbent (tubes and valves). The number of moles of methane really stored in the sample holder alone was then obtained by application of the van der Waals equation of state for methane. At the end of each isotherm, the maximum amount thus stored was also checked by weighing the vessel. The delivery, which was calculated by differentiating the amounts (measured by the isotherm) stored at 3.5 and 0.1 MPa, was recovered by weighing the vessel again, after allowing the methane to be released at room temperature and normal pressure. For each material, a comparison of what was deduced from the isotherms and what was obtained from the weighing was thus performed. Identical results for the stored amounts on one hand, and for the delivery amounts on the other hand, were always obtained within average and maximum uncertainties of  $\pm 5\%$  and  $\pm 10\%$ , respectively. In addition, all the pore textures were systematically investigated but are not detailed here; developments of the method and discussion of the results may be found elsewhere.<sup>44</sup> Especially, the micropore volumes  $V(\text{N}_2)$  and  $V(\text{CO}_2)$  were obtained by application of the theory of Dubinin–Radushkevitch<sup>45</sup> to the adsorption isotherms of nitrogen at 77 K and  $\text{CO}_2$  at 298 K, respectively. The micropore size distributions were calculated using the Dubinin–Stoeckli method<sup>46,47</sup> applied to the nitrogen sorption isotherms at 77 K. Finally, the mesopore volumes  $V(\text{C}_6\text{H}_6)$  and their distributions of sizes were determined by application of the Kelvin equation and capillary condensation theory<sup>48–50</sup> to the adsorption isotherms of benzene at 298 K.

A few storage isotherms of the as-poured adsorbents powders, showing the molar capacity  $Q$  (in units of moles of methane stored per kilogram of material into the vessel filled with it) of the anthracite activated with NaOH at different activation temperatures and  $R = 3$ , are given in Figure 3(a). Type I-like isotherms, according to the IUPAC classification,<sup>23</sup> are obtained. However, at the highest equilibrium pressures (typically  $> 2 \text{ MPa}$ ), such isotherms are rather straight, evidencing that methane does not adsorb anymore but is simply compressed in the largest pores (mesopores, macropores, and intergranular voids). It was then interesting to calculate the true adsorption capacity ( $Q^*$ ) of the materials, assuming that adsorption occurs within the micropores alone. For that purpose, the volume occupied

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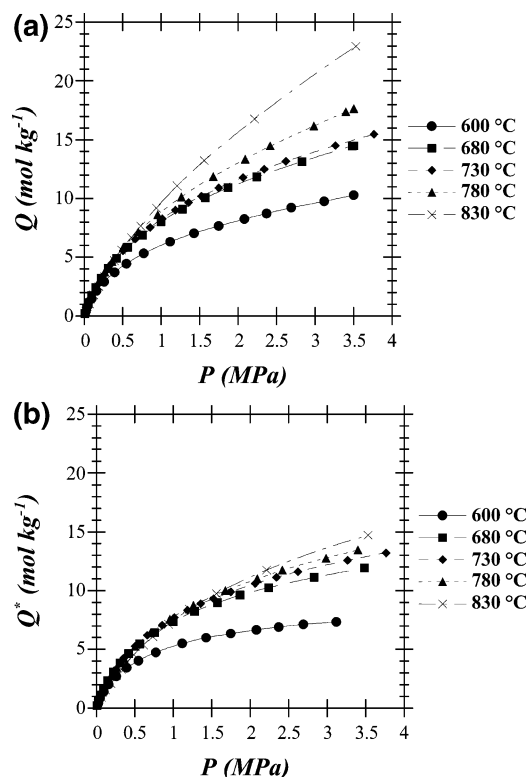
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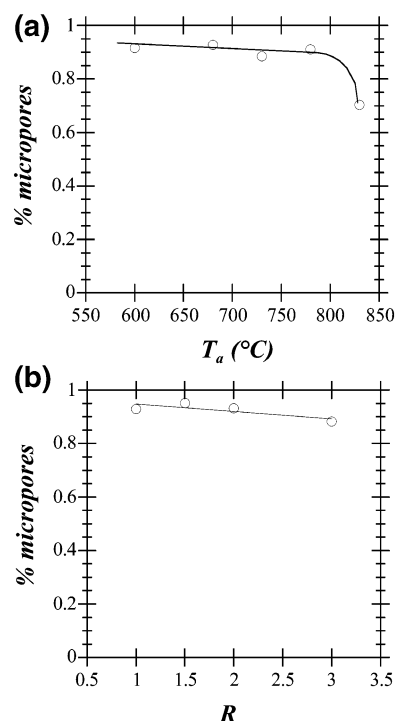
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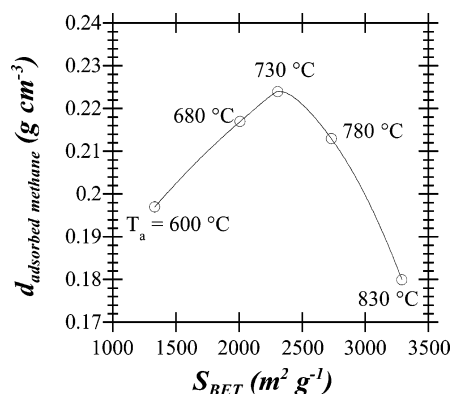
**Figure 3.** (a) Measured molar methane uptake (20 °C),  $Q$ , of the anthracite activated with NaOH at several temperatures  $T_a$  with a fixed NaOH/carbon mass ratio ( $R = 3$ ). (b) Calculated molar amount of methane at 20 °C ( $Q^*$ ), stored only in the micropores of the same materials.

by the C atoms (assuming a bulk density of 2.2 g/cm<sup>3</sup> for the carbonaceous backbone) and the volume of the micropores ( $V(N_2)$ ) were subtracted from the volume of the storage vessel. The number of moles of methane purely compressed in the remaining spaces was thus calculated, and, hence, the amount of methane stored only in the micropores of the materials could be derived. The “corrected” storage isotherms, i.e., taking into account only the fraction of methane that is present within the micropores, are presented in Figure 3b. It can be observed that the straight high-pressure portions of the curves in Figure 3a have disappeared and typical Langmuirian (Type I) isotherms are now obtained.

**Choice of the Most Suitable Preparation Parameters and Ultimate Pore Texture Refinements.** Whatever the  $R$  or  $T_a$  value, highly microporous materials were prepared, as shown in Figure 4a and b, wherein the micropore fractions of the total pore volume, expressed by the ratios  $(V(N_2) + V(CO_2))/(V(N_2) + V(CO_2) + V(C_6H_6))$ , were plotted. With such materials, very large BET surface areas are obtained (up to 3300 m<sup>2</sup>/g); however, the best gas storage performances are not directly associated with their absolute values, because the pore widths are crucial. Thus, high areas may be obtained either with ultrafine micropores, which are too narrow for methane adsorption, or with numerous wider pores, in which the sorbed phase is not suitably densified. In other words, the greatest density of adsorbed methane does not correspond to the most developed surface area, as evidenced by Figure 5, for example. Such results of calculated density were obtained by dividing the mass of methane trapped in the micropores only (obtained through the value of  $Q^*$ ) by the corre-



**Figure 4.** Micropore fraction of the pore volume within an anthracite activated with NaOH: (a) at several temperatures  $T_a$  with a fixed NaOH/carbon mass ratio ( $R = 3$ ), and (b) at several  $R$  values, keeping the activation temperature fixed at  $T_a = 730$  °C.

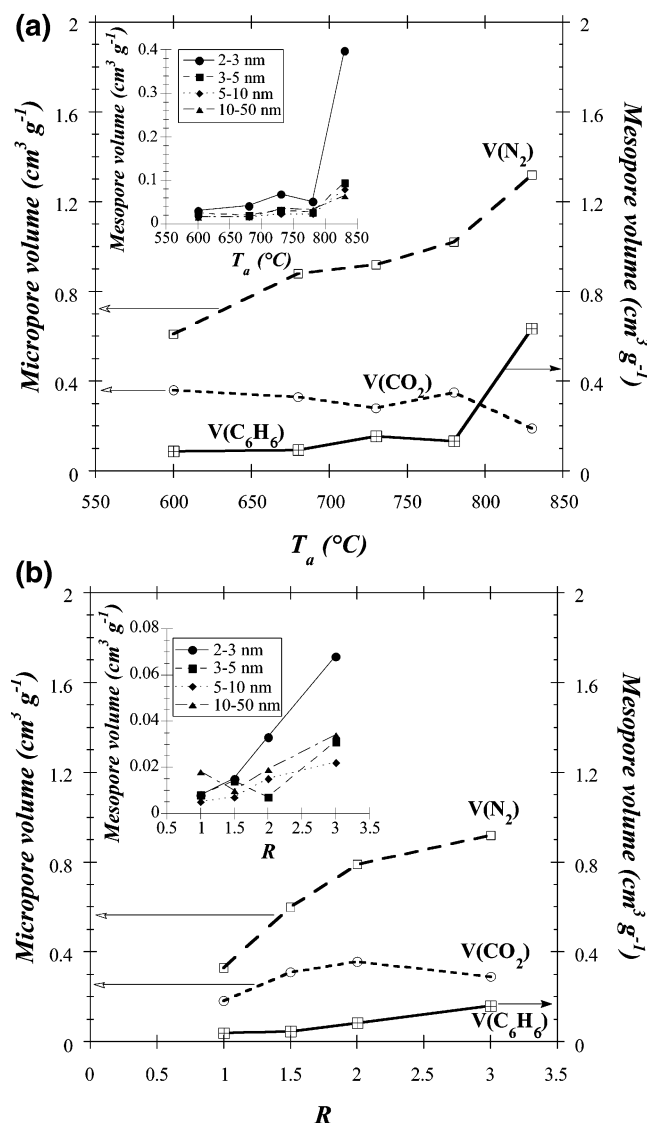


**Figure 5.** Calculated density of the methane adsorbed within the micropores, as a function of the BET surface areas of anthracite activated at various activation temperatures (given on the plot), and keeping a constant NaOH/carbon mass ratio of  $R = 3$ .

sponding micropore volume. It may be seen that densities of ~0.2 g/cm<sup>3</sup> are attained; these values are ~10 times greater than that of compressed methane at the same pressure. Thus, the benefit of adsorption for storing methane is clearly demonstrated here.

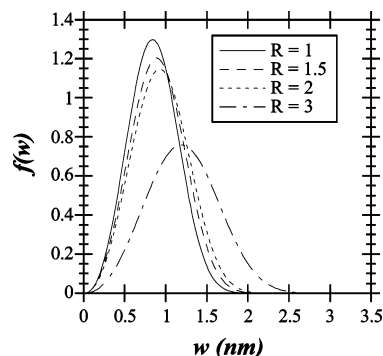
Figure 6a shows the evolution of both types of micropore volumes and mesopore volumes, as a function of the activation temperature at a fixed NaOH/anthracite weight ratio of  $R = 3$ . Given the respective molecular diameters of CO<sub>2</sub> and N<sub>2</sub>,  $V(CO_2)$  represents the volume of the ultramicropores, which have effective pore widths of 0.33 nm <  $w$  < 0.7 nm, whereas the difference  $V(N_2) - V(CO_2)$  corresponds to the volume of the supermicropores, such that 0.7 nm <  $w$  < 2 nm.<sup>44</sup> From the pure point of view of methane storage, only the supermicropore volume should be maximized, because





**Figure 6.** Micropore ( $V(N_2)$  and  $V(CO_2)$ ) and mesopore ( $V(C_6H_6)$ ) volumes of an anthracite activated with NaOH: (a) at several temperatures  $T_a$  with a fixed NaOH/carbon mass ratio of  $R = 3$ ; (b) at several  $R$  values, keeping the activation temperature fixed at  $T_a = 730$  °C. Insets show the detailed mesopore volumes as a function of their widths.

the  $CH_4$  molecules are efficiently and reversibly adsorbed in such pores. In contrast, ultramicropores generate highly attractive potentials; hence, methane is strongly retained and can desorb only at subatmospheric pressure. Now, one must get the maximum deliverable amount of methane under the standard operation conditions of the storage vessel, i.e., the gas should be released while the pressure is decreased from 3.5 down to 0.1 MPa. Consequently, ultramicropores are responsible of what could be termed the “irreversible capacity” (though, as explained above, the phenomenon is not really irreversible, and pumping on the material would be enough to desorb the remaining methane), while the supermicropores account for the “reversible” capacity. According to Figure 6a, both ultramicropore ( $V(CO_2)$ ) and mesopore ( $V(C_6H_6)$ ) volumes remain almost constant, as long as  $T_a$  is less than 780 °C. Because the total micropore volume  $V(N_2)$  increases as the activation temperature increases, such an increase is due to the development of supermicroporosity alone



**Figure 7.** Micropore size distributions, derived from application of the Dubinin–Stoeckli method to the nitrogen adsorption isotherms at 77 K, of anthracite activated at several  $R$  values and a fixed activation temperature of  $T_a = 730$  °C.

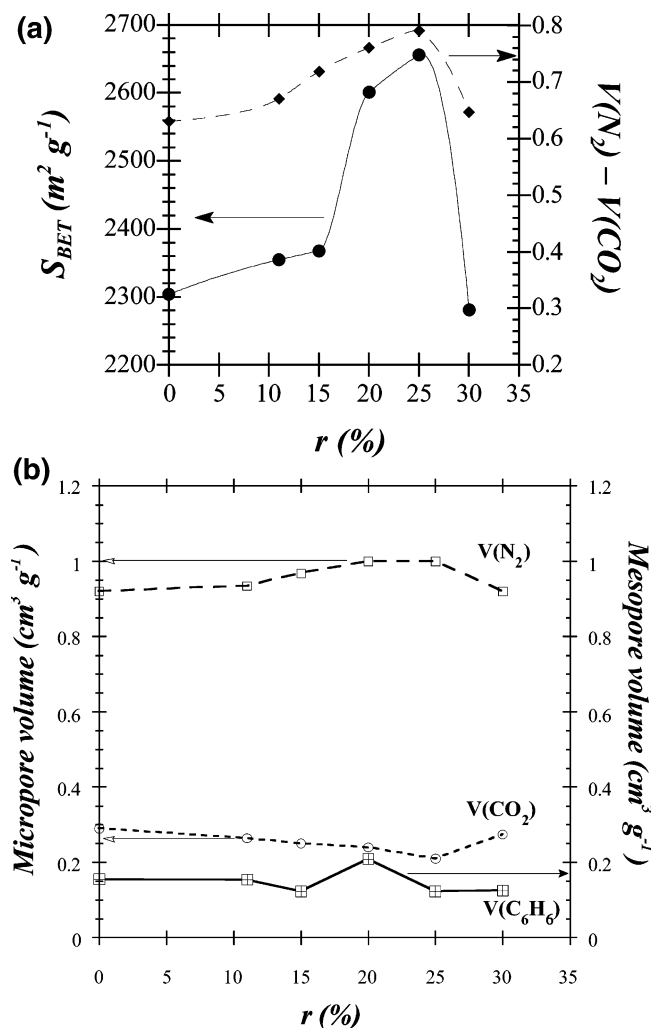
(because  $V(CO_2)$  is constant), which phenomenon is very favorable. However, reaching a temperature of 830 °C leads to non-negligible mesopore volumes, which should be avoided, even if the micropore volume is the highest at such a  $T_a$  value. Indeed, the lower the volume of useless large pores, the higher the mass of adsorbent that can be introduced into a given storage vessel. Hence, as demonstrated below, more volumes of methane may be stored in the carbons that lead to the sorbed phase having the highest density. Finally, note that the narrowest mesopores are determined to be the most sensitive to the activation temperature (see the inset of Figure 6a).

Figure 6b is the same as Figure 6a but now involves varying the value of  $R$  at a fixed activation temperature of  $T_a = 730$  °C. The microporosity develops while  $R$  increases. As long as  $R$  is  $< 2$ , both the ultramicropore and mesopore volumes remain almost constant and, hence, an increase of the supermicropore volume prevails, which is again very favorable. Higher  $R$  values lead to higher mesopore volumes, which should be avoided for the same reasons as previously stated. At this point of the paper, it seems that conditions of  $T_a = 730$  °C and  $R = 2$ , which both lead to very high supermicropore volumes (in which the density of adsorbed methane is the highest) without creating additional mesoporosity, are the best activation parameters. Indeed, Figure 7 clearly shows that the material prepared following such experimental conditions presents a narrow micropore size distribution, centered on a value close to the optimal effective width of 0.8 nm.

The effect of adding controlled amounts of water to the anthracite powder before mixing it with the NaOH lentils was also investigated. A wetting ratio ( $r$ ) was defined as the weight ratio of water to anthracite, and experiments that varied  $r$  were performed, keeping  $T_a$  and  $R$  fixed at 730 °C and 3, respectively. It may be observed in Figure 8a and b that an optimum exists at  $r \approx 20\%–25\%$  of wetting; however, the effect is low (pore volumes vary by  $\sim 10\%$ ) and just corresponds to an adjustment of the pore texture. A very interesting point is that, at such an ideal value of  $r$ , the supermicropore volume is the highest, whereas the ultramicropore volume is the lowest. This means that the deliverable capacity of the adsorbent is the highest at such an optimal wetting ratio.

Ultimate refinements of the pore texture may be achieved through post-carbonization of the material in





**Figure 8.** (a) BET surface area and supermicropore ( $V(N_2) - V(CO_2)$ ) volume and (b) micropore ( $V(N_2)$  and  $V(CO_2)$ ) and mesopore ( $V(C_6H_6)$ ) volumes of an anthracite wetted at several water/anthracite weight ratios ( $r$ ) and next activated with NaOH, keeping  $T_a$  and  $R$  fixed at 730 °C and 3, respectively.

an inert atmosphere, followed by a moderate physical post-activation using either steam or  $CO_2$ . Both treatments lead to the widening of the ultramicropores, thus becoming supermicropores, without appreciable modification of the other pore characteristics.<sup>51</sup> Since more supermicropores and less ultramicropores are obtained, higher reversible storage capacities are expected.

As a last remark, it should be stressed that, regardless of the activation parameters, the presence of a low amount of mesoporosity is unavoidable and even necessary for gas transfer throughout the adsorbent; otherwise, charging and emptying of the storage tank is strongly hindered.

### Storage Capacities of the Adsorbents and Role of Processing

**Molar Storage Capacities.** So far, the storage capacity of the materials ( $Q$ ) and that of their micropores alone ( $Q^*$ ) were expressed in units of moles stored per kilogram of active carbon. Such quantities are representative of the intrinsic sorption properties

of the considered material but do not correspond to the actual behavior of a tank filled with it. Indeed, depending on the amount of adsorbent that can be introduced in a vessel having a given size, more-or-less STP volumes of methane can be stored. This is the reason the storage capacities should also be expressed in units of  $V/V$ , according to the following equation:

$$Q'(V/V) = Q(\text{mol/kg}) \times M \times v \times d_{\text{app}} \quad (1)$$

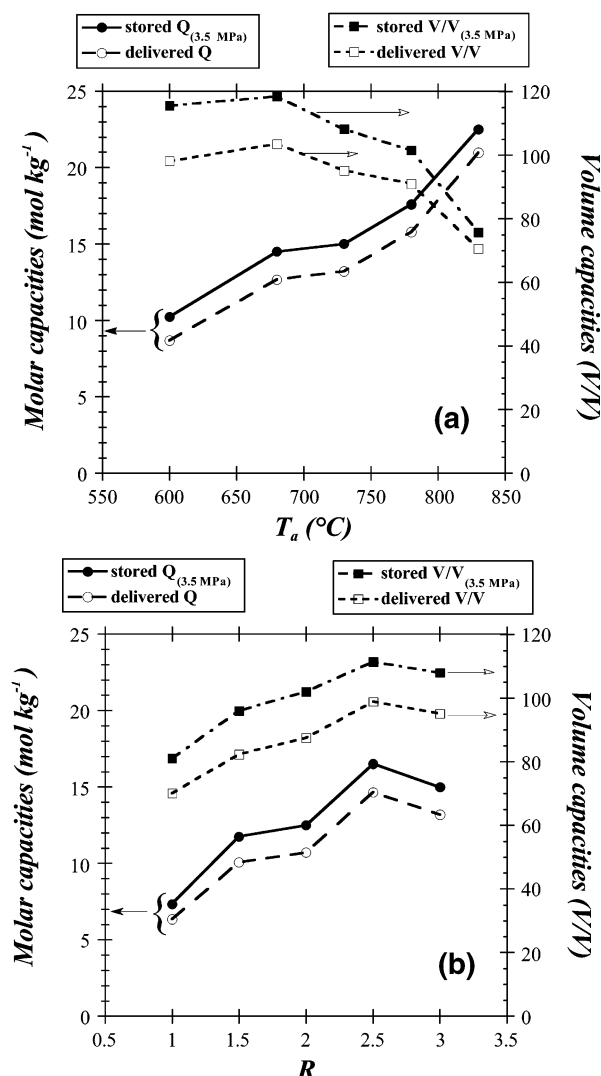
In eq 1,  $d_{\text{app}}$  is the apparent density (in units of  $g/cm^3$ ) of the adsorbent bed (uncompacted, so far),  $M$  is the molecular weight of methane ( $M = 16$  g/mol), and  $v$  is the volume occupied by 1 g of methane under the STP conditions ( $v = 1.5$  dm<sup>3</sup>/g). Getting high values of  $Q$  (in units of mol/kg) may be achieved, as observed previously, by a deep activation of the carbonaceous precursor. However, doing this, much porosity is created and, hence, the apparent density of the resultant material decreases rapidly. Since  $Q$  (in units of mol/kg) and  $d_{\text{app}}$  vary in opposite ways, an optimum value of  $Q'(V/V)$  should exist.

Such a maximum of  $Q'(V/V)$  is observed for the materials that have been activated at  $T_a = 680$  °C with  $R = 3$  (see Figure 9a), whereas the optimum appears at  $R = 2.5$  for materials activated at  $T_a = 730$  °C (see Figure 9b). The deliverable amounts of gas are also given on the corresponding plots; such quantities are indeed very useful, because they correspond to what is actually released by the storage tank while its inner pressure decreases from 3.5 MPa down to 0.1 MPa. It should also be emphasized that the molar capacities measured at 3.5 MPa are close to 20 mol/kg. These values, which are obviously below the theoretical limit given in the second section of this paper, are nevertheless the highest ever found in the open literature. Indeed, the best result reported so far was 15.6 mol/kg (including, similar to our own data, the gas phase) with Kansai Maxsorb material,<sup>52</sup> whereas 15.5 mol of methane stored per kilogram of adsorbent were measured in activated mesocarbon microbeads.<sup>15</sup> Finally, more-typical results, although very interesting, involve a maximum of 14 mol/kg, using potash-activated anthracites.<sup>29</sup> Such exceptional performances are attributed to the pore texture of the activated anthracite, which is really optimized for the intended application. However, expressing them in units of  $V/V$ , the storage capacities are rather disappointing, because they are hardly above average. Many standard (and usually commercial) active carbons indeed present volume storage capacities of  $\sim 100 \pm 20$  V/V.<sup>12</sup> The reason lies on the very low density of the packing of active carbon powder, preventing any efficient filling of the storage tank by the adsorbent. A processing of the latter thus seems to be necessary, because the target is a delivery of 150 V/V.

**Processing of the Adsorbent.** So far, the storage properties of the loose-packed activated anthracites (i.e., those simply poured into the vessel) were reported. Reducing the dead space within the storage tank may be achieved in various ways, such as the use of mixtures

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**Figure 9.** Storable and deliverable molar capacities, both measured for a vessel full of activated carbon ( $Q$ ), and calculated in the micropores only ( $Q^*$ );  $Q$  and  $Q^*$  are given in units of mol/kg. Also shown are the storable and deliverable volume capacities of the same vessel full of activated carbon (in units of V/V): (a) effect of the activation temperature  $T_a$  at a fixed NaOH/carbon mass ratio of  $R = 3$  and (b) effect of  $R$  at a fixed activation temperature of  $T_a = 730$  °C.

of grains of well-chosen different sizes,<sup>53–56</sup> the preparation of compact monoliths using binders,<sup>2,9,57,58</sup> and uniaxial compression of powders (with or without additives). Only two methods—the mixture of grains and powder compression—are introduced here, because making monoliths is not believed to be so advantageous, given the expected partial filling and closure of the pores by the binder. A bimodal blend was prepared using the

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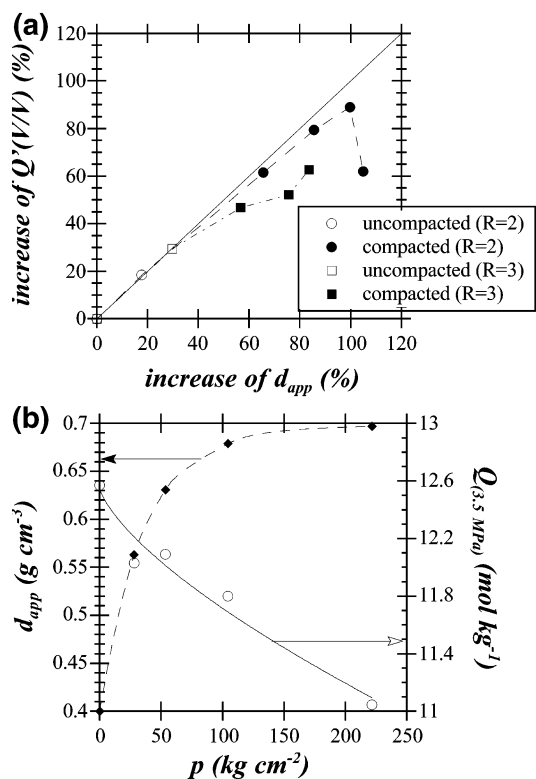
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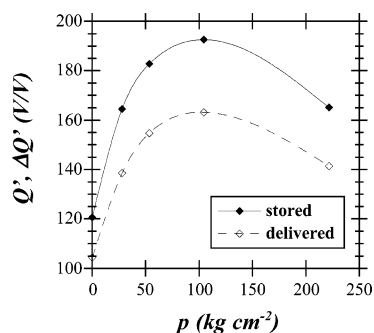


**Figure 10.** (a) Experimental effect of both mixing two granulometric fractions and pressing the blend, on the relative increase in volume storage capacity  $Q'(V/V)$ , plotted versus the relative increase of apparent densities of the powders. Anthracites activated at a same temperature (730 °C) with two values of  $R$  are compared. (b) Effect of compaction pressure ( $p$ ) both on the apparent density ( $d_{app}$ ) of the bimodal activated anthracite powder ( $T_a = 730$  °C,  $R = 2$ ) and on the molar storage capacity measured at 3.5 MPa.

granulometric 100–200  $\mu$ m fraction mixed with the 0–100  $\mu$ m fraction, in such a way that the mass ratio of the biggest grains to the smallest grains is 3/1. This mixture was next introduced into a cylindrical stainless-steel tube and compacted uniaxially at various pressures. Two anthracites, activated at 730 °C with different NaOH/carbon ratios ( $R = 2$  and 3) were investigated; the greater the burnoff (the higher  $R$ ), the more brittle and the more easily crushed the material.

Preparation of a mixture of two granulometric fractions obviously does not change the pore texture parameters (details may be found elsewhere<sup>59</sup>); however, it does lead to an important increase—up to 30%—in the volume capacity, thanks to the almost-identical increase of the apparent density. Increases of both  $Q'(V/V)$  and  $d_{app}$  are then strictly proportional for the uncompact material, as seen in Figure 10a. Application of compaction pressures  $p$  of up to 100 kg/cm<sup>2</sup> on the bimodal powder produces a significant compaction, whereas the application of higher pressures does not change the apparent density of the packing as much, as shown in Figure 10b. The effect of  $p$  on the volume storage capacity is clearly evidenced in such a way that the relative increase of  $Q'$  is lower than that of  $d_{app}$  (see Figure 10a). As suspected, the more-brittle carbon ( $R = 3$ ) is much more influenced by pressure than its less-

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**Figure 11.** Volume storage ( $Q'$ ) and delivered ( $\Delta Q'$ ) capacities of the anthracite ( $R = 2$  and  $T_a = 730$  °C) measured as a function of the compaction pressure  $p$  applied on the powder.

activated counterpart ( $R = 2$ ). In addition, as shown in Figure 10b, the molar storage capacities  $Q$  measured at 3.5 MPa decrease, on average, with the applied pressure. Such a phenomenon was attributed to a partial pore collapse occurring upon compaction of the material.<sup>59</sup> Because  $Q$  and  $d_{app}$  vary in opposite ways while  $p$  increases, the volume storage capacities  $Q'(V/V)$  are expected to have an optimum value at a given  $p$ .

The absolute measured volume storage capacities are plotted as a function of the applied compaction pressure  $p$  in Figure 11 for the anthracite activated at  $R = 2$  and  $T_a = 730$  °C. The latter material is indeed more easily studied than that prepared with  $R = 3$  at the same temperature, for which the compaction-induced reduction of  $Q_{3.5 \text{ MPa}}$  was observed for applied pressures as low as  $p = 30$  kg/cm<sup>2</sup>. In Figure 11, the presence of an optimum in V/V is clearly seen, beyond which the amounts of methane that can be stored and delivered are decreasing functions of the pressure. Indeed, it was recently demonstrated that pressing onto the powdery active carbon induces both the increase of  $Q_{0.1 \text{ MPa}}$  and the decrease of  $Q_{3.5 \text{ MPa}}$ . This phenomenon, evidenced by pore texture investigations,<sup>59</sup> is due to the fact that some supermicropores may become ultramicropores within which methane is strongly adsorbed, whereas some mesopores may become supermicropores that are slightly too wide to adsorb methane efficiently. As a result, the amount of deliverable methane ( $\Delta Q = Q_{3.5 \text{ MPa}} - Q_{0.1 \text{ MPa}}$ ) is reduced. An increase in the volume storage capacity  $Q'(V/V)$  is then possible only if the relative loss of  $\Delta Q$  is compensated by a more-rapid relative increase in the apparent density. This happens below an optimal pressure at which the number of deliverable V/V is the highest, as observed in Figure 11. Conversely, above such an optimal compaction pressure, pore collapse prevails and, hence, the resultant volume capacity decreases. At a pressure of  $p \approx 100$  kg/cm<sup>2</sup> applied to the bimodal carbon powder ( $R = 2$ ), both the storage and the deliverable capacities—193 and 163 V/V, respectively—are, to the best knowledge of the authors, the highest ever reported so far in the open literature. Indeed, very elevated storage capacities were formerly reported, but never that high: 186 V/V stored in a monolith that was composed of AX-21 active carbon bound with 2% poly(vinyl alcohol) (delivery unknown),<sup>58</sup> 166 V/V stored for both compressed active carbon fibers and potash-activated anthracite, for deliveries of 150 and 142 V/V, respectively.<sup>2</sup> 160 V/V stored were also

reported with compressed carbon nanohorns.<sup>60</sup> The highest deliverable capacity ever published was 152 V/V in a PX-21 active carbon-based monolith<sup>61</sup>—10 V/V lower than our result. Hence, preparing and processing the adsorbent as detailed in the present paper readily allows one to exceed clearly the recommended target of 150 deliverable V/V.

### Systems and Processes for Methane Storage.

Beyond that which purely involves the adsorbent itself, other practical aspects that are required for the conception of a storage system by adsorption are worth consideration. Because such aspects were not the purpose of the present paper, no detailed notions were developed here. However, because of the primary importance, with regard to the real application of methane as a fuel in vehicles, a few engineering concepts should be briefly reviewed.

First, recall that most of the studies so far have involved pure methane, although natural gas is actually thought to be an alternative fuel. Now, natural gas is a mixture, and the other gas present may have a harmful effect on the storage capacities of the adsorbent. Indeed, the few heavier hydrocarbons adsorb preferentially on the carbon surface; CO<sub>2</sub> is also strongly retained, and, hence, after several filling–emptying steps of the tank, the storage performances decrease dramatically.<sup>9,62,63</sup> Therefore, preadsorption systems (which are known as guard beds) must be provided to “purify” natural gas and, as far as possible, allow the admission of methane alone inside the reservoir.

In addition, adsorption is an exothermal phenomenon; hence, the filling or emptying of the tank induces increases or decreases in the temperature of the adsorbent, respectively. In both cases, the storage capacities are reduced, because less gas can adsorb onto a warmer surface, and obviously the gas desorbs with more difficulty from a colder material. Moreover, the adsorption–desorption kinetics are also strongly influenced by such thermal effects, leading in both cases to a slowing of the charging–discharging processes. Thus, it is necessary to increase the thermal conductivity of the adsorbent bed through the use of both additives and a suitable vessel geometry, to promote heat transport.

Finally, the problem of gas diffusion throughout the adsorbent must be addressed. Low diffusion of the gas inside the pore network causes considerable durations of the filling/emptying steps, which are associated with high thermal gradients within the material. Again, well-designed geometries, such as the presence of channels, should minimize such problems.

All the previously listed drawbacks lead to degraded performances, with respect to the deliverable capacities of a given material measured under thermodynamical equilibrium conditions, using pure methane. This is the reason preparing the best material, even better than the formerly fixed target, is so important. Moreover,

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much work remains to be done at the engineering level before natural gas can be used as a common commercial fuel for vehicular applications.

### Conclusions

Methane storage is a valuable alternative to more-conventional fuels; however, its very low intrinsic density constitutes a major disadvantage that must be solved. Reaching a density that is 150 times greater than that at standard temperature and pressure (STP) was suggested for an operational vehicle system using adsorbed natural gas and working at 3.5 MPa and 25 °C. In the present work, the superiority of carbonaceous materials for such a purpose was recalled, and the features of the most efficient adsorbent were briefly reviewed. The way of preparing suitable active carbons that have the optimal pore texture characteristics was

detailed, and both the best precursor and the best preparation route were identified. Arguments were given to suggest that fine anthracite powders that have been activated with sodium hydroxide (NaOH) under some definite conditions (including temperature, the NaOH/carbon mass ratio, the presence of water, and post-treatment) lead to the highest molar storage capacities. However, such as-made materials still exhibit rather average volume capacities, which could nevertheless be significantly enhanced through a suitable processing (including mixing of grains of different sizes and subsequent moderate compaction). Using such conditions, outstanding (record) performances in both stored ( $\sim 195$  V/V) and delivered ( $\sim 165$  V/V) amounts of methane were experimentally observed, clearly exceeding the aforementioned target of 150 V/V.

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