

CH₄ STORAGE ON COMPRESSED CARBONS

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ABSTRACT

The uptake of CH₄ in three commercially-produced carbons before and after physical and chemical modification were studied using a specially designed cell within a high pressure TGA. The uptake capacities in non-compacted and compacted carbons and their pore size distributions were compared. After compaction, a carbon having 75-38 μ m particles adsorbed more CH₄ than the same carbon having larger particles of 1700-425 μ m even though the resultant density of the later sample was greater. Compaction of graphite powder produced significant microporosity, imparting capacities of 25 ml CH₄ at STP/ml carbon. Even though greater microporosity in carbons increases CH₄ storage capacities, high microporosities usually leads to low piece densities and difficulties during compaction. Hence, methods to improve piece density while maintaining CH₄ capacities were investigated. One method involved the mixing a highly microporous carbon with graphite and then compacting the mixture. A blend of 75:25 by volume (carbon : graphite) contained the same adsorption capacity on a volume CH₄/volume carbon basis as did the pure carbon sample; the blend had better compaction properties. Another method involved chemical deposition on and within the carbon. Diethylsilane was impregnated on and in a highly microporous carbon resulting in greater piece density and increased CH₄ uptake capacity.

INTRODUCTION

The commercial utilization of microporous carbons to store natural gas at low pressures will require the optimization of many factors including: maximizing the pore volume around 1.1 nm¹; minimizing adsorption/desorption cycle times²; and, increasing the volume-per-volume (v/v) storage capacities, i.e. volume of CH₄ stored-per-volume of carbon used. Optimization and production of suitable carbons has been studied by several researchers³⁻⁶. In transportation applications, the CH₄ sorbent will ultimately need to be contained within a fixed volume, thereby requiring relatively high densities which produce desirable v/v storage capacities.

Previous work has shown that treating activated carbons with surfactants can improve their compressibility and reduce the work needed for densification⁷. However, the CH₄ storage capacities of these carbons were not determined. The present study investigated changes in the compressibility and CH₄ uptake of microporous carbons when physical modifiers were added before compaction.

EXPERIMENTAL

The compaction properties of three carbons and their CH₄ uptake were studied. Three commercially-made carbons, including Barnebey-Sutcliffe A207 (two particle size fractions, 75-38 μ m and 1700-425 μ m), Amoco Super A, and Alfa Aesar graphite were used. The N₂ BET surface areas of these materials were 850, 3000, and 5 m²/g, respectively. Mixtures of Amoco Super A with graphite were also densified and studied; these mixtures were 100:0, 75:25, and 50:50 Amoco: graphite on a volume basis.

In order to prevent expansion of the carbons after compaction, a special reactor was designed for use in the Cahn C1100 high pressure thermal analyzer (HPTGA). Two reactor configurations, shown in Figure 1, were used depending on whether CH₄ storage on compacted or non-compacted (loose) carbons was being measured. The sides and bottom of the cylindrical reactor were made of porous (2 μ m) stainless steel, the top of which was a solid, 3.1 mm thick disk. For loose carbons, this closing disk was placed above and supported by the hanger rod; for compacted carbons, the disk was placed over the carbon and then secured by the hanger rod, thereby preventing expansion during the HPTGA measurements. The procedures of Sosin and Quinn⁸ were used to calculate CH₄ storage capacities and pore size distributions. The densities of loose and compacted carbons were determined by knowing the weights of the carbons contained in the known reactor volume.

Densification of the Amoco carbon was studied after deposition of diethylsilane (DES). DES was chosen because it is a starting material for microporous thin films; a porous coating on the carbon would be desirable during CH₄ adsorption and desorption⁹. Two procedures were used to deposit

the DES on the carbon. In each case, two grams of Amoco carbon were treated. In one case, the carbon was soaked in 5 ml of DES for 2 hours and in the other case the carbon was soaked in a 30% solution of DES in CCl_4 for 30 minutes. Excess DES was decanted and the DES plus carbon were filtered using #1 qualitative filter paper. The carbon was subsequently air dried for 30 minutes, and then heated to 300°C in air for 15 minutes.

RESULTS

Compaction studies on two different particle size distributions, $75\text{-}38\mu\text{m}$ and $1700\text{-}425\mu\text{m}$, of the Bamebey - Sutcliffe A207 carbon were performed. Larger particles have a higher nascent density than finer particles and were anticipated to have higher compaction densities; larger particles in a loose packing situation were anticipated to have a lower density because of the voids due to irregular particle shapes. These anticipations were qualified by the data where loosely packed $75\text{-}38\mu\text{m}$ and $1700\text{-}425\mu\text{m}$ particles had densities of 0.49 and 0.44 g/ml, respectively, whereas compressed samples had maximum attainable densities of 0.82 and 0.91 g/ml, respectively. For each particle size distribution, the CH_4 storage capacity increased with increased packing density of the carbon (Figure 2). However, the highest storage capacity obtained for the A207 carbon was for the compressed $75\text{-}38\mu\text{m}$ powder even though it did not have the highest packing density.

Maximum compaction densities of only 0.34 g/ml were attainable using 100% of the Amoco carbon. It was very difficult to compact. Graphite, however, has a relatively high bulk density and is easily compacted to 1.22 g/ml. The CH_4 uptake on loose graphite is very low but compaction increases it significantly (Figure 3). In an attempt to improve the compaction properties of pure Amoco carbon, varying mixtures of carbon and graphite were prepared and subjected to CH_4 uptake determinations. Figure 4 shows the results for these blends in comparison to the pure Amoco carbon. With the 50:50 Amoco : graphite mixture, the maximum attainable density was 0.63 g/ml, almost twice that of the compacted pure Amoco carbon. The CH_4 uptake capacities increased with increased compaction densities for all blends. Interestingly, the CH_4 uptake on the compacted 75:25 Amoco : graphite mixture was the same as for 100% Amoco carbon.

The possibility of using chemical deposition on and within the pores of the Amoco carbon as a way to increase compressibility was also explored. Maximum compaction densities of 0.38 and 0.44 g/ml were attained for the high and low concentrations of DES, respectively. Even though these densities were only slightly greater than for the pure Amoco, the CH_4 uptake on the DES treated carbons was greater than on the pure carbon (Figure 5). The data suggest that DES impregnation warrants further investigation.

Pore size distributions were determined from the CH_4 isotherms. Comparison of the pore size distribution of compressed Amoco carbon relative to the loose, pure carbon indicated that compression significantly enhanced the pore volume for pores having diameters around 1.1 nm (Figure 6); pores of this dimension are believed to be optimum for CH_4 storage¹. Pore size distributions were also determined for compressed mixtures of Amoco : graphite and for the DES treated Amoco carbon (Figure 7). The total pore volume from pores with dimensions of 0.38-2.0 nm correlated well with the total CH_4 uptake (Figure 8). Plotted in Figure 8 are the average values of all replicates for the untreated and each different physically modified compressed carbon. These data also indicated similar pore volumes for the compressed, pure Amoco and for the 75:25 Amoco:graphite samples. The DES treated Amoco, especially the less severely treated material, had the highest pore volumes which was consistent with their highest CH_4 uptake capacities.

SUMMARY AND DISCUSSION

During this study, methods were explored to improve the compaction properties of porous carbons to increase the amount of CH_4 stored per unit volume of carbon. The particle size of the starting material was important and it appears that, even though larger particle can be compacted to higher densities, greater microporosity was developed during the compaction of fine powders.

Amoco Super A, a highly micro-porous carbon with low bulk density, has been shown to have a higher CH_4 uptake capacity compared to all other carbons studied during this work¹⁰. Maximum compaction densities of this carbon under the experimental conditions were low (0.34 g/ml) in comparison to graphite (1.22 g/ml). Compaction of pure graphite resulted in the development of some microporosity, which is considered responsible for uptake of 25 ml (STP) CH_4 per ml graphite. The compaction properties of a blend of graphite with the Amoco carbon were improved over those of the carbon alone and a blend of 75 : 25 carbon : graphite on a volume basis resulted

in the same amount of CH₄ adsorption as the pure carbon. These results have important implications for improving the economics of CH₄ storage on activated carbon, i.e. inexpensive graphite was substituted for the expensive activated carbon and yet the CH₄ uptake capacity was not compromised.

The role of the graphite and DES has yet to be elucidated. The data in Figure 4, where the 0.20 g/ml density sample from the 75:25 mixture has a CH₄ uptake capacity of 29 v/v, the 0.20 g/ml density sample from the 50:50 mixture has a CH₄ uptake capacity of 14 v/v and the pure Amoco carbon has a capacity of 37 v/v, suggest that in loose mixtures the effect of graphite is nearly linear in graphite concentration where it plays the role of a diluent, i.e. less Amoco carbon implies less CH₄ storage. In compressed mixtures, the diluent effect is still observant but not as predominant. Under compaction, the graphite could occupy macro-voids and provide some microporosity.

The DES coating method was chosen because of its potential to provide a porous micro-coat on and in the carbon. Quite interestingly, the data indicate that the DES treatment improved the carbon's compressibility and increased its microporosity. The DES coating did not appear to change the microporosity of non-compacted carbon.

CONCLUSIONS

The two methods for improving the compaction properties of a highly microporous carbons appear worthy of further investigation relative to fundamental and applied areas of study. Both blending carbons with a material having a higher bulk density and the chemical deposition on or within the carbon improved compaction properties and increased CH₄ uptake. Both methods appear to enhance the microporosity only after sample compaction.

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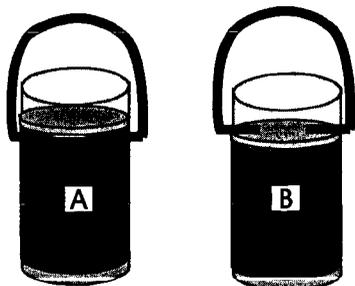


Figure 1. Reactor configurations for CH₄ storage determinations on loose (A) and compressed (B) carbons.

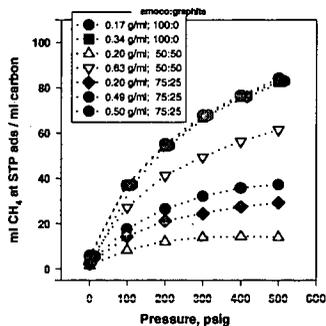


Figure 4. CH₄ storage on loose and compressed mixtures of Amoco Super A and graphite.

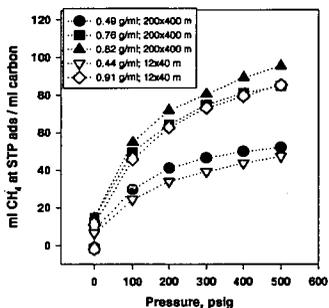


Figure 2. CH₄ storage on loose and compressed 75-38µm and 1700-425µm particle fractions of an activated carbon.

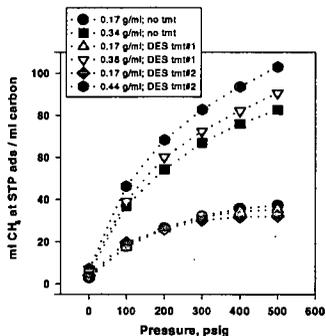


Figure 5. CH₄ storage on loose and compressed untreated and DES treated Amoco Super A carbon.

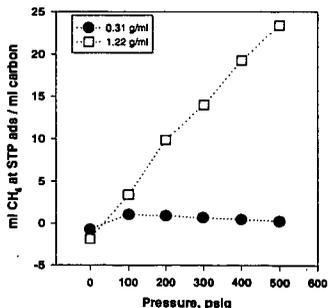


Figure 3. CH₄ storage on loose and compressed graphite.

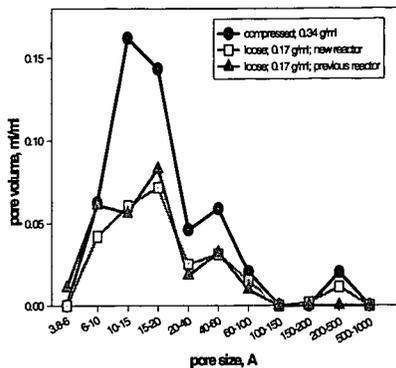


Figure 6. Pore size distributions for loose and compressed Amoco Super A carbon.

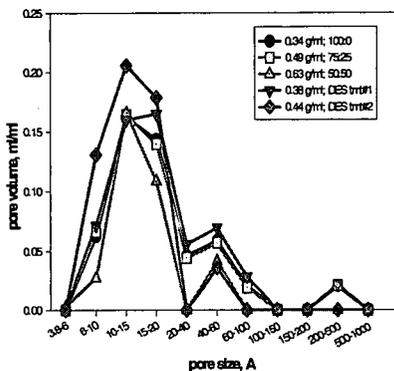


Figure 7. Comparison of the pore size distributions of compressed untreated carbon, carbon - graphite mixtures, and DES treated carbons.

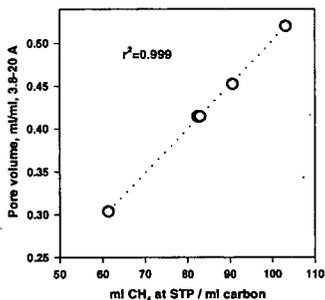


Figure 8. Correlation of pore volume of 3.8-20 Å pores with CH₄ storage capacity.