MODIFICATION OF ACTIVE CARBONS
FOR NATURAL GAS STORAGE SYSTEMS

B. Buczek and L. Czepirski

Faculty of Fuels and Energy, University of Mining and Metallurgy,
30-059 Cracow, Poland

Introduction

Development of efficient storage capabilities is an important factor in the utilization of natural gas as an energy carrier. Natural gas is an alternative to liquid fuels in a variety of applications, ranging from metal welding, home heating to vehicular fuel. It has been shown that natural gas should be preferred as a fuel for internal combustion engines. The use of natural gas as a vehicular fuel, an application where storage volume is limited, has necessitated the use of high-pressure storage, 200 atm, to give an adequate if not entirely satisfactory driving range. The disadvantage of compressed natural gas is that its energy density is about 30 % of that of gasoline. Gas is stored in heavy steel cylinders and filling a tank requires an expensive multistage compression facilities. This disadvantage can be eliminated by using low-pressure storage systems containing adsorbents when the high density of surface phases is exploited [1-2].

The aim of this study was to test the improvement of the properties of active carbon for natural gas storage systems. The method of successive removal of external layers from a particle surface as produced by abrasion in a spouted bed was used for the preparation of samples.

Experimental

Granulated active carbon of type A (Poland) obtained by activation of hard coal with steam was subjected to working in a spouted bed [3-4]. The time of process was chosen in order that the amount of carbon abraded from the surface of the pellets 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 A20, A40, A60 and A80.

To testify the influence of bulk density on storage capacity active carbon A40 was ground and sieved to obtain fraction 0.1 - 0.2 mm. Composite sample (Amix) was next prepared by mixing 75 wt % of sample A40 and 25 wt % of narrow fraction. This procedure doesn't change distinctly the sorption properties with respect to methane, but increases the bulk density.

In order to characterize the changes in properties of active carbons densimetric and adsorption measurements were made. The results are given in Table 1.

Table 1. Properties of active carbons under study

	A	A20	A40	A60	A80	Amix
d_{He} gcm^{-3}	2.402	2.366	2.314	2.289	2.254	2.314
d_{Hg} gcm^{-3}	0.630	0.726	0.800	0.828	0.845	0.805
d_{bulk} gcm^{-3}	0.447	0.467	0.507	0.515	0.530	0.625
V_{mi} cm^3g^{-1}	0.304	0.300	0.295	0.291	0.285	0.295
V_{ma} cm^3g^{-1}	0.867	0.655	0.523	0.480	0.455	0.515
S_{BET} m^2g^{-1}	886	855	837	802	769	837

The measurements of storage capacity were conducted by volumetric technique in an experimental system which has been described elsewhere [4-5]. The storage capacity was determined in the desorption mode. This procedure has a sound practical basis, because the cylinders with the compressed gaseous fuel are not completely emptied, but are discharged to some residual pressure. Thus, at any given pressure, the amount of of the available gas is the difference between the amounts stored at that pressure and the residual pressure. It should be noticed that complete recovery of gas is practically possible using vacuum desorption system.

To determine the gas storage capacity as a function of pressure, the discharge was stopped at various pressures, keeping the tank in constant temperature (298 K), and the volume of gas for that pressure was measured.

Results and Discussion

The amount of gas stored per tank unit volume is defined here as a storage density. It is expressed as a sum of gas adsorbed and that in the gas phase (compressed in the inter- and intra-particles voids). A comparison of the results with the compressed gas density shows the

improvement in methane storage density of active carbon-containing tanks over hollow ones. The improvement is appreciable at low pressures but decreases as the pressure increases. Changes of storage density in adsorption storage system were also characterized by the enhancement factor (ratio of storage density in adsorption system and compressed gas density in the hollow tank at the same pressure).

In further considerations the value of storage pressure was chosen as 35 atm 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 a containers by using small two-stage air-cooled compressors or directly from gas transmission lines. In Table 2 the values of enhancement factor at 35 atm for all carbons under study are listed.

Table 2. Enhancement factor at 35 atm

Sample	F
A	2.03
A20	2.08
A40	2.18
A60	2.17
A80	2.15
Amix	2.46

Traditionally, adsorption has been measured on a mass basis, but for storage capacity the adsorption must be measured per unit volume; thus, the packing and piece density of the adsorbent becomes important. When a vessel is packed with adsorbent it can be viewed as being divided into the following parts: the void between carbon pieces, the macropore volume, the volume occupied by carbon skeleton and the micropore region. The storage tank utilization for carbons under study is illustrated in Figure 1 for carbons under study.
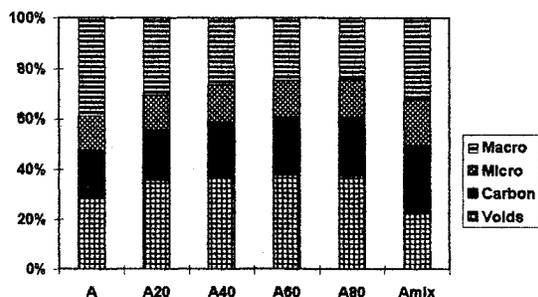

Figure 1. Storage tank utilization

As can be seen to achieve greater methane storage densities, the bulk density of the carbon should be increased by eliminating as far as is possible voids and

macropores without decreasing the micropore volume (macropores and large mesopores play little or no role in contributing to methane adsorption especially at temperatures well above the critical temperature).

The increase of micropore volume causes to increasing in part of gas adsorbed in total storage capacity, and the other hand, the increase of bulk density minimizes the dead spaces between particles. A further gain can be made by using a carbon having a low macropore volume. If these are not done the the storage capacities will be low.

By abrasion of external layers of grain active carbons with better adsorptive properties, smaller voids and improved attrition strength were obtained.

For granular carbon, improvement in packing can be achieved by particle selection. An experiments with composite sample Amix show an improvement in bulk density by varying the particle size distribution. This method of adsorbent preparing allows to obtain good tank packing from active carbon with rather weak adsorption properties.

In both cases investigations indicated that methane storage density can be increased up to 20 - 25 % over commercial carbon.

Conclusions

According to the data obtained it can be conclude that active carbons appear to be a suitable medium for the storage of natural gas. An adsorptional characteristics 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, micropore volume becomes important factors influencing the storage density. Results indicate that there is still room for improvement in the performance of these systems.

Acknowledgements

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