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## CARBON HONEYCOMB STRUCTURES FOR ADSORPTION APPLICATIONS

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**Abstract**—Activated carbon honeycomb structures based on synthetic precursors are described. These strong, highly durable honeycombs are continuous interpenetrating structures of activated carbon and a ceramic with adjustable broad range of carbon percentage (5–95 wt%). Dynamic adsorption performance of a particular honeycomb structure containing 18 wt% carbon is described with respect to various adsorbates, i.e. butane, toluene, formaldehyde, isopropanol etc., and the importance of space velocity in determining the adsorption performance as well as the effect of structural parameters on the performance is shown. © 1998 Elsevier Science Ltd. All rights reserved.

**Key Words**—A. Activated carbon, A. carbon honeycombs, D. adsorption properties.

### 1. INTRODUCTION

Activated carbon is a very important material industrially, with applications in a variety of areas [1] such as adsorbents in air and water pollution control, catalysts in the chemical and petrochemical industries, electrodes in batteries and supercapacitors, and purifiers in the food and pharmaceutical industries. Typically activated carbon is made from naturally occurring materials such as wood, coal and nutshell flour [2,3] etc. via high temperature, inert atmosphere processing followed by activation to create porosity in the nanometer size range. This porosity imparts special adsorption characteristics to carbon and makes it useful in the variety of applications mentioned above. As a result of the natural raw materials used as well as the necessary processing steps associated with the manufacture, the material is obtained in a finely powdered form, and is granulated later to make it suitable for handling on a large scale [1]. In spite of the widespread use of this type of product, there are some drawbacks associated with it. First, the variations in the natural material make it difficult to control the properties of the carbon from batch to batch. Secondly, the granular material has to be used in traditional packed beds in many of the pollution control applications. Although functional, such beds have inherent drawbacks such as high pressure drop associated with the flow through the packed media, particle entrainment, channeling etc. For applications such as battery electrodes fine powders may only be used with binders and metallic current collectors, which result in poor utilization of the carbon properties. To obtain carbon with controlled and reproducible properties, synthetic starting materials may be used. The synthetic materials typically include polymeric resins. Several studies [4–6] have been carried out on synthetic raw material-

back of the variability in raw material source and have the added advantage of control of the carbon properties through control of the synthetic material structure. In spite of these advantages the synthetic material-based carbons have not been widely available commercially presumably due to high cost. Recently a new type of product, activated carbon fibers based on synthetic raw materials has been introduced. A number of studies of the properties of these fibers and the performance advantages the fibers demonstrate, have been published [7–9]. The fibers, however, have not found widespread commercial use. One of the drawbacks of the fibers is that these small diameter ( $\sim 10 \mu\text{m}$  diameter) fibers have to be made into a structural shape to put into a device and this requires more difficult procedures such as weaving into shapes. These procedures are expensive. Availability of activated carbon in a monolithic form with controlled adsorption properties is thus desirable.

The main objective of the various devices in industrial applications is to make the special nanoporosity in the carbon accessible to a flowing stream or more accurately the components in the stream, so that these components may be adsorbed and removed from the stream. The better the efficiency of the device in doing so, the better the carbon is utilized. It is thus important that the device has as high a geometric surface area per unit volume as possible. In the case of the packed beds, although the surface area per unit volume is high, in many cases all of it may not be accessible to the fluid stream because of the preferential flow patterns that may be established. Another problem with the packed beds is that the carbon pellets in the beds are sufficiently large in diameter to prevent full utilization of carbon because of the diffusional resistance associated with diffusion through the macropores before the components are

A natural structural shape that may eliminate the problems associated with the traditional products mentioned above is the honeycomb shape. This shape is known to have a very high geometric surface area to volume ratio, a feature which has resulted in widespread use of honeycomb structures in applications such as automotive catalyst carriers. The high surface area provides high contact efficiencies between the substrate and the flow stream. If activated carbon is made available in the honeycomb form, its adsorption capacity may be utilized better and a more efficient device design may result. The pressure drop for a honeycomb structure based system will be significantly lower than a packed bed system, with the extent of decrease in pressure drop depending on the structural parameters of the honeycombs.

Although attempts have been made to form activated carbon honeycombs and some industrial products such as ozone filters in laser printers have resulted, these honeycomb products are not widely used. The main reason for the commercial honeycombs not being successful is that these honeycombs have poor durability. The honeycombs are fabricated mainly by extruding finely powdered carbon into honeycomb shapes with a polymeric binder. The bonding between the carbon particle and the binder is typically poor which results in low strength, low durability honeycombs. In liquid streams the liquid preferentially adsorbs at the interface between the particle and the binder weakening the interface still further and severe durability problems result. These honeycombs therefore have been used only in less demanding applications such as for ozone removal in laser printers.

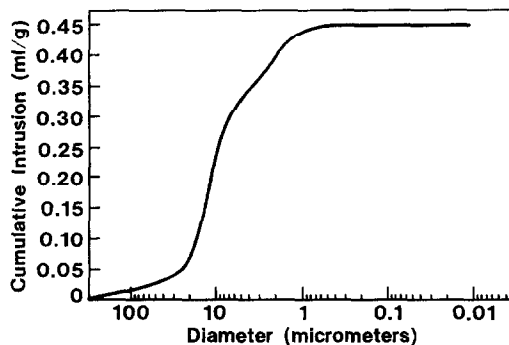
A new class of activated carbon honeycombs have been developed, which eliminate the binders associated with the honeycomb structures mentioned above. These highly adsorbent honeycombs have a continuous carbon structure. Since no binders are used, these inert high strength honeycombs are highly durable and provide an attractive alternative to the traditional packed bed system. In the following one of the concepts for fabricating these honeycombs is presented. The dynamic adsorption performance of any activated carbon system is the key to determining the usefulness of the system in any application. Although the major advantage of the honeycomb structure is the very open structure which results in a low pressure drop, this same open structure may result in poor adsorption performance. Preliminary data is thus presented on dynamic adsorption performance of one type of such a honeycomb structure with various adsorbates and the effect of some of the process and structural parameters on this performance is discussed.

## 2. CONCEPT AND EXPERIMENTAL DETAILS

The honeycombs discussed in this report were

carbon. In principle the process is as follows. Highly porous ceramic honeycombs are first fabricated. These honeycombs are fabricated from various ceramic compositions starting with clays. Cordierite-based compositions, which are used for fabricating low thermal expansion honeycombs for automotive catalyst support were used for this work. The honeycombs are commercially available from Corning Inc., Corning, NY. Various clays are mixed together with polymeric binders and extruded through steel dies in honeycomb shapes. The honeycombs are then fired to high temperatures ( $\sim 1500^{\circ}\text{C}$ ) to burn out binders and to react and sinter clays to form cordierite honeycombs. These honeycombs may be fabricated with a wall thickness of anywhere from 0.1 mm and higher and with cell densities as high as 95 cells per square cm. The cells may be rectangular, triangular, hexagonal or other shapes. Another important factor that can be adjusted is the wall porosity. By utilizing appropriate compositions, the wall porosity may be adjusted from 10% to 70%. Most of the work described in this report was done with cordierite honeycombs with 62 cells per square cm, a wall thickness of 0.19 and 0.29 mm and wall porosity of  $\sim 50\%$ . The mean pore size for these honeycombs is ten microns. Figure 1 shows the pore size distribution of the honeycombs measured by the mercury porosimetry technique.

The honeycomb is impregnated with high carbon yield polymeric resin of low viscosity. The resin is allowed to soak into the ceramic honeycomb structure. The excess resin is then drained and the resin-coated honeycomb is subjected to a drying and curing cycle to crosslink the resin. The resin forms an interpenetrating network with the ceramic. The cured honeycomb is then subjected to carbonization and activation in an inert atmosphere to form the composite carbon-ceramic honeycomb. The resin chosen for this work was a phenolic resole from Occidental Chemical Co., Niagara Falls, NY, because of two important characteristics. This resole has a viscosity of 100 cP. This low viscosity allows the impregnation and draining step to be carried out with ease. In addition the inexpensive phenolic resins have a very high carbon yield ( $\sim 50\%$  of the cured weight), thus



reducing the cost of the carbon produced. The aqueous resole contains about 65% solids. The honeycombs are simply dipped in the resin, allowed to soak for a few minutes and then drained of the excess resin by blowing air through the cells, before being subjected to a drying and curing process. The coated honeycombs are air dried and then dried at 95°C and cured at 150°C to crosslink the resin. Most of the cured resin remains in the cell wall porosity with a thin layer of resin on the surface. The coated honeycomb is then subjected to a carbonization and activation process. The carbonization is carried out at 900°C in nitrogen. The activation is carried out at the same temperature in carbon dioxide to obtain burnoff in 25–30% range. On carbonization a ceramic–carbon composite structure is formed. This structure is monolithic with carbon forming a continuous structure inseparable from the ceramic backbone. As the SEM micrographs show, it is difficult to see the boundary between the carbon and the ceramic. The SEM's of the ceramic honeycomb and the composite honeycomb are shown in Fig. 2.

Figure 2(a) shows the polished cross section of the ceramic as well as the composite carbon honeycomb. It is clear from the micrograph that the wall thickness of the honeycomb does not change significantly as a result of the carbon impregnation and the large

porosity in the honeycomb wall is not strongly affected. Figure 2(b) shows a high magnification view of the fracture surface of the honeycombs. It is clearly seen that the carbon has formed on the ceramic and also occupied the small pores in the wall. The activation step generates the desired porosity in the carbon for adsorption without affecting the strength of the structure significantly. The carbon–ceramic composite structure has 30–40% higher strength than the precursor ceramic honeycomb. Table 1 shows the comparison of the strength of the honeycombs.

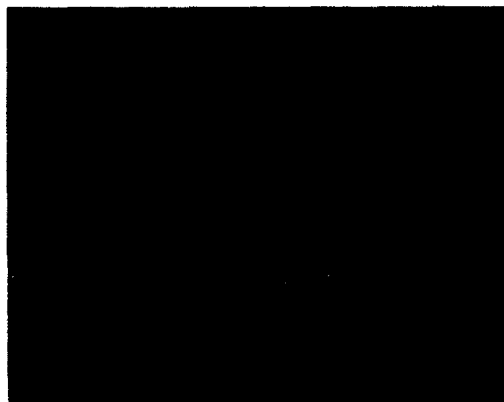
The dynamic adsorption properties of the honeycombs mentioned above were measured with an apparatus, the schematic of which is shown in Fig. 3. As shown in the figure various gases such as nitrogen, butane and toluene stored in pressurized tanks are metered through flowmeters in appropriate proportions and mixed before passing through the sample

Table 1. Axial crush strength of the honeycombs (2.54 mm min<sup>-1</sup> speed)

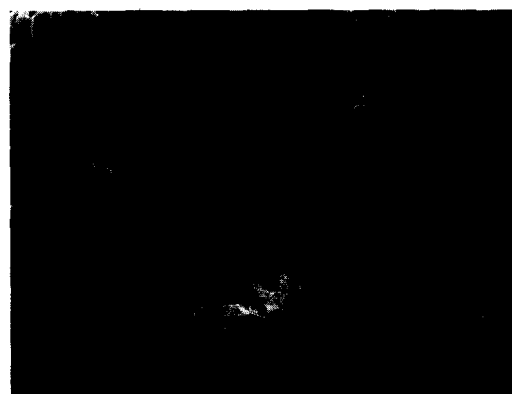
Ceramic honeycomb (0.19 mm wall)	6.3 MPa (±10%)
Composite carbon honeycomb (0.19 mm wall)	8.6 MPa (±6%)
Composite carbon honeycomb (0.29 mm wall)	13.8 MPa (±8%)



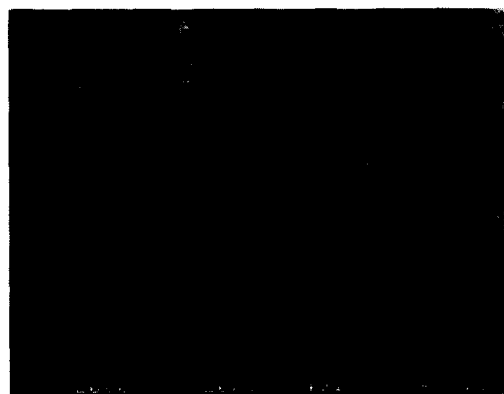
(a)



(b)



(a)



(b)

### Schematic Of Dynamic Adsorption Apparatus

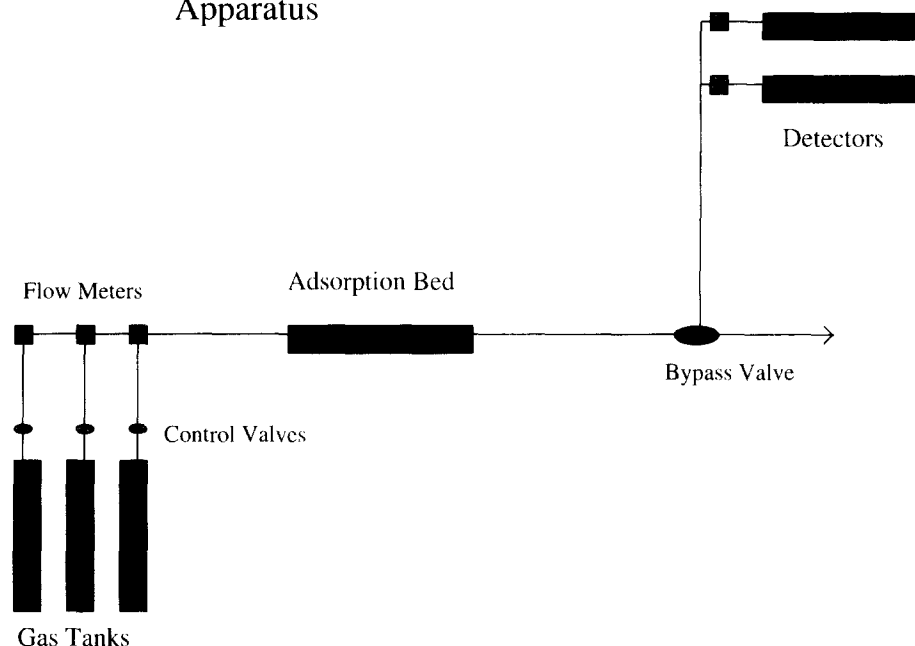


Fig. 3. Schematic of dynamic adsorption apparatus.

chamber. A small fraction of the mixed gases is diverted to the hydrocarbon detector. The calibrated detectors measure the hydrocarbon levels in the gas streams. All the equipment is computer controlled and the data is automatically stored and plotted to generate the breakthrough curves. The adsorption performance of the samples is measured as a function of time. Adsorption isotherms of the carbon are measured on an Omnisorp 100 from Coulter Inc. using standard procedures. Although methods have been developed to fabricate anywhere between 5 and 100 wt% carbon honeycombs, all the data given in this report was generated on first generation honeycombs with about 18 wt% carbon.

### 3. RESULTS AND DISCUSSION

The adsorption performance of the honeycombs depends on several material and process parameters. The material parameters include the carbon adsorption porosity on the honeycomb, the carbon percentage as well as the wall thickness of the honeycomb. The process parameters include the flow rate and concentration of the adsorbate, the adsorption potential which is dependant on the carbon structure as well as the adsorbate properties such as molecular weight. Although these carbon honeycombs have been made with a range of carbon structures which affect the adsorption performance, the carbon structure used for this work is described by a type I isotherm shown in Fig. 4. The carbon in this case is thus essentially microporous although some adsorp-

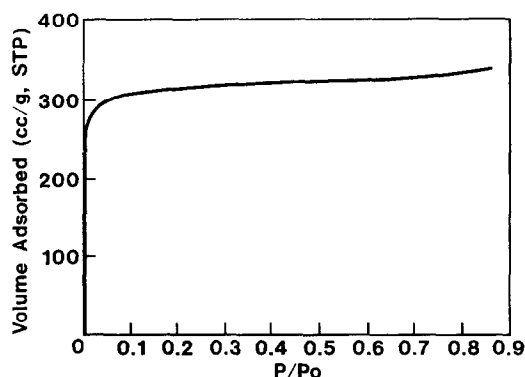


Fig. 4. Nitrogen adsorption isotherm of carbon.

gen adsorption isotherm was obtained at liquid nitrogen temperature. A TEM micrograph of the carbon structure is shown in Fig. 5. As the figure shows the carbon has a very regular structure with platelet spacing of 0.7–0.8 nm. This carbon structure is unusual and changes very significantly as a function of material and process parameters. Detailed studies of these structures will be published separately.

The adsorption performance of a device is measured in terms of the efficiency of removal of a certain constituent from a flowing stream. The performance is generally given in terms of a breakthrough curve, which shows the ratio of effluent concentration to influent concentration as a function of time [10]. The breakthrough capacity, i.e. amount adsorbed until the effluent to influent concentration reaches 0.05

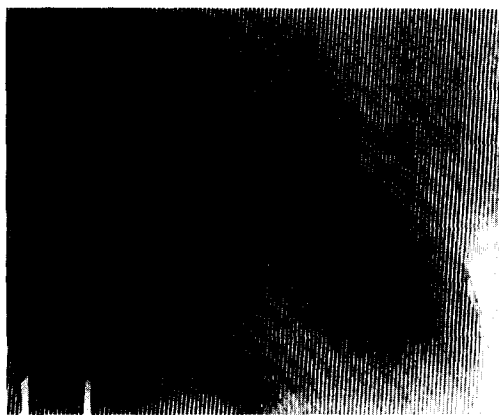


Fig. 5. TEM of carbon nanostructure.

tration of adsorbate and the amount of carbon in the honeycomb. In the literature, the breakthrough curve is given as a function of surface velocity calculated from volumetric flow rate divided by the empty cross-sectional area of the bed.

Although honeycomb structures may have advantages mentioned above such as low pressure drop, an important factor may substantially affect the performance negatively. Honeycombs have straight flow paths with very small cell dimensions. Under standard conditions encountered in practice, the flow through the honeycomb cell is laminar. Laminar flow means that there is very little mixing of the fluid stream during the flow through the honeycomb. As a result the efficiency of contact between the carbon surface and the contaminant to be removed may be very low and the adsorption efficiency may be negatively affected, especially at the high flow rate low concentration conditions encountered in practice. Experiments were thus done to evaluate adsorption efficiencies for butane and toluene, an aliphatic and an aromatic hydrocarbon, at 80 ppm concentration. These two hydrocarbons at the specified concentration are used as model compounds for adsorption behavior in certain industrial applications. Formaldehyde and acetaldehyde adsorption performance was evaluated at 30 ppm concentration. These two components are present in diesel exhaust. Finally, isopropanol adsorption performance was evaluated at 80 and 300 ppm concentration. Isopropanol is a typical solvent in solvent recovery applications. The data obtained with all these compounds at the specified concentrations and flow rates is thus expected to give an idea of the performance of these new structures under the dynamic conditions encountered in practice.

Figure 6 shows the dynamic adsorption performance of a 400 cell honeycomb with 0.19 mm wall thickness for butane adsorption at 80 ppm inlet concentration. The honeycomb was 2.54 cm in diameter and 3.8 cm long. The adsorption performance was evaluated at a flow rate of  $15,000 \text{ cm}^3 \text{ min}^{-1}$  of the

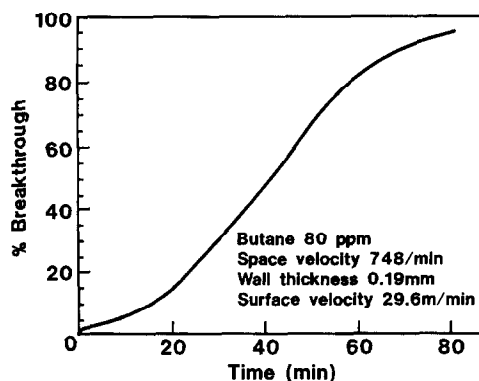
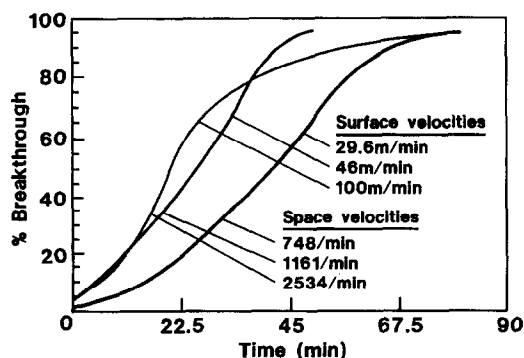


Fig. 6. Breakthrough curve for butane, thin-walled honeycomb (0.19 mm wall).

shows, the effluent concentration is 1.6 ppm or 2% of the influent at one minute. There is thus an immediate breakthrough. As the adsorption sites are filled up, the effluent concentration begins to increase and eventually reaches 95% of the influent level, i.e. 76 ppm at 75 minutes. Integrating the area above the curve gives the total adsorption capacity of the honeycomb. In this case the capacity is 127.9 mg. Since there is immediate breakthrough, it is clear that the length of the honeycomb is not sufficient to develop the mass transfer zone fully. The surface velocity in this case is  $29.61 \text{ m min}^{-1}$ . The honeycomb was then removed from the apparatus and regenerated in a  $150^\circ\text{C}$  oven. The experiment was then repeated with the same honeycomb at the same concentration of butane (80 ppm) but at a surface velocity of  $46 \text{ m min}^{-1}$ . The data showed that there was immediate breakthrough and the initial adsorption efficiency was 95% (4 ppm breakthrough) in this case. Increasing the surface velocity further to  $100 \text{ m min}^{-1}$  results in a further decline in initial efficiency and the initial effluent concentration is 6 ppm. Figure 7 shows a comparison of these three curves. The nature of the curves is similar to the curves obtained from packed beds and so there does not seem to be a heavy penalty associated with using an open honeycomb structure with straight flow



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