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Improvement of Hydrogen Storage Capacity for Active Carbon

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Abstract. The porous structure of activated carbon modified by successive removal of external layers from a granule surface as produced by abrasion in a spouted bed was investigated. Procedure used for activated carbon modification is the way to minimization voids and macropores without decreasing the volume of adsorbing pores. The concept of hydrogen adsorption storage in modified samples was analysed. The amount of hydrogen that can be stored in an adsorption system depends on the hydrogen volumetric uptake and densimetric characteristics. The results show that the cryoadsorption technique could provide a viable method for hydrogen storage.

Keywords: adsorption, activated carbon, hydrogen storage

1. Introduction

In the present century hydrogen will be the most important source of energy and will replace petroleum and petroleum-derived products in the next future. Hydrogen is an almost ideal fuel, both because of its unlimited accessibility and for ecological reasons; the product of its combustion—water vapor—is neither any gaseous contamination nor a component of greenhouse gases. Nowadays hydrogen is applied in industrial processes, but may be also used as a source of house lighting and heating energy, for production of electricity, and as fuel for car engines. Fuel cells, applying reaction between hydrogen and oxygen for production of electricity have been for a long time used in the space technology. Application of hydrogen as fuel should give a possibility of storage and transfer of the high quality energy, i.e. the energy of a high exo-energetic ratio (Berry, 1996).

Due to its low density, one of the main obstacles to the widespread use of hydrogen in energy sector is an efficient storage technology. At present, the methods of hydrogen storage are to liquefy and store in refrigerated containers, which is very expensive, or to store it in high-pressure gas cylinders at room temperature. Unfortunately, low storage density of hydrogen for the latter technique is a significant drawback. Between alternatives have been considered (chemical storage in irreversible hydrogen carriers like methanol or ammonia, reversible metal and chemical hydrides and adsorption in porous media), the latter one seems to be the most promising (Kiyobayashi, 2002; Dillon and Heben, 2001; Chachine and Bose, 1994; Noh et al., 1987). Thanks to the high density of adsorbed phase, adsorptive storage system could allow the storage of a high density of hydrogen at much lower pressures than compression and higher temperatures than liquefaction.

The aim of this study was to test the improvement of the properties of commercial activated carbon for hydrogen storage systems. The method of successive removal of external layers from a granule surface of active carbon was used for the preparation of samples. Characterization of the pore structure as well as densimetric properties of the modified samples were also undertaken to establish a link between pore structure and hydrogen storage capacity.

2. Material and Methods

A commercial granulated activated carbon **2RL** (*Norit*, The Netherlands) obtained by activation of peat char with steam was selected to study of cryogenic hydrogen storage.

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Table 1. Properties of samples under study.

Property	**2RL**	**C20**	**C42**	**C63**	**C83**
True density, d_{He} (g cm^{-3})	2.285	2.254	2.181	2.135	2.076
Apparent density, d_{Hg} (g cm^{-3})	0.663	0.692	0.718	0.727	0.747
Bulk density, d_b (g cm^{-3})	0.413	0.447	0.458	0.472	0.479
Total porosity, ε_t (cm^3 cm^{-3})	0.710	0.693	0.671	0.659	0.640
Bed porosity, ε_b (cm^3 cm^{-3})	0.377	0.354	0.362	0.351	0.359
Total pore volume, V_{po} (cm^3 g^{-1})	1.071	1.001	0.934	0.907	0.857
Volume of micropores, W_o (cm^3 g^{-1})	0.447	0.453	0.461	0.428	0.406
Energy of adsorption, E_o (kJ mol^{-1})	21.4	20.9	20.6	20.8	20.9
Micropore width, x_{mi} (nm)	0.56	0.58	0.59	0.58	0.58
Volume of mesopores, V_{me} (cm^3 g^{-1})	0.120	0.087	0.082	0.067	0.067
Mesopores surface area, S_{me} (m^2 g^{-1})	108	102	104	86	82
BET surface area, S_{BET} (m^2 g^{-1})	1280	1290	1300	1210	1130

Carbon was subjected to working in a spouted bed (Buczek and Czepirski, 1987; Buczek, 1993). The time of the process was chosen in order that the amount of carbon abraded from the surface of the particles in the form of dust was increased by about 20 wt.% for each successive sample. As a result of this process, particles of active carbon with surface layers removed to different degrees were obtained and designated **C20**, **C42**, **C63** and **C83**.

The structural characteristics of obtained samples were determined from the argon adsorption/desorption isotherms at 77 K. Densimetric parameters were measured using helium pycnometer for true (skeletal) density and mercury pycnometer at 0.1 MPa for apparent density. Results of the measurements and calculations are given in Table 1.

The measurements of hydrogen adsorption isotherms 77 K and pressure up to 40 atm were made using a volumetric system described before (Czepirski, 1996). It is capable of operating in both adsorption and desorption mode with accuracy $\pm 1\%$.

3. Results and Discussion

Comparing parameters characterizing carbons porous structure it can be seen that attrition process in spouted bed changes of pore structure with a granule radius. These radial changes in the texture result from the nature of the activation process. During abrasion, highly converted external layers (with a greater proportion of macropores) are removed. Simultaneously during the treatment in the spouted bed, granules change in shape and geometric dimensions (tendency to ovalization is observed), as well as, their density undergo the changes.

Traditionally, adsorption is measured on a mass basis, however an application such as gas storage, where storage volume is limited, the adsorption per unit volume must be measured; thus, the bulk and apparent densities of the adsorbent becomes important. When a tank is packed with adsorbent it can be viewed as being divided into the following parts: the void between carbon granules (intervoids), the macropore volume (intravoids), the volume occupied by carbon skeleton and the micropore region. The storage tank utilisation for samples under study is presented in Fig. 1.

It can be seen that procedure used for activated carbon modification is the rational way to minimization as far as is possible voids and macropores without decreasing the volume of adsorbing pores. One ought so

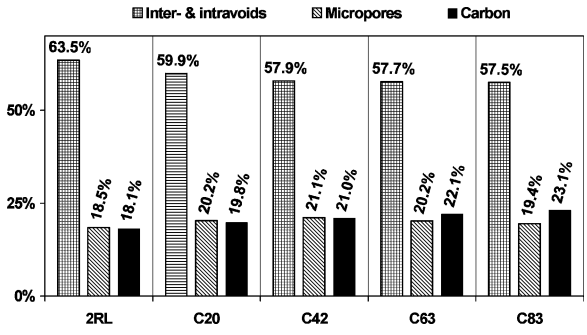

Figure 1. Storage tank utilization.

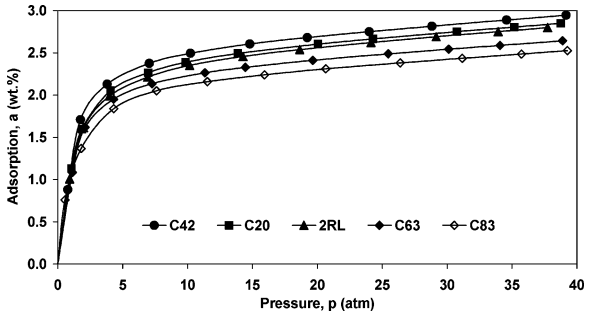

Figure 2. Adsorption isotherms of hydrogen on samples under study.

to suppose that in the case of gas storage, volumetric uptake and densimetric characteristics are the keys adsorption and packing properties that determine the most effective storage capacity.

Because of adsorption isotherm is one of the most important property determining activated carbon performance in storage systems, hydrogen adsorption isotherms were measured at 77 K. They are presented in Fig. 2 as plots of mass of hydrogen adsorbed per unit weight of carbon. The values of adsorption for samples under study are comparable with those cited in literature for different active carbons (Nijkamp et al., 2001).

Experimental isotherms and densimetric characteristics were applied for calculation of amount of gas stored per tank unit volume defined here as the volumetric storage capacity. It could be expressed as the sum of the capacity of adsorbed molecules on the carbon surface plus the volumetric capacity due to compression in the inter- and intraparticle void space (Zhou et al., 2004). Figure 3 shows hydrogen storage capacity for sample **C42**. Changes of capacity in adsorption storage system were also characterized by the enhancement factor (ratio of storage capacity in adsorption storage system and compressed gas density in the hollow tank at the same pressure.

A comparison of hydrogen capacities in adsorption system with compressed gas density shows the improvement of active carbon—containing tanks over hollow ones. The improvement is appreciable at low pressures but decreases as the pressure increases. The results show that it is possible to store by adsorption on activated carbon approximately the same amount of hydrogen at 15 atm and 77 K that can be stored at 120 atm in a compressed system of the same volume. Taking into account the excess of gas in tank filled with carbon compared with that in hollow tank, it could be simply demonstrated that optimum pressure range for hydrogen storage at 77 K is about 15 atm.

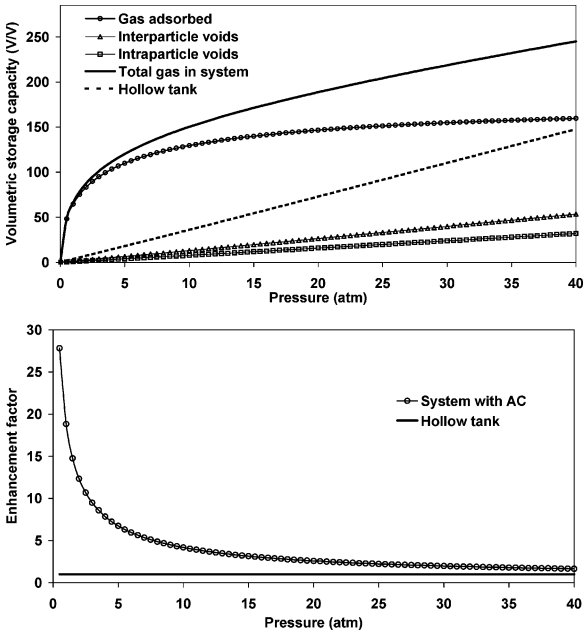

Figure 3. Plots of hydrogen storage capacity and enhancement factor vs. pressure for sample **C42**.

In further considerations this value of storage pressure was chosen from a practical point of view. As it is known, high-pressure storage requires relatively large and costly compressors, while low-pressure adsorption storage gives the possibility to refuel containers by using small two-stage air-cooled compressors. In Table 2 the storage capacities of hydrogen stored at 15 atm, values of enhancement factor, as well as, parameters of the micropore volume and surface area on the unit volume basis are listed. The results stay in the good agreement with those presented by Benard and Chachine (2001).

For all modified samples storage capacity was 9–18% higher than for commercial carbon **R42**. An advantage of proposed method of the modification is

Table 2. Hydrogen storage parameters.

Property	**2RL**	**C20**	**C42**	**C63**	**C83**
Storage capacity at 15 atm (VV^{-1})	146	159	171	155	169
Enhancement factor	2.69	2.93	3.16	2.85	3.12
$W_o * d_b$ ($cm^3\ cm^{-3}$)	0.185	0.202	0.211	0.202	0.194
$S_{BET} * d_b$ ($cm^3\ cm^{-3}$)	529	577	595	571	541

that during abrasion, the external layers with high conversion are removed what allow us to achieve greater storage capacities by eliminating voids and macropores while increasing the micropore volume (carbon **R42**). For sample **R83** it was possible to change the bulk density advantageously, but unfortunately with considerable decrease in the micropore volume.

To achieve greater hydrogen storage densities, the bulk density of the carbon should be increased by eliminating as far as is possible voids and macropores without decreasing the volume of micropores (macropores and large mesopores play little or no role in contributing to hydrogen adsorption especially at temperatures well above the critical temperature).

It can be seen that the storage capacity is linearly proportional to product of the micropore volume and the bulk density (or the specific surface area and the bulk density). These indexes give a better indication of the characteristics of adsorbent suitable for adsorption storage than the usually used surface area or bulk density.

Conclusions

The phenomenon of intensive attrition in the spouted bed was used to prepare activated carbons with different physicochemical properties within granule. The goal of this study was to evaluate the suitability of modified carbons for hydrogen storage.

According to the data obtained it can be conclude that active carbons appear to be a suitable medium for the storage of hydrogen. An adsorptional characteristics on volumetric basis and packing density become the most desirable parameters of a good carbonaceous material for adsorption storage systems. The packing and piece density of the adsorbent, as well as, the volumetric methane uptake become important factors influencing the storage capacity.

From the presented data it results that the low temperature adsorption of hydrogen (cryoadsorption) on active carbon is a viable method of hydrogen storage. This method is comparable both with storage in tanks of hydrogen compressed to at least 150 atm, and with hydrogen storage in tanks containing metal hydrides.

Adsorption storage seems to be not only economical, but also has a psychological advantage over high-pressure compression storage as far as consumers are concerned. Because of hydrogen adsorption storage is rather new method, still much more work is needed to clarify the potential of carbon materials as hydrogen storage media.

Acknowledgments

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