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Oak Ridge, Tennessee 37831
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LOCKHEED MARTIN ENERGY RESEARCH CORP.
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ACTIVATION AND MICROPORE STRUCTURE DETERMINATION OF ACTIVATED
CARBON-FIBER COMPOSITES

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SYNOPSIS

Rigid, high surface area activated carbon fiber composites have been produced with high permeabilities for environmental applications in gas and water purification. These novel monolithic adsorbents can be produced in single pieces to a given size and shape. The project involves a collaboration between the Oak Ridge National Laboratory (ORNL) and the Center for Applied Energy Research (CAER), University of Kentucky ¹⁻⁴. The carbon fiber composites are produced at the ORNL and activated at the CAER using different methods, with the aims of producing a uniform degree of activation, and of closely controlling pore structure and adsorptive properties.

The unusual properties of the composites offer potentially unique solutions to a range of environmental and catalytic applications. An open structure, combined with the presentation of the reactive surfaces for adsorption or catalysis in the form of narrow diameter fibers allows direct access of the contacting fluid with minimal mass transfer limitations, and very high rates of adsorption, desorption, and reaction. Hence, efficient adsorption or desorption can be achieved at short contact times and with low pressure energy requirements.

The main focus of the present work has been to find a satisfactory means to uniformly activate large samples of carbon fiber composites (dimensions up to 12x7x6 cm, or up to about 166 gram) and produce controlled pore structures. Two different processes have been developed using activation in steam or CO₂ and a less conventional method involving oxygen chemisorption and subsequent heat treatment. Steam activation was found to be the more cost efficient method. Different furnace configurations were evaluated. The preferred choice uses a perforated manifold for distribution of the activating gas. Oxygen chemisorption gives very uniform activation but requires extensive reaction times because of the long processing time.

Several environmental applications have been explored for the activated carbon fiber composites. One of these was to evaluate the activated composites for the separation of CH₄-CO₂ mixtures, and an apparatus was constructed specifically for this purpose. Samples activated to low burnoff (5-7% wt loss) with low surface areas (from 300-500m²/g) gave much better separation of CO₂ and CH₄, than samples produced at higher burnoff. It appears that the narrow pore size distribution created at low burn-offs is advantageous in the separation of CO₂ and CH₄. Since the higher separation efficiency was obtained at low burn-off, the materials can be produced at a relatively low cost.

The activated samples have also been characterized for their efficiency in adsorbing and desorbing CO₂. The samples with the most narrow average pore size show the highest CO₂ working capacity. These results are in excellent agreement with the results for the separation of CO₂ from CH₄. The maximum CO₂ working capacity occurs with samples at a burnoff of around 10% which is also the optimum burn-off for the separation of CO₂ and CH₄.

The composites were further evaluated in the cyclic recovery of volatile organics. The

Amendments to the Clean Air Act of 1998 have enforced the use of more efficient carbon canisters in US automobiles to recover evaporated gasoline. The standard evaluation method for this application is the butane working capacity test which is a carbon's ability to adsorb and desorb gasoline light ends. The two most important criteria for high butane working capacity carbons are high density and a large proportion of pores in the small mesopore range (from 20-50 Å). Several other practical applications of activated carbons also require wide pores, such as cyclic adsorption and desorption of volatile organic compounds (VOCs). The pore diameter of the pitch-based carbon fibers were found to be too narrow and were therefore not useful for such applications. Future work will focus on obtaining fibers from alternative precursors that give wider pore size distributions.

The activated carbon fiber composites have also been tested for possible water treatment applications by studying the adsorption of sodium pentachlorophenolate, PCP (a common herbicide/wood preservative). The composite specimen showed superior performance to a commercial water treatment carbon. The breakthrough time for PCP was at 1396 column volumes for the composite and 146 column volumes for commercially available Norit-Hydarco 4000 granular water treatment carbon. It is considered that the superior performance of the carbon fiber composite is due to the low diffusional resistance that it presents, allowing easy access of the adsorbate to the micropore network.

INTRODUCTION

The current project has its origins in research that was conducted at the Oak Ridge National Laboratory (ORNL) in the 1980s⁵, when a carbon fiber composite material was developed as a low-density, mechanically strong thermal insulator for a radioisotopic heat source on spacecraft for the Galileo and Ulysses Missions. The basis for the present project was to examine the feasibility of adapting the process to produce high surface area adsorbents through the activation of similar composites, by development of porosity in the carbon fibers. One of the principal changes, compared to the original work, was to focus on low cost carbon fibers that are produced from isotropic pitches although other types of fiber are also included in the studies. In recent years, a great interest has developed in the activated forms of isotropic carbon fibers, where high surface areas can be produced by partial gasification in steam or other oxidizing gas^{6,7}. Moreover, while porosity can be generated in most types of carbon fiber, low-modulus fibers produced from isotropic pitch are particularly suited for activation due to their unique structure in which the random packing of small crystallites allows for the development of an extensive pore structure.

Activated carbon fibers are of interest in several areas of adsorption and environmental protection due to their novel properties that make them more attractive than conventional forms (powder or large-size carbons) for certain applications^{1,2}. Among the possible applications, activated carbon fibers are of interest for the adsorption and recovery of organic vapors; the clean up of landfill gas i.e separation of methane and carbon dioxide, the removal of SO_x and NO_x from flue gases; the improvement of air quality; and water treatment^{8,9}.

Difficulties in handling and utilizing activated fibers can be surmounted by their incorporation into composites, such as woven and non-woven fabrics, felt, and paper. This research is concerned with the development of a rigid activated carbon fiber composite material that can be produced in single pieces to a given size and shape. Because of the potential molecular sieve properties, the composites have been termed activated carbon fiber composite molecular sieves, or CFCMS.

The unique properties of the activated carbon fiber composites offer potentially unique solutions to a range of environmental problems. An open structure, combined with the presentation of the reactive surfaces for adsorption or catalysis in the form of narrow diameter fibers allows direct access of the contacting fluid with minimal mass transfer limitations, and very high rates of adsorption, desorption, and reaction. Hence, efficient adsorption or desorption can be achieved at short contact times and with low pressure energy requirements.

The research described in this report is the result of a collaborative effort between the ORNL and the University of Kentucky, Center for Applied Energy Research(CAER). Carbon fiber composites have been prepared at ORNL and sent to the CAER for studies of activation, the characterization of pore structure and other properties, and studies of adsorptive behavior. The specific objectives of the research are listed below;

- * Prepare and supply activated rayon fibers to ORNL for production of mesoporous Carbon Fiber Composites (CFC)
- * Investigate steam activation of CFC from ORNL. Determine relationships between activation conditions and uniformity of product, and between burnoff and porosity and shrinkage.
- * Supply fibers synthesized at CAER to ORNL for incorporation into CFC material.
- * Develop methods to assess potential of activated CFC for gas separation.

EXPERIMENTAL

Composite Preparation

Carbon fiber composites were prepared at ORNL¹ by vacuum molding from water slurries containing powdered phenolic resin and chopped isotropic petroleum pitch fibers, (P-200, ~ 17.5 μm diameter, average length 380 μm , supplied by courtesy of Ashland Carbon Fibers Division, Ashland Inc.). The slurry is vacuum molded into tubular, plate or rod configuration, followed by drying, curing, and carbonization to about 650°C. The carbon fiber composites are supplied to the CAER in the form of plates (28x12x1.5cm), rectangular or cylindrical shapes¹.

Activation

The normal method of activation is by reaction in steam or CO_2 at temperatures between 800-950°C. Carbon atoms are removed by gasification reactions

creating a network of pores and simultaneously reducing the yield of material as the pore structure develops. The rate of reaction is dependent upon the concentration of the reactant gas and the temperature. In order to effect uniform activation of composites it is therefore important to ensure that the gas concentration and temperature are maintained uniformly throughout the sample.

In attempting to uniformly activate relatively large composite samples (4.5" diameter, 6" long) in steam or CO_2 , different reactor configurations and conditions have been investigated. Originally a Lindberg Blue M laboratory box furnace was used, in which the specimen was contained in a sealed stainless steel cylindrical chamber of diameter 6", and height 6". Water was pumped into the reaction chamber and vaporized at the bottom when steam flowed upwards through a perforated stainless steel plate, and was distributed around the composite, Figure 1. This furnace configuration leads to non-uniform activation since the gas stream did not have free access to the center of the composite, and the reaction products, CO and H_2 , will further serve to dilute the steam leading to poor surface area development in the center and upper parts of the sample.

Figure 1: Configuration of steam supply in Lindberg Blue M activation furnace: perforated plate at bottom

In a later, more successful arrangement, steam was introduced at several points along the length of the composite. A 4900 W Lindberg furnace was acquired with an inconel chamber of dimensions 6"x 4" x 12". The activating agent, steam or CO₂ was supplied through 4 connected stainless steel distributor tubes that run along the four long corners of the furnace, Figure 2. The distributors are drilled with holes 2 mm in diameter and spaced about 1" apart along their length. The end result is to create a uniform flow of the activating agent in the chamber and around the sample. The design was developed from the previous experience, where uniform activation was achieved with small samples by introducing the steam at different points around the sample. By this configuration, concentration gradients in the activating gas are reduced.

Figure 2: Configuration of steam supply in activation furnace.

Steam activation was carried out at temperatures from 800-900°C for reaction times of 0.5-3 hrs using a mixture of steam and nitrogen. The flow rate of water was 50-140cc/hr and of nitrogen, 2-3 lpm. Activation in pure CO₂ was carried out at temperatures from 850-950°C, for reaction times of 1-3 hours. The flow rate of CO₂ was varied from 2-3 l/min with the same multiple point gas introduction configuration.

A less conventional method of activation involved a combination of oxygen chemisorption and carbonization. The method was first described by Nandi et al¹⁰ and has been researched more recently by Quinn et al¹¹. The procedure involves the chemisorption of oxygen at low temperatures (e.g. <250°C) followed by heat treatment in nitrogen or other inert gas at temperatures up to about 900°C. It appears that slow oxygen chemisorption produces a uniform distribution of surface oxygen groups that are then thermally decomposed to remove carbon as CO and CO₂. Because of the limited oxygen uptake at low temperatures it is necessary to complete several cycles before there is appreciable surface area development. The samples were exposed to an atmosphere of 50% O₂ in N₂ at temperatures ranging from 170-240°C for periods of 1-6 hours. They were subsequently heat treated in nitrogen to 850-925°C, for 1-3 hours, when the removal of carbon as carbon oxides should lead to a uniform surface area development. It is known that CO₂ is released at temperatures from 300-800°C with a maximum at about 350°C while CO is released at temperatures from 500-900°C with a maximum at 700°C.

Characterization

Porosity

Surface area and pore size distributions were measured on a 10 port automated surface area analyzer, OMNISORB 610. The high efficiency of the instrument allows the measurement of surface areas, as well as the characterization of pore sizes down to 4 Å diameter, using nitrogen at 77K as the adsorbate. Surface areas were determined from the isotherms by the BET method¹², and pore volumes by the D-R method (micropores) and the BJH method (mesopores)¹².

Butane Working Capacity Test

The butane working capacity (BWC) was developed as a measure of the effectiveness of activated carbons that are used to trap hydrocarbons released by evaporative losses from vehicle fuel systems (used in evaporative loss control devices, or ELCDs). It is also a useful indication of the properties of activated carbons with respect to other applications. Essentially, the BWC is the difference between the saturation adsorptive capacity of butane, and the amount retained upon the carbon after purging under specified conditions. The retained butane is too strongly adsorbed to allow facile desorption. The tests were performed according to ASTM method D5228-92. According to the procedure, the activated carbon sample is outgassed under vacuum at 150°C for 4 hours, packed in a constant volume bed according to a standard procedure (ASTM D 2854), and immersed in a constant temperature water bath at 25°C. Butane is then passed through the activated carbon sample at a flow rate of 250cc/min for 900 seconds. The sample is then weighed, and gas is adsorbed for another 600 seconds. When the sample has reached constant weight, the bed is desorbed with dry air that is passed through the sample at a flow rate of 300mL/min for 2400 seconds. The difference in mass between the adsorbed and desorbed state is the BWC and is expressed as mass of butane per unit volume of carbon. We also report CO₂ working capacities that were determined using the same procedure.

Permeability of Composites to Liquid Flow.

Previously we have reported on the high permeability of the composites to the flow of gases. We have now extended these measurements to include the flow of liquids. Specimens for permeability testing were cut from a composite sample using a hole cutter with 1/2 inch diameter. The samples were about 5.7 cm long, giving a total specimen volume of about 12.5 cc. The samples were firmly sealed into heat shrink tubing and mounted in a simple apparatus that was used for the water flow permeability test. The water flow was varied between 8-170 ml/min or 4-90 gpm/ft². The differential pressure was measured using a digital pressure gauge upstream of the sample. The pressure drop was determined as the difference between this pressure and atmospheric pressure.

Liquid Phase Adsorption: Herbicides.

The adsorptive capacity of an activated carbon composite sample for sodium pentachlorophenolate (PCP) was measured by sealing a 2.0 g sample of carbon into

polyolefin tubing to create a column of volume 8 cm³ and length 6 cm. Plugs of quartz wool were fitted at the column ends to contain the bed. A peristaltic pump, Pulsafeeder - Mec-o-matic VSP-20, located downstream of the column continuously drew a 40 ppm solution of sodium pentachlorophenolate (NaC₆Cl₅O) from a reservoir and through the column. The concentration of PCP in the column effluent stream was monitored via a UV-Vis spectrophotometer (Varian, Series 634) fitted with a 10 mm path length flow-through quartz cell, at a wavelength of 317.5 nm. Column breakthrough was determined as the point where the ratio of effluent to inlet PCP (C/Co) was equal to 0.3. The flow rate of PCP solution through the column was held constant at 1 ml.min⁻¹. An equivalent experiment was conducted using a granular Norit commercial water treatment carbon to provide a basis for comparison.

RESULTS AND DISCUSSION

Uniformity of Steam and CO₂ Activation

Samples of dimensions up to 12 cm x 7 cm x 6 cm and weighing up to 166 g were activated by steam or CO₂ using the second furnace configuration. The uniformity of activation was determined by measuring BET surface areas and micropore volumes on samples taken from 3 or 6 different positions in the composite, as indicated in Figure 3. The results are shown in Table 1. The standard deviation of BET surface area for steam activated samples ranged from 0.5-10%, and for CO₂ activation from 5-8%. At similar burnoff the surface area and pore width is the same but the CO₂ activation is slower.

Table 1: Uniformity of activation of carbon fiber composites

ID	B. off	HTT	Time	BET area	pore width	micro pore vol.	stdev BET
	(%)	(°C)	(hr)	(m ² /g)	(Å)	(cc/g)	(%)
Sample ID Activating Agent							
Steam							
181	9	850	1	484-487	6.4-6.5	0.23-0.24	0.5
185	19	877	1	465-568			10.0
182	25	900	2	812-867	7.3-7.6	0.41	4.6
186	25	877	2	803-914			6.3
106	27	800	4	762-865			9.0
109	41	877	2	1089-1109			1.3
CO₂							
179	5	850	3	390-431	6.7-8	0.19-0.21	5.7
180	11	900	3	426-469	6.2-6.9	0.21-0.23	4.9
126	20	900	3	632-578	6.6-6.3		6.3

NOTE: sample #178: 20 gram, sample #>178: 50-60 gram, sample #190 sample: 166 gram * sample was physically disrupted, and split along plane perpendicular to settling direction during formation of composite

Figure 3: Position of samples for surface area measurement

Dimensional Changes

It is found that there is an overall shrinkage of the composites during activation and the volume decrease can be related to the extent of weight loss, Figure 4. A linear relationship exists to about 35% burnoff, but at higher values there is a steeper increase in shrinkage. There is a similar path for steam and CO_2 at least up to ~45% burnoff. Moreover, for burnoffs over 50% and above 850°C , the extent of contraction induces sufficient stresses to split the composite and destroy its physical integrity.

Figure 4: Volume change of composite with burnoff

Uniformity of Activation in Steam

Although it was found that samples up to ~ 150 g can be uniformly activated, the difficulty of attaining this objective increases with sample size. This is a pertinent issue, since in many practical applications, there may be a requirement to produce much larger monoliths. Sample SM12, a cylinder of carbon fiber composite was produced at ORNL to a diameter of 11.4 cm and length 21 cm, and was divided into three sections each 6.9-7.8 cm long with the same diameter. The sections weighed between 140-180 grams. In order to try to achieve more uniform activation it was decided to examine the effect of progressively lowering the steam activation temperature from 875°C in steps of 25°C down to 800 °C. The samples were all activated to a burnoff of 24-28% under the conditions given in Table 2. The surface area distributions through the three samples are given in Figures 5a-c.

Activation is most uniform under conditions of low temperature (800°C) and long reaction times (14 hrs), which is attributed to the low reaction rate that allows the steam to diffuse throughout the sample. Hence, the center of the sample is activated to nearly the same extent as the periphery. The mean rate of activation (burnoff/g sample/minute) is shown in Table 2. The reaction rate increases by about 27% upon increasing the temperature from 800 to 825°C and by another 50 % upon increasing temperature from 825 to 850°C. The samples activated at 800°C do not exhibit stress cracks, while at 850°C, stress cracks occur. Stress cracking may be related to non-uniform activation and leave differential shrinkage in the sample.

The activation energy for steam activation was determined to be 126kJ/mol from a plot of the rate of carbon burnoff versus reciprocal absolute temperature (Arrhenius plot and is consistent with data in the literature. The activation energy is slightly higher than for the activation of coal and wood based carbons but lower than for the activation energy for carbon fibers¹³. In practical terms, activation at 800°C proceeds too slowly to be of value. It is anticipated that further improvement can be made in activating at higher temperatures and achieve low standard deviations in surface area distribution by further changing furnace configurations and conditions.

Table 2: Burnoff and surface area for steam activation at different HTT.

ID	HTT (°C)	time (hr)	start wt (g)	burnoff(B.O.) (%)	rate of B.O.St dev (g/g.hr) BET(%)	
OR267	800	14	172	26.7	0.019	17
OR 272	825	10	189	24.2	0.024	20
OR 267	850	8	133	28.7	0.036	23

a) HTT=850°C, 8
hrs

b) HTT=825°C, 10 hrs

c) HTT=800°C, 14 hrs

Figure 5 a-c: Distribution of BET surface area in samples activated at three different temperatures.

Uniformity of Activation by Chemisorption

The chemisorption of oxygen coupled with carbonization has been investigated as an activation technique for achieving uniform activation and a narrow pore size distribution. The chemisorption of oxygen is performed at 200-250°C when oxygen can attach onto the active sites of the carbon as illustrated in Figure 6a^{10,11}. The amount of oxygen uptake eventually reaches a limiting value. As long as sufficient time is allowed for the oxygen to diffuse to all of the available surface, the extent of chemisorption should be uniform throughout the sample. Upon subsequent heat treatment to elevated temperatures (up to 925°C in this work), the removal of carbon as CO and CO₂ will result in the formation of micropores.

Figure 6: Reaction mechanisms for the chemisorption /carbonization technique

The average surface area and pore volume is shown for the different reaction conditions used in Table 3. The chemisorption temperature was varied from 160-250°C. Increasing the chemisorption temperature from 225 to 250°C gave sufficient uptake of oxygen to triple the BET surface area upon heat treatment to 900°C, Table 3¹⁴. The carbonization temperature was varied from 850-925°C. Heat treatment to 850°C is not sufficient to achieve significant microporosity, and heat treatment to 925°C also gives low surface area. The optimum upper temperature for maximizing the production of narrow micropores appears to be around 900°C. Over a single treatment cycle, the surface area development in large composites was found to be very uniform with a deviation in surface area within the samples (3 samples taken for measurement throughout the composite) of

only 3-6% for a chemisorption temperature of 250 and carbonization temperature of 900 or 925°C, Table 3. This deviation cannot be distinguished from the experimental reproducibility.

In order to increase the surface area further, the cycles of oxygen adsorption and heat treatment were repeated several times. The surface area increased slightly with each step, to about 440 m²/g after a total burnoff of 9%, Figure 7. For each cycle of activation, new narrow micropores are opened. It was also found that the average pore width is reduced as the burnoff is increased, contrary to the case with steam activation.

Table 3: Activation of carbon fiber composites by oxygen chemisorption/carbonization.

Sample#	Chemisorp.		Carboniz.		Burnoff (wt%)	Surface area (m ² /g)	stdev (%)	pore volume (cc/g)	
	T(°C)	t(hr)	T(°C)	t(hr)				micro	meso
221	225	3	900	2	4	150	20	0.11	0.03
216	250	3	850	2	5	315	19	0.15	0.07
218	250	3	900	2	6	387	6	0.20	0.0
219	250	3	925	2	6	230	3	0.13	0.03

Figure 7: Increase in surface area for each cycle of oxygen chemisorption/carbonization. (Each data point shows a new cycle).

Compared to the uniformity of surface area development produced in large samples by steam activation (which ranged from 17 % at an activation temperature of 800°C to 22% at 850°C), the oxygen chemisorption technique gives a much more uniform activation. However, the disadvantage of using this technique compared to steam activation is the extended processing time required to achieve a certain burnoff. The activation time necessary to achieve a 9 % burnoff is shown in Figure 8 for steam activation at different temperatures and oxygen chemisorption/carbonization. As can be seen from the Figure, a far longer processing time is needed to achieve the same burnoff for the chemisorption technique. It is therefore expected that the oxygen chemisorption technique will be non-economical on a commercial scale.

Figure 8: Reaction times for activation to 9% burnoff by steam activation at different HTT and oxygen chemisorption/carbonization.

Activation of Poly Acrylo Nitrile(PAN)-Based Carbon Fibers and Composites

PAN-based carbon fibers and PAN-based carbon fiber composites were activated in an attempt to produce composites with wider pore size distributions than those from the petroleum pitch based fibers. PAN-based Fortafil P-200 composites were supplied by ORNL. A range of different carbonization/ activation conditions was investigated to optimize surface area development. The results are shown in Table 4. The highest surface area obtained was about 680 m²/g. The optimum conditions for surface area development are carbonization at 700° C followed by steam activation at 800 °C. The surface areas are still appreciably lower than those that can be generated in conventional pitch based carbon fibers, and it was found that there was no significant broadening of the pore size distribution.

Table 4: BET surface area and porosity of PAN based carbon fibers

Sample#	Carboniz		Steam Activ		Burnoff (wt%)	Surface area(m ² /g)	
	T(°C)	t(hr)	T(°C)	t(min)		BET	mesopore
254	600	120	700	300	39	336	2
229	700	120	750	240	46	413	3
230	700	120	800	180	86	670	11
222	-	-	877	60	95	679	9
255	850	15	850	30	56	370	2
257	900	15	850	30	37	261	2
258	1000	15	850	30	30	106	1

Applications

Gas Separation

The unique properties of the activated composites - narrow, unimodal pore structure, high surface area, rapid rates of adsorption and desorption, and the ability to form specific shapes of high permeability and strength - suggest that, among other applications, they may be suitable for molecular separation on the basis of size and shape. The system CH₄ - CO₂ was selected as a model mixture, following studies of the adsorption of these gases by TGA which showed that the activated carbons have a high capacity for adsorbing CO₂ (up to 10 wt%) while much less methane is adsorbed (less than 1 wt%)¹⁵.

An apparatus was constructed to examine the effectiveness of the activated carbon fiber composites for gas separation, Figure 9. Samples were tested using a mixture of 75% CH₄ and 25% CO₂. The composition and flow rate of the emergent gases were detected as a function of time using a mass spectrometer and a mass flow meter. The sample was sealed in place using a rubber seal. Helium was first purged through the system and when the gas analysis indicated that virtually pure helium was emerging at the outlet, the valve was switched and the 75%CH₄/ 25% CO₂ mixture introduced at a fixed controlled flow rate (usually 50 ml/min). The outlet flow rate and composition were then monitored and recorded for 10 minutes. Initially, for an activated sample there is a period of time when the outlet flow is very low, as most of the CH₄ and CO₂ flowing into the sample is adsorbed. Then, relatively pure methane begins to be detected. After about 10 minutes, the outlet gas composition has returned to that of the original mixture 75% CH₄, 25% CO₂. The volumes of gas produced per gram of composite with 95%, 90% and 85% CH₄ concentration were then calculated.

The volumes of effluent gas produced at 95 and 90% methane concentration are shown in Table 5 as a function of burn-off for pitch-based composites. Samples activated to low burnoff (5-7% wt loss) and low surface areas (from 300-500m²/g) show excellent

separation of CO₂ and CH₄, compared to samples produced at higher burnoff (10-30% wt. loss, surface area 500-1000m²/g). There appears to be no benefit in producing composites at burnoffs higher than 10%. The influence of average pore diameter on the separation process and production of high purity methane is shown in Figure 10. From these data, the optimum pore diameter is seen to be in the range 0.7 - 1.0 nm. The greater separation efficiency obtained at low pore diameters and therefore low burn-off means that the most effective CFCMS can be produced at relatively low cost.

Figure 9: Schematic Arrangement of Apparatus for testing Gas Separation.

Table 5: Volume of CH₄ produced at 95-85% concentration from a mixture of 75%CH₄/25%CO₂

Sample	Cumul. vol of CH ₄ out(cc)-off		Burn agent	Activation		BET sa	pore vol	pore diameter	
	95%	90%		temp (°C)	time (hr)				
			(wt %)			(m ² /g)(cc/g)		(Å)	
SA124	-	47	24	CO ₂	900	3	632	0.2	5.8
SA139	33	69	8	H ₂ O	850	1/4	444	0.26	12.0
SA 132	35	67	8	CO ₂	850	2	424	0.19	7.6
SA 135	39	78	12	CO ₂	850	4	548	0.23	5.9
SA 136	44	80	7	CO ₂	1000	1/60	291	0.11	11.0
SA 137	53	87	7	CO ₂	950	1/6	397	0.13	8.8

Figure 10: Relationship of average pore diameter to volume of effluent gas produced with high CH₄ purity.

CO₂ Working capacity

The CO₂ working capacities of the composites were determined using a test similar to the standard test for butane working capacity. The CO₂ working capacity for four different samples is shown in Table 6. Interestingly, the specimen with the highest CO₂ working capacity has a burnoff of only 9% and a BET surface area of 484 m²g⁻¹, while a sample with 25% burnoff and a surface area of 850m²g⁻¹ has a significantly lower CO₂ working capacity. The samples with the most narrow average pore size show the highest CO₂ working capacity. These results are in excellent agreement with the results for the separation of CO₂ from CH₄. The maximum CO₂ working capacity occurs with samples at a burnoff of around 10% which is also the optimum burn-off for the separation of CO₂ and CH₄.

Table 6: CO₂ working capacities for composite samples

Sample #	SA 183	SA181	SA182	SA179
Apparent density(g/cc)	0.35	0.33	0.29	0.40
Burn-off (%)	19	9	25	5
BET surface area(m ² g ⁻¹)	559	484	850	393
Average pore size(A)	6.1	6.4	7.4	8.0
CO ₂ working capacity, W/W(%)	8.8	10.3	9.9	9.2
CO ₂ working capacity, W/V(g/100mL)	3.0	3.4	2.9	3.1
CO ₂ adsorbed W / W %	5.4	9.9	10.4	10.1
CO ₂ adsorbed W / V g / 100 mL	1.9	3.3	3.4	3.4
CO ₂ retained W / W %	-3.4	-0.4	0.8	0.8
CO ₂ retained W / V g / 100mL	-1.2	-0.1	0.3	0.3

[NOTE: The CO₂ adsorption numbers for SA 183 and 181 are too low, probably due to air being adsorbed onto the carbon after outgassing and before CO₂ adsorption. The experimental procedure was altered to avoid this phenomenon in the other runs.]

Butane working capacity, BWC

The purpose of the BWC test is to investigate how the adsorptive properties of the activated composites compare to those of commercial granular carbons that are currently used in evaporative loss control devices (ELCD) in automobiles. The ELCD canister takes up gasoline evaporated during refuelling and evaporation due to temperature changes during the day. The gasoline is desorbed from the canister by a flow of ambient air and recycled to the engine. The commercial carbons have a BWC of around 15 g/100 mL.

Pitch-based carbon fibers have narrow micropores and would not normally be useful for such applications as the adsorbed vapours would be strongly retained. Because of this, carbon fiber composites were activated to high burnoffs in order to attempt to create wide porosity. In these cases, the surface area is high, up to 1800 m²/g, but the composites still have a low proportion of mesopores. Another problem associated with activation to burnoffs higher than ~40% is that cracking and delamination of the composites occurs. A further obstacle to producing the performance expected of an evaporative loss control device is the low density of the composites. The density of the standard composites as received from Oak Ridge is about 0.23 g/cc. In order to compete with the BWC of commercial carbons the density must be increased to around 0.35 - 0.4 g/cc. In the research reported here, samples A and B were ground and packed as a powdered bed to a density of 0.39 and 0.36 cc/g respectively. The results of the BWC tests are shown in Table 7. Both samples have butane adsorption capacities within the commercial range of evaporative loss control devices for automobiles, 9.7 and 8.6 g/100 ml. This is significantly lower than that of commercial carbons, including wood-based sample produced at the CAER, Table 7. One reason for the low performance of the pitch based carbon fiber composite is the narrow pore size distribution that gives high retentivity of butane. The average pore size for wood based carbons is usually around 20-50A, allowing much more effective desorption. The

pitch based activated carbon fibers are therefore not suitable for butane or gasoline vapor storage. However, if the composites were made from a more mesoporous fiber, the butane working capacity could be increased.

In an attempt to improve the performance of the composites, an electrical current was applied to two of the composites during the air desorption stage in order to increase the sample temperature and aid desorption. A current of 4 A was applied for 25 seconds to give a temperature increase of about 50 °C for samples C** and D**. As can be seen in Table 7, the butane retentivity for sample D decreased from 1.8 g/100 ml to 0.8 g/100 ml when the current was applied. However, the BWC is still only 4.1 g/100 ml and the highest BWC obtained on an activated composite was 5.5 g/100 ml which is still very low.

Even with the application of an electric current during the desorption stage, it does not seem feasible to produce a purely pitch-based carbon fiber composite with high performance for butane adsorption.

Table 7: Butane Working Capacity (BWC) of activated carbon fiber composites

ID	A	A2*	B*	C**	D	D**	Wood^^
BET surface area (m ² /g)	1380	1380	1057	1728	1126	1126	1798
density (g/cc)	0.25	0.39	0.36	0.25	0.21	0.21	0.28
BWC [W/V] (g/100 ml)	5.5	9.7	8.6	4.6	3.1	4.1	14.5
butane activity [W/V] (g/100ml)	10.0	11.6	10.2	6.9	4.9	4.9	14.5
butane retentivity[W/V](g/100 ml)	4.5	1.9	1.6	2.3	1.8	0.8	0

* composite ground and packed to high density; ** current applied to composite to desorb butane, 4 A for 25 seconds, temperature increase ~ 50°C; ^^Wood-wood based commercial carbon

Adsorption of VOC's

The dynamics of adsorption of volatile organic compounds (VOCs) onto pitch-based activated carbon fiber composites was investigated using butane as a test adsorbent and compared to that of beds of granular activated carbon (GAC). During adsorption in activated carbon beds, the shape of the mass transfer zone is one of the most important working parameters with respect to the economics of operation of the carbon bed. The mass transfer zone (MTZ) defined below, is dependent upon the adsorbent, the concentration of the adsorbate and the contact time. A schematic of the typical progress of the mass transfer zone through an adsorber bed is shown in Figure 11¹⁶. The adsorbate front progresses through the bed until the concentration in the outlet stream starts to increase. When the outlet concentration is unacceptably high (usually above 10% of initial concentration), the breakthrough point is reached and the bed has to be regenerated. At this point, only part of the bed is totally saturated, Figure 11, and a proportion of the adsorbate is unused. Thus the efficiency of bed use is dependent upon the shape of the mass transfer profile and, ideally it is defined as a sharp boundary across the bed diameter.

$$MTZ = \frac{\text{total bed depth}}{(t_{st}/(t_{st} - t_B) - X)}$$

where t_{st} = time required to saturation; t_B = time required until breakpoint;
 X = degree of saturation in the MTZ

The mass transfer zone in an activated carbon fiber composite bed should be significantly shorter than in a bed of GAC. The two main reasons for this are; the narrow diameter of the carbon fibers giving little diffusion resistance and therefore high rates of adsorption; and high accessibility of the adsorbate to the fiber due to the open architecture of the composite. Both these factors result in a very short and steep mass transfer zone. Examples of the difference in mass transfer zones in beds of activated carbon fiber composite and a granular activated carbon are shown in Figure 12. The calculated mass transfer zone for the composite is 24% of the total bed length while it is about 88% for the granular bed. This means that at breakthrough 76% of the adsorbent has been saturated for the composite and only 12% for the granular bed^{17, 18}.

Figure 11: Stages of adsorption and resulting outlet concentrations. (From "Air Pollution Control Equipment", eds. L. Theodore and A. J. Buonicore, ETS Inc. 1992, p.93)¹⁶

Figure 12: Mass transfer profile for an activated carbon fiber composite and GAC(Calgon F-400).

Adsorption of Herbicides from Water

Pitch-based activated carbon fiber composites have also been tested for possible water treatment applications by studying the adsorption of sodium pentachlorophenolate, PCP (a common herbicide/wood preservative). A breakthrough plot for PCP in the carbon fiber composites and a commercial carbon specifically designed for water treatment (Norit Hydarco) is shown in Figure 13¹⁹⁻²². The breakthrough time for the composite was found to be almost 1400 column volumes, whereas it was closer to 150 column volumes for the granular carbon - a factor of about nine. At first sight, the difference in the performance of these carbons is surprising, since they are of comparable surface area. However, we believe that the superior performance of the carbon fiber composite is due to the narrow diameter of the fibers (15 - 20 μm) that essentially minimizes mass transfer limitations, and allows much faster rates of adsorption (and desorption) than is possible over large granules. A second factor is that the contacting fluid enjoys free access to the adsorbent surfaces. Essentially, the composite can be viewed metaphorically as a situation in which the granules have been "peeled open" to allow the adsorbent to readily access all of the inner adsorbent surface, which can otherwise only be approached by diffusion through an extensive pore network.

Adsorption of PCP via Packed Columns 40 ppm Na-PCP

Figure 13: Adsorption of the herbicide sodium pentachlorophenolate, PCP from water for a composite sample and a commercial granular activated carbon.

Liquid Phase Pressure Drop of Activated Composites

One of the most important parameters when considering a carbon for water treatment applications is the pressure drop that is developed over the adsorbent. We have previously reported pressure drops for gas flow, and we have also determined the pressure drop developed due to the flow of a liquid. The pressure drop over a 12.5 cc bed of composite at different flow rates of water is shown in Figure 5 along with data from the literature on pressure drop for a granular bed of activated carbon. The composite samples shown have comparable pressure drops to that for the bed of granular carbon, over the range of flow for which it was tested. The differences in pressure drop for the two composite specimens are due to differences in the density of the precursor composite.

Figure 14: Pressure drop of water over two carbon fiber composites at different densities and a granular bed(from literature)

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