

# METHANE STORAGE BY ADSORPTION IN ACTIVE CARBONS DENSIFIED BY COMPRESSION

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## Introduction

Adsorption in active carbons is now accepted as being one of the most attractive methods of storing methane for both gas transportation and automotive applications. Indeed, high uptakes may be reached at much lower pressures than those required by simple compression. The amount of methane that can be stored in active carbons may be measured in terms of either moles adsorbed by kilogram of adsorbent ( $Q$ ), or STP volumes adsorbed by volume of adsorbent ( $V/V$ ). Both quantities are related to each other through the apparent density  $d_{app}$  of the adsorbent, according to :

$$V/V = Q \text{ (mol kg}^{-1}\text{)} \times M \times v \times d_{app} \text{ (g cm}^{-3}\text{)} \quad (1)$$

where  $M = 16 \text{ g mol}^{-1}$  is the molecular weight of methane and  $v = 1.5 \text{ dm}^3 \text{ g}^{-1}$  is the volume occupied by 1 g of methane in the STP conditions. Usually, the more activated the carbon, the higher its molar storage capacity but the lower its density. Hence,  $Q$  and  $V/V$  vary in opposite ways.

A few years ago, the Atlanta Gas Light Adsorbent Research Group (AGLARG) suggested the target of 150  $V/V$  deliverable at 3.5 MPa and room temperature for a viable application of methane adsorption to natural gas vehicle [1]. For a given fixed  $Q$ , increasing the value of  $V/V$  may be achieved by a suitable densification of the activated carbon through different methods such as : suitable mixtures of grains of well chosen different sizes [2-5], preparing compact monoliths using binders [6-8], and uni-axial compression of powders (with or without additives). The last two methods – monoliths preparation and powder compression - may lead to degraded intrinsic storage capacities, due to partial filling and closure of the pores by the binder, and collapse of the pore texture, respectively. In the present study, the effect of preparing a bimodal mixture on the volume storage capacity of a given active carbon is investigated. Next, increasing uni-axial pressures are applied to the same powdery mixture : the evolution of both pore textures and related stored amounts of methane are discussed.

## Experimental

The studied active carbon is an anthracite chemically activated with NaOH following a protocol detailed elsewhere [9], using an initial weight ratio hydroxide / carbon  $R = 2$  and an activation temperature of 730 °C. The main features of the non compacted

“unimodal” powder (grain sizes ranging from 100 to 200  $\mu\text{m}$ ), namely apparent density, BET surface area, micropore volumes and methane storage capacities, are presented in Table 1. The micropore volumes  $V(\text{N}_2)$  and  $V(\text{CO}_2)$  (from  $\text{N}_2$  adsorption at 77 K and  $\text{CO}_2$  adsorption at 298 K, respectively), were determined using the Dubinin-Radushkevitch method. The mesopore volumes and their distribution of sizes were determined by application of the Kelvin equation and capillary condensation theory to the adsorption isotherms of benzene at 298 K, and are given in Table 2. A bimodal blend was prepared using the same granulometric fraction 100 – 200  $\mu\text{m}$  mixed with the fraction 0 – 100  $\mu\text{m}$ , in such a way that the mass ratio of the biggest grains to the smallest ones is 3 / 1. This mixture was next introduced into a cylindrical stainless tube and compacted uni-axially at the various pressures listed in Tables 1 and 2.

Table 1 : Main features of the activated anthracite submitted to various conditions.

Sample	Pressure ( $\text{kg cm}^{-2}$ )	$d_{\text{app}}$ ( $\text{g cm}^{-3}$ )	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V(\text{N}_2)$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V(\text{CO}_2)$ ( $\text{cm}^3 \text{g}^{-1}$ )	$Q_{0.1 \text{ MPa}}$ ( $\text{mol kg}^{-1}$ )	$Q_{3.5 \text{ MPa}}$ ( $\text{mol kg}^{-1}$ )	V/V
unimodal	0	0.34	1797	0.79	0.357	1.78	12.49	102
bimodal	0	0.40	1800	0.80	0.360	1.70	12.57	139
bimodal	28	0.55	1561	0.68	0.383	1.90	12.03	163
bimodal	53	0.54	1630	0.73	0.298	1.85	12.09	183
bimodal	104	0.51	1204	0.53	0.151	1.74	11.8	192

$d_{\text{app}}$  is the apparent density of the adsorbent,  $S_{\text{BET}}$  its BET surface area,  $V(\text{N}_2)$  the micropore volume and  $V(\text{CO}_2)$  the ultramicropore volume (see text),  $Q$  the mass storage capacity at the equilibrium methane pressure given in index, and V/V the volume storage capacity at 3.5 MPa.

Table 2 : Mesopore volumes of the same material.

Sample	Pressure ( $\text{kg cm}^{-2}$ )	$V_{\text{meso}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	2-3 nm ( $\text{cm}^3 \text{g}^{-1}$ )	3-5 nm ( $\text{cm}^3 \text{g}^{-1}$ )	5-10 nm ( $\text{cm}^3 \text{g}^{-1}$ )	10-50 nm ( $\text{cm}^3 \text{g}^{-1}$ )
bimodal	0	0.084	0.033	0.070	0.015	0.019
bimodal	28	0.063	0.027	0.013	0.012	0.011
bimodal	53	0.069	0.030	0.014	0.010	0.015
bimodal	104	0.042	0.017	0.008	0.008	0.009

$V_{\text{meso}}$  is the total mesopore volume, and the mesopore-size distribution of volumes is detailed according to the ranges of widths listed in the Table.

Given the respective molecular diameters of  $\text{CO}_2$  and  $\text{N}_2$ ,  $V(\text{CO}_2)$  represents the volume of the ultramicropores, which effective pore widths  $w$  obey  $0.33 < w < 0.7 \text{ nm}$ , while the difference  $V(\text{N}_2) - V(\text{CO}_2)$  corresponds to the volume of the supermicropores, such that  $0.7 < w < 2 \text{ nm}$  [9]. From the pure point of view of methane storage, only the supermicropore volume should be maximized, since the  $\text{CH}_4$  molecules are efficiently and reversibly adsorbed in such pores. By contrast, ultramicropores generate highly attractive potentials, hence methane is strongly retained and can desorb only at subatmospheric pressure. Now, one needs to get the maximum deliverable amount of methane in 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 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.

The storage capacities of the different samples were measured at 20 °C into a classical volumetric device using highly accurate pressure transducers. For each adsorbent, the methane uptake was determined point to point by discontinuous introduction of the adsorbate into the sample holder (inner volume  $\approx 1.6 \text{ cm}^3$ ), up to 3.5 MPa. 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). At the end of each isotherm, the maximum amount thus stored was also accurately checked by weighing the vessel before and after allowing the methane to be released at room temperature and normal pressure.

## Results and Discussion

The pore texture was expected to be influenced by the pressure applied to the powder. Indeed, preliminary experiments dealing with a more brittle carbon, i.e., the same anthracite activated with NaOH but with an initial weight ratio hydroxide / carbon  $R = 3$ , evidenced the following facts. Compression at about  $30 \text{ kg cm}^{-2}$  of a bimodal powder makes the apparent density increase by 43 %, while the number of V/V stored at 3.5 MPa increases from 108 up to 145, i.e. by 34 % only, see Figure 1(a). Such a result is very interesting by itself, since it shows that reaching the aforementioned famous target of 150 V/V is quite possible. According to Eq. (1),  $d_{\text{app}}$  increasing faster than V/V means that the mass capacity  $Q$  is lowered upon pressing on the powder. Pore collapse should thus occur upon compaction, since  $Q_{3.5 \text{ MPa}}$  was shown to be directly correlated to the micropore volume  $V(N_2)$  [9]. The compaction-induced lowering of  $Q_{3.5 \text{ MPa}}$  was observed for an applied pressure as low as  $30 \text{ kg cm}^{-2}$ , hence finding the pressure at which an optimum of volume storage capacity is attained was assumed to be more easily achieved with a tougher adsorbent (i.e., less activated, with  $R = 2$ ).

Preparing a mixture of two granulometric fractions of the latter material obviously does not change the pore texture parameters, as seen in Table 1, but leads to an increase of about 35 % of the volume capacity thanks to that, almost identical, of the apparent density. Increases of both V/V and  $d_{\text{app}}$  are then strictly proportional for the uncompacted material, as seen in Figure 1(a). Applying pressures up to  $100 \text{ kg cm}^{-2}$  on the bimodal powder produces a significant compaction, while applying higher pressures does not change so much the apparent density of the packing, as seen in Figure 1(b). Pressure effects on the volume storage capacity are clearly evidenced, in such a way that V/V increases slower than  $d_{\text{app}}$ , see Figure 1(a). As suspected, the more brittle carbon ( $R = 3$ ) is much more influenced by pressure than its less activated counterpart ( $R = 2$ ). Additionally, as shown in Figure 1(b), the methane mass storage capacities  $Q$  measured at 3.5 MPa decrease, on average, with the applied pressure. Since  $Q_{3.5 \text{ MPa}}$  and  $d_{\text{app}}$  vary in opposite ways while  $p$  increases, the volume storage capacities (V/V) are expected to have an optimum value at a given compacting pressure.

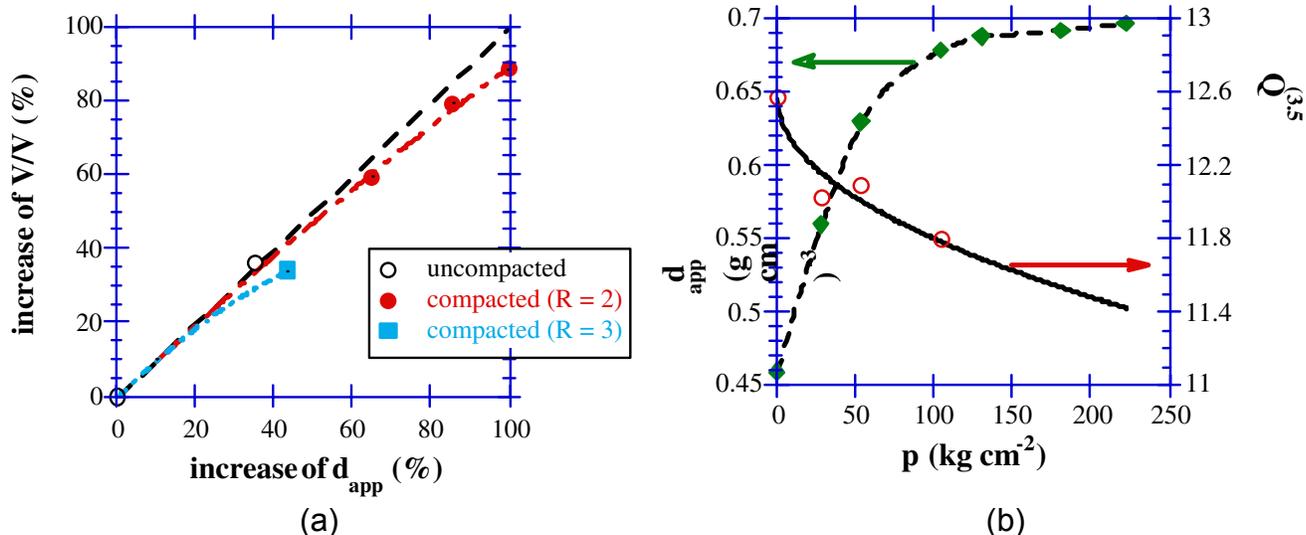


Figure 1. (a) The effect of both mixing two granulometric fractions and pressing the blend on the relative increases of volume storage capacities ( $V/V$ ), plotted vs the relative increase of apparent densities of the powders. (b) The effect of pressure both on the apparent density ( $d_{app}$ ) of the bimodal activated anthracite powder and on the methane mass storage capacity measured at 3.5 MPa.

As seen in Tables 1 and 2, the pore volumes decrease with  $p$ , on average, just like  $Q_{3.5 \text{ MPa}}$ . However, the decrease of the mesopore volume is not related to an increase of the supermicropore volume ( $V(N_2) - V(CO_2)$ ) and similarly, the decrease of the supermicropore volume is not related to any development of ultramicroporosity ( $V(CO_2)$ ). Hence, since all the pore volumes that were measured are decreasing functions of the pressure, this means that a number of pores become unavailable for adsorption. Therefore, the expected phenomenon according to which mesopores become supermicropores upon compaction, while former supermicropores become ultramicropores does not seem to happen. The only exception to this statement could be the drop of the mesopore volume at 28 kg cm<sup>-2</sup> (of about 0.05 cm<sup>3</sup> g<sup>-1</sup>), which seems to be compensated by the increase (of about 0.06 cm<sup>3</sup> g<sup>-1</sup>) of the ultramicropore volume. However, it is strange that some mesopores are directly converted into ultramicropores at such a low pressure, without clearly becoming first supermicropores. Hence, it seems that pressing the material only lead to degraded storage performances. Thus,  $Q_{3.5 \text{ MPa}}$  is found to decrease slightly with pressure, just like the micropore volume  $V(N_2)$ . However,  $Q_{0.1 \text{ MPa}}$  remains almost constant, while the ultramicropore volume clearly decreases. This phenomenon should be due to the narrowing of the corresponding slit pores, leading to enhanced adsorption properties. Correlating the pore volumes to the methane storage capacities is thus not obvious, due to the expected pressure-induced shift of the pore-size distributions.

Pressing on the powdery materials finally induces the decrease of  $Q_{3.5 \text{ MPa}}$  while  $Q_{0.1 \text{ MPa}}$  remains almost constant. Hence, the mass deliverable amounts of methane  $\Delta Q = Q_{3.5 \text{ MPa}} - Q_{0.1 \text{ MPa}}$ , should decrease with the applied pressure. An increase of the volume storage capacity ( $V/V$ ) is then possible only if the relative loss of  $\Delta Q$  is compensated by a more rapid relative increase of apparent density. This happens below an optimum

pressure at which the number of deliverable V/V is the highest, quite exceeding the target of 150. Figure 2 depicts such a situation : the absolute volume storage capacities were plotted as a function of the applied pressure  $p$ , for the anthracite activated at  $R = 2$ . The presence of an optimum may be seen, beyond which the number of volumes of methane that can be stored are decreasing functions of the pressure.

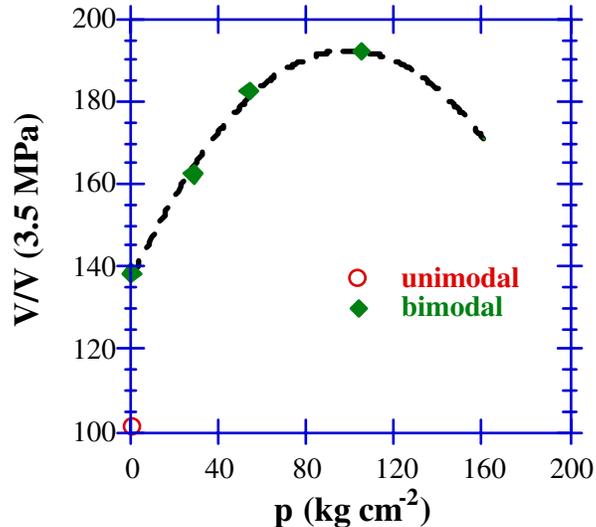


Figure 2. Volume storage capacity of the anthracite activated with NaOH (weight ratio hydroxide / carbon  $R = 3$ ) as a function of the pressure applied on the powder.

## Conclusions

The influence of compressing an active carbon on its intrinsic adsorption capacity was demonstrated. Experimental observations were explained on the basis of pore collapse, making all the pore volumes to decrease, on average, with the applied pressure. The pressure-induced reduction of the porosity is explained by the closure and / or the unavailability of a growing number of pores, without interconversion of a family of wide pores into a family a narrower ones. The reversible storage capacity is found to decrease, while the “irreversible” one remains almost constant. The net effect is a loss of deliverable methane storage capacity, which can be compensated - to some extent - by the pressure-induced increase of apparent density. Since these two latter antagonistic phenomena are present, an optimum of applied pressure exists and was evidenced for the investigated material. With such an optimal applied pressure, adsorbents leading to deliverable volume capacities higher than the target of 150 V/V suggested by the AGLARG may be obtained.

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