

METHANE HYDRATE FORMATION IN WATER-SATURATED ACTIVE CARBONS

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Introduction

Due to its cheapness, abundance, and clean burning, methane is an interesting alternative fuel. Unfortunately, its very low density (methane is a supercritical gas in STP conditions) restricts seriously the field of its possible applications [1,2]. In recent papers [3,4], storing more than 200 STP volumes of methane per volume of adsorbent (i.e., 200 V/V) was shown to be feasible through hydrate formation in ordinary wetted commercial active carbon at 2 °C and 10 MPa. Indeed, typical isotherms were obtained, all exhibiting a marked step occurring near the expected formation pressure of methane hydrates, thus supporting their occurrence within the porous materials. Such critical pressures were shown to depend on the water-filled-pore size distribution, but were found to be always above 3.5 MPa.

However, such results were obtained while the weight ratio $R = \text{water} / \text{carbon}$ was kept constant (R close to 1), and was thus not optimised. Especially, the pore volume was not saturated by water, and it was suspected that more methane hydrate could be formed if more water was added. Therefore, finding both lower formation pressures for methane hydrates and higher stored amounts was assumed to be possible. In the present work, the same active carbons as before are described and investigated in identical T-P conditions, but in such a way that their pore volume was saturated by water. Such materials were chosen because of their pore textures, ranging from purely microporous to highly mesoporous. Methane storage isotherms, combining both adsorption and hydrate formation are then given and discussed. Finally, considerations about charge / discharge kinetics of a storage vessel full of water-saturated active carbon are also developed.

Experimental

Four active carbons produced and supplied by Pica France, whose main characteristics are gathered in Table 1, were investigated. The NC series corresponds to mainly microporous carbons, and derives from coconut shell chars activated with steam at several burn-offs. Picazine is a highly mesoporous material (however with a non negligible micropore volume) which originates from pinewood chemically activated with orthophosphoric acid. All these materials were ground and sieved in order to keep the granulometric fraction 100 – 200 μm . The carbons were wetted with various amounts of water (see below), and were then introduced into a high pressure vessel made of stain-

Table 1 : Pore texture (in the dry state) of the carbonaceous adsorbents.

Carbon	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{μ} ($\text{cm}^3 \text{g}^{-1}$)	V_{m} ($\text{cm}^3 \text{g}^{-1}$)	$V_{\mu} + V_{\text{m}}$ ($\text{cm}^3 \text{g}^{-1}$)
NC58	1000	0.405	0.049	0.454
NC86	1587	0.570	0.088	0.658
NC120	2031	0.814	0.141	0.955
Picazine	1967	0.65	0.72	1.37

S_{BET} is the BET surface area, and V_{μ} and V_{m} are the micropore and the mesopore volumes, respectively.

less steel, to which a cooling jacket was fitted. A volumetric device, which was described elsewhere [3], was placed into a thermostated glove box (2 ± 0.1 °C). For each adsorbent, the methane uptake was measured point to point by discontinuous introduction of the adsorbate into the sample holder (inner volume $\approx 24 \text{ cm}^3$), up to pressures close to 8 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

While methane storage isotherms within dry carbons are typical langmuirian (type I) curves, see Fig.1, those of wet adsorbents are stepwise (type IV) and such a shape was interpreted as follows [3-5]. The first part corresponds to classical physisorption within the smallest pores ; the amounts of methane thus stored are much lower than in dry materials, due to the presence of water that both fills and blocks a number of pores and diffusion pathways throughout the pore network. Then, at some critical pressure, the methane uptakes increase rapidly and, while $R \approx 1$, become higher than those measured for dry carbons, see Fig. 2. Such jumps correspond to the formation of hydrates within the largest pores. The formation pressures of hydrates are higher than those found in bulk water at the same temperature (i.e., 3.18 MPa), due to the additional capillary pressure that must be exceeded before the hydrates can form. Increasing the equilibrium pressure then forces hydrates to occur in smaller pores, until a plateau is reached if the pores were initially almost filled with water (e.g., for NC58). Otherwise, most of the water available for forming hydrates is consumed, and simple compression of methane occurs in the remaining empty pores, leading to positive slopes at the end of the isotherms (e.g., for the other adsorbents).

Basing on these conclusions, more methane was thought to be stored in adsorbents containing more water than that corresponding to $R \approx 1$ only. Additionally, forming hydrates at the lowest possible pressure, 3.18 MPa, was expected since saturating the pore volume with water leads to the filling of the largest pores, thus resembling the case of free water. The four adsorbents of Table 1 were thus wetted until the saturation of the pore volume is reached, and methane uptakes were measured in the same conditions.

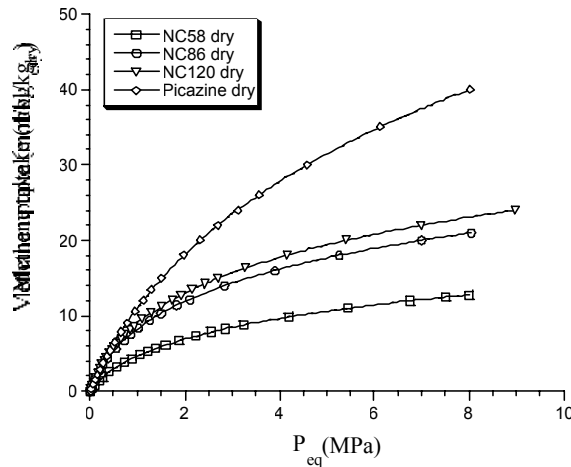


Figure 1. Mass methane uptake at 2 °C of the four adsorbents in the dry state.

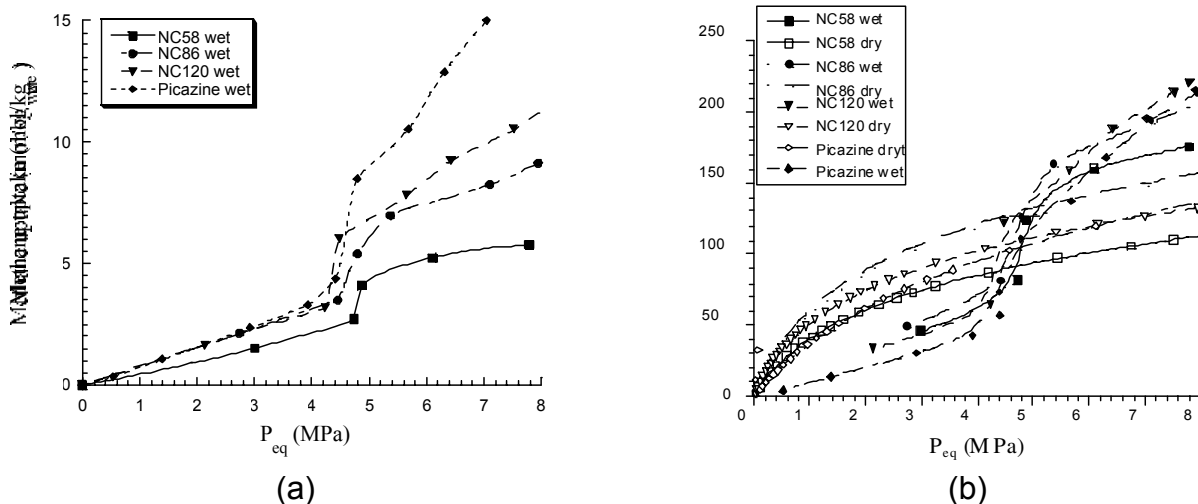


Figure 2. (a) Same as Figure 1, but the adsorbents are wetted with a constant weight ratio water / carbon $R \approx 1$. (b) Comparison of data of Figures 1 and 2(a), with the methane uptakes expressed in units of V/V .

Saturation was assumed to be achieved by adding the minimum amount of water making the carbon powders to become sticky pastes. A very encouraging result was obtained with NC58, as shown in Figure 3(a), since the new formation pressure is exactly that of the bulk hydrate. Hence, large uptakes may be reached at much lower pressures than those required with the unsaturated wet carbon. Even better results were expected with the three other adsorbents, since more water could be introduced in their more developed porosity. However, the opposite was observed, as seen in Figures 3(b)-(d) and, surprisingly, greater pore volumes completely filled with water lead to lower storage performances. For both NC120 and Picazine, the uptakes are even lower than what can be stored by simple adsorption on dry materials. While plotting the greatest amounts of methane stored at 8 MPa as a function of the weight ratio water / carbon R , curves exhibiting maxima are obtained, as shown in Figure 4.

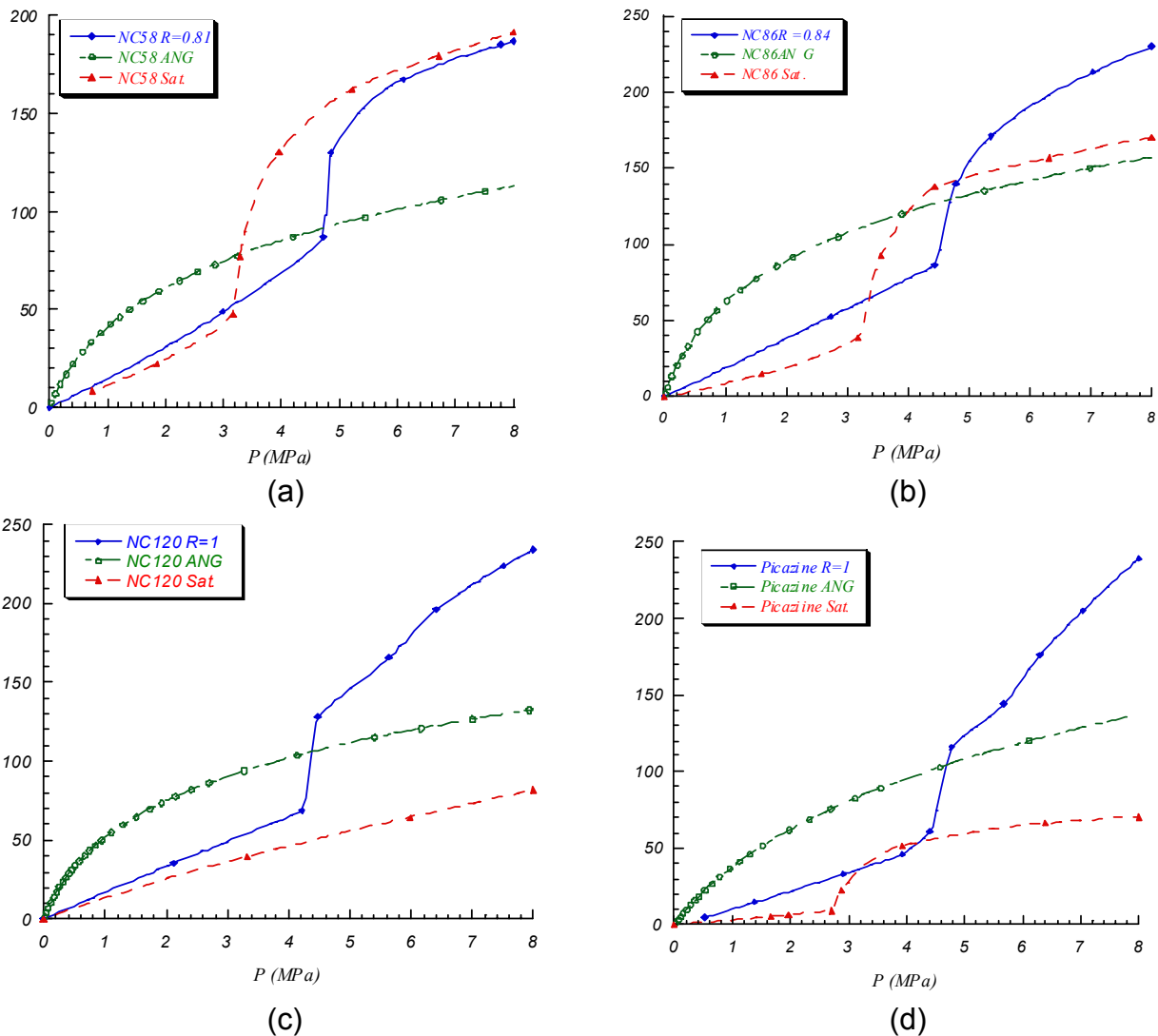


Figure 3. Volume methane uptakes measured with the 4 active carbons which pore volumes were saturated (“sat.”) with water. The data corresponding to materials wetted with a constant weight ratio water / carbon (“ $R \approx 1$ ”) and to adsorption on dry carbons (“ANG” : adsorbed natural gas) are given for comparison.

The existence of an optimum R_{opt} in the water content was already suggested in previous works [5,6]. It may be seen that, except for NC58, the former value $R \approx 1$ was already very close to such an optimum, in agreement with the results of Figure 3. This finding is rather surprising, given the very different pore textures of the materials presented in Table 1. Thus, for $R < R_{opt}$, more hydrate can be formed by adding more water inside the pore volumes, i.e., by increasing R . But above R_{opt} , diffusion of gaseous methane is more and more difficult because diffusion pathways become increasingly scarce throughout the pore network. Since methane has a very low solubility in water, hydrates cannot form inside the material, and hence only a few of them may occur at the periphery of the grains.

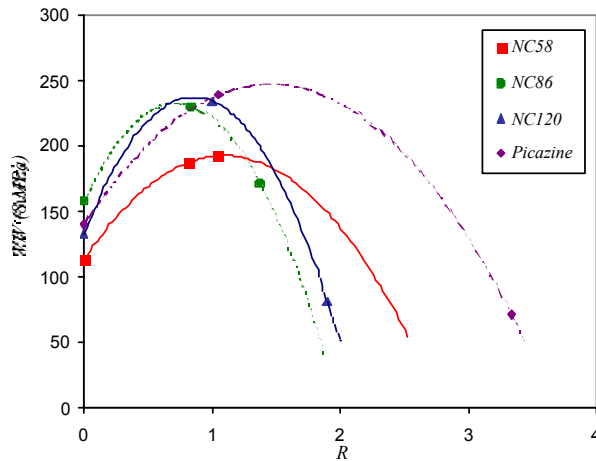


Figure 4. Methane uptakes at 8 MPa in water-saturated adsorbents vs the weight ratio water / carbon R .

A major problem of storing methane through hydrate crystallization within porous media lies on their extremely slow formation kinetics, making the filling a tank to be a very long process. Above the formation pressures, first-order kinetic laws were evidenced [3,4], according to :

$$\ln(V/V_{eq}) \propto kt \quad (1)$$

where V is the STP volume of stored methane measured as a function of time, V_{eq} is the adsorbed amount at equilibrium, t is the time and k a kinetic constant. Unlike free water, wherein increasing the pressure speeds up hydrate formation [7], the kinetic constants are seen to decrease in wet carbons submitted to growing pressures, as seen in Figure 5. Since the kinetics of formation of the hydrate only depends on the temperature [8], such a slowing down phenomenon is again attributed to the increasing difficulty of methane to diffuse throughout the water-filled pore network already containing hydrate crystals.

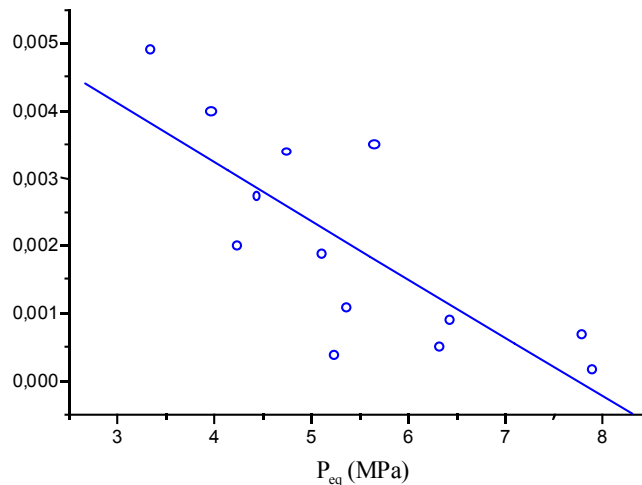


Figure 5. Kinetic constants of hydrate formation vs equilibrium pressure for the NC series of adsorbents.

Finally, it should be noticed that discharging a storage tank full of methane hydrates crystallized inside wetted carbons is very rapid and almost complete, unlike emptying of methane adsorbed on dry materials. Unfortunately, much water evolves during the process, and therefore is irreversibly lost. Readjusting the water content in order to come back to the value of R_{opt} is thus required before a subsequent filling of the tank.

Conclusions

Storing methane by hydrate formation within wetted active carbons is possible but requires both high pressures, at least 3 MPa, and low temperatures, close to 0 °C. Additionally, the water content has to be correctly chosen, otherwise no real benefit exists as compared with either adsorbed or compressed methane. Indeed, an optimum was clearly evidenced : at low water contents, the formation pressures of hydrates are rather high, and hence even higher pressures must be reached for storing large amounts of natural gas. Conversely, at high water contents, formation pressures are those of the bulk hydrate, but the diffusion of gaseous methane throughout the pore network is drastically hindered, and only a very few methane is stored. It was shown here that, despite the very different pore textures of the investigated adsorbents, the optimum weight ratio water / carbon R_{opt} is close to 1. Even if R_{opt} was easily reached, problems still remain in the filling / emptying processes, namely extremely slow storage kinetics and irreversible lost of water, respectively.

References

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