

TREATMENT OF ACTIVATED CARBONS FOR DENSIFICATION

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Keywords: Surfactant, densification, activated carbon

ABSTRACT

Although activated carbons can have very high surface areas and micropore volumes, their adsorption capacity is generally achieved at the expense of density. Decreased density limits the applicability of carbons for adsorption storage of compressed natural gas and vehicular fuels, even though their potential use has been shown to offer advantages where storage volume is limited.

In this study, activated carbons were treated with surface active agents to increase their bulk and pressed densities. This treatment, along with a hydraulic pressing procedure, are described in which the carbon densities are enhanced without significant adverse effects on their adsorbent properties. It is also shown that surface active agent treatment decreases the work needed to densify the carbons and that specificity in densification is influenced by the ionic character of the agent. As a result, even higher volumes of adsorption storage is expected relative to untreated adsorbents, especially for carbons having very high surface areas ($\sim 2000 \text{ m}^2/\text{g}$) and low densities ($\sim 0.2 \text{ g/cc}$).

INTRODUCTION

In general, the N_2 adsorption surface areas of activated carbons are very high, and in the range $600 - 2800 \text{ m}^2/\text{g}$. As a consequence, they have inherently low densities (\sim or $< 0.4 \text{ g/cc}$), and the amount or mass of carbon that can be accommodated in a limited volume is restricted. Ideally, a combination of high surface area, microporosity, and high density would be desirable for particular applications; for example, in the storage or adsorption of hydrogen, methane, or natural gas, it is imperative to maximize density while maintaining surface area and microporosity(1-4).

The purpose of this communication is to address the concept of densifying activated carbons produced from fossil resources with a surface active agent while maintaining reasonable levels of microporosity and adsorption capacity. The process uses low concentrations of inexpensive additives called surface active agents (surfactants) to enhance densification. These commercially available surfactants are anionic, cationic or amphoteric in nature and are interacted with activated carbons before or during densification processes that could be used in the carbons industry. This process was devised to enhance the density of activated carbon at a lower and more economical work input while maintaining inherent surface area and porosity in comparison to that obtained when using standard compaction, extrusion or pelletization without the addition of surface active agents.

EXPERIMENTAL

Three commercial activated carbons were used in the study; they were supplied by Amoco Research and Development, Norit N. V. Activated Carbon, and Sutcliffe Speakman Carbons Ltd. The BET surface areas and densities for each carbon respectively are as follows: 2600 m²/g, 2000 m²/g, 850 m²/g and 0.18 g/cc, 0.21 g/cc, and 0.38 g/cc.

Two surfactants were used in the experiments and are classified as anionic and cationic in charge. These surfactants were dissolved into distilled de-ionized water with stirring at a temperature at which dissolution was rapid, ~ 50° C. Surfactant concentrations in the range 0 - 1.0% by weight were used, since at levels in excess of approximately 1.0% surfactant solubilities typically reach a critical point of saturation, thereby causing unwanted agglomeration and formation of micelles. The activated carbons were treated and then heated to approximately 50° C with stirring. This temperature is not a factor controlling the effects of the surfactant on carbon density, but rather enable it to uniformly deposit and interact with the carbon without causing excess water boil-off or surfactant decomposition. The solution-carbon mixture was then filtered and dried at temperatures of 100-200° C to remove excess water. As a control to verify the attributes of surfactant addition, each of the samples was also treated with only distilled, de-ionized water (i.e. 0% surfactant) using a procedure identical to that used for preparing surfactant treated samples.

Apparent density measurements of the carbons were obtained in accordance to ASTM procedure D-2854 (5). This procedure is commonly practiced in industry. Carbon samples are fed through a feed funnel into a 100 ml graduated cylinder. The apparent density is then calculated as grams of carbon per unit volume. Any mechanical or vibrational packing effects were minimized in an effort to measure true inherent apparent densities.

Secondly, the pressed density of the carbons were obtained through the use of a pressing/pelleting technique. In determining pressed density, a cylindrical stainless steel die was used with a hydraulic press to supply the pressure on a graduated plunger. A premeasured mass of activated carbon was compressed under a steadily increasing hydraulic force of 0 - 89,000 N. By using the cylindrical volume (V) relationship ($V=4\pi r^2h$, where r is the radius of the plunger and h is the height of compacted carbon in the die) the change in volume vs. pressure was obtained. The volume of the pressed carbons was calculated using predetermined hydraulic forces - 11,125, 22,250, 44,500, 66,750, and 89,000 N; and, at these forces, the density was calculated using the mass per volume relationship $\rho=m/v$, where m was the premeasured mass of the sample before pressing. In addition to the density measurements, work and force relationships were calculated using standard equations to look at potential ramifications of the procedure.

Surface area measurements were performed on the control and the surfactant treated samples to evaluate effects of the treatment on adsorption capacities. Standard nitrogen adsorption (6) using a static volumetric flow process was used, employing a Coulter Omnisorp 100CX sorption system. All surface areas were calculated using the standard BET equation between relative pressures of 0.05 - 0.25. All samples were pretreated under similar conditions to ensure uniformity in data interpretation.

RESULTS AND DISCUSSION

Figure 1 displays the percent increase in apparent density relative to the standard data given in Table 1 for the carbons when treated with a 0.4 and 0.8% anionic surfactant. The maximum increase in apparent density is near 11% for the Norit activated carbon when using 0.8% by weight surfactant. The increased density of the 0.8% treated carbons suggests a cumulative effect which entails the ability to sufficiently cover the activated carbon surface with a minimum surface layer of surfactant. It has also been determined that treatments at concentrations of 1.0% or greater can cause decreased density in comparison to a 0.8% treatment. Hence, there is a maximum in density as a function of surfactant concentration rather than an increasing density with increasing surfactant concentration.

Using a cationic surfactant, the apparent density changes relative to the standard are displayed in Figure 2. The maximum increase in apparent density is 9% for the Amoco activated carbon when using a 0.8% surfactant treatment. The effects of cationic surfactant treatment are significantly different than the effect of the anionic surfactant treatment. This specificity is probably related to fundamental physical and chemical differences between the surfactants and their interaction with the carbons. This suggests possible inherent charge differences between the particles have been neutralized in the surfactant densification procedure. In addition, the data displayed in Figures 1 and 2 imply that a variable control of carbon density might be possible with either step-wise anionic/cationic treatments or amphoteric surfactants.

Figure 3 illustrates the work input needed to compact the Amoco activated carbon powder through a range of densities. The work-density plots for the Norit and A207 samples show similar behavior. Commercially it is imperative to increase carbon densities to maximize either the mass incorporated into a limited volume and/or to produce compacted pellets or extrudates which are resistant to decrepitation (1-4). Analysis of the data in Figure 3 show that the work required to achieve a particular density is significantly less for a sample that has been treated with surfactant. In the case of the Amoco activated carbon, the work input needed to compact the carbon to densities between 0.7-1.4 g/cc decreases by approximately 35% after treatment. This work input data implies that there is a potential and significant economic benefit to using surfactants during compaction, extrusion, or pelletization. It is also, however, imperative to retain specific or reactive surface area of the carbons if surfactant treatment is to be used during carbons processing.

Nitrogen BET surface areas of the pressed carbons are displayed in Figure 4. In general, the precision of the surface area measurement is (+/-) 5%. Within this precision limit, anionic and cationic surfactant treatments did not cause significant changes in the surface areas of the carbons. Surface area analysis on the carbon in their powdered, unpressed form showed similar results except for a marked decrease in surface area for the cationic treatments. Hence, the benefit of surfactants for powdered carbons, in which both density and surface area are considered, is dependent on the ionic character of the surfactant.

CONCLUSIONS

Surfactant treatment has shown to be beneficial in the densification of high surface area activated carbons for potential natural gas storage applications. This simple and inexpensive procedure has been shown to increase the densities of activated carbons without significantly inhibiting their adsorption storage potential. For applications in which storage volume is limited at certain pressures, a combination of high density and porosity can be achieved through a combination of surfactant treatment and hydraulic pressing of activated carbons. It is known that activated carbons can contain either positively or negatively charged surfaces and that the magnitude of the charge can be influenced by chemical treatment of the carbon (7-10). In the examination of anionic and cationic surfactant treatments, it appears that selective neutralization and alteration of surface charge is surfactant dependent. The action of the surfactants in enhancing carbon density and in decreasing the work necessary to produce a densified carbon is therefore tentatively related to the elimination or minimization of surface charge.

ACKNOWLEDGEMENTS

Appreciation is extended to Amoco Research and Development, Norit N. V. Activated Carbon and Sutcliffe Speakman Carbons Ltd. for supplying the activated carbon samples.

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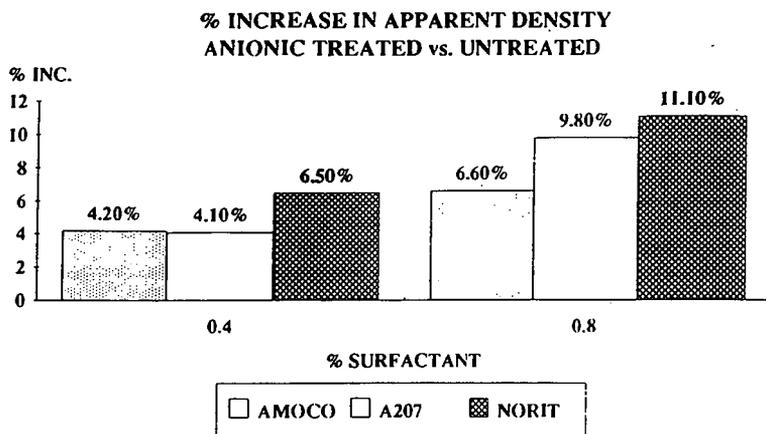


Figure 1.

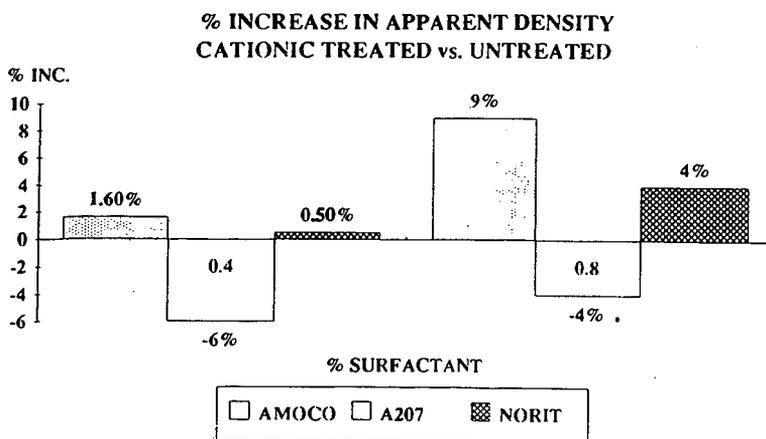


Figure 2.

AMOCO ACTIVATED CARBON
Work vs. Density

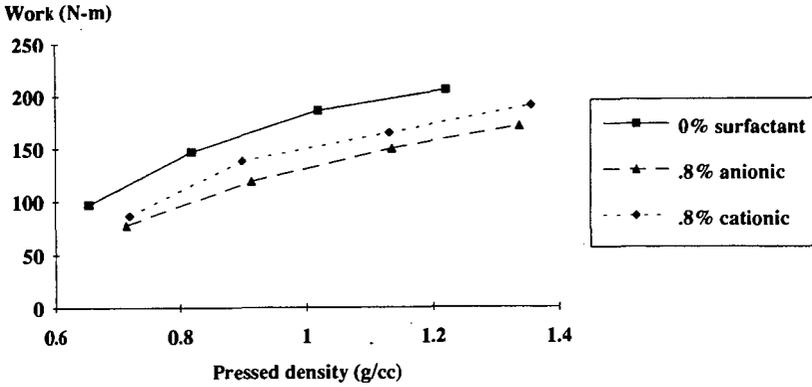


Figure 3.

SURFACTANT TREATED PRESSED CARBONS
BET SURFACE AREA

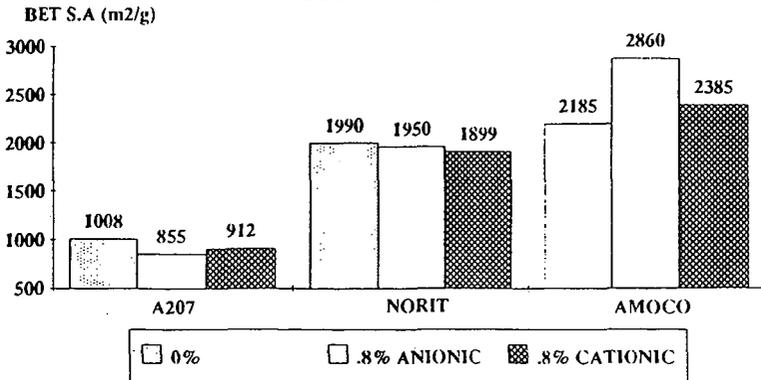


Figure 4.