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TOPICAL REPORT

ACTIVATION AND MICROPORE STRUCTURE DETERMINATION OF CARBON-FIBER COMPOSITE MOLECULAR SIEVES

Reporting Period: 30th March, 1994 - 14th April, 1995

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SUMMARY

The progress of research in the development of novel, rigid, monolithic adsorbent carbon fiber composites is described. Carbon fiber composites are produced at ORNL and activated at the CAER using steam or CO_2 under different conditions, with the aims of producing a uniform degree of activation through the material, and of closely controlling pore structure and adsorptive properties. The principal focus of the work to date has been to produce materials with narrow porosity far use in gas separations.

Carbon fiber composites are prepared at ORNL, usually in plate or tubular form, by vacuum molding from water slurries containing phenolic resin and chopped isotropic petroleum pitch fibers. The composites are activated at the CAER in steam or CO_2, using samples of dimensions up to 1.5 x 4 x 12 cm that are cut from the original plates. One of the objectives is to produce uniformly activated composites, which is especially critical when attempting to active large monoliths. It has been found that there are appreciable variations in the density and permeability of the as-formed composites that must relate to the forming technique. These variations are expected to exert some influence on the rate and extent of reaction and surface area development. In attempting to uniformly activate the composites, two reactor configurations have been investigated. In the more successful arrangement, 'steam "is introduced at several points along the length of the composite. A reduction in steam partial pressure from 95 vol% to 44vol% significantly improvedthe uniform&y of surface area distribution. Activation with CO_2 was still better, which is attributed to the much slower reaction rate than with steam.

Measurements of composite dimensions have shown that there is an overall shrinkage during activation. A direct correlation is found between dimensional shrinkage and burnoff, and is similar for CO_2 and steam activation. The causes of the shrinkage are not yet clear. At levels of burnoff above about 40%, the extent of contraction is sufficient to produce stresses that result in fracture.

Activated composites have been evaluated for the separation of CH_4-CO_2 mixtures, and an apparatus has been constructed specifically for this purpose. Samples activated to low burnoff (5-7% wt loss) with low surface areas (from 300-500m²/g) give much better separation of CO_2 and CH_4, than samples produced at higher burnoff, and there appears to be no benefit in producing

composites at burnoffs higher than 10%. The greater separation efficiency obtained at low burn-off means that the most effective CFCMS can be produced at relatively low cost. Continuing work will attempt to define the parameters that influence this gas separation, and whether these are applicable to other gas mixtures.

Five samples of CFCMS have been recently prepared for shipment to British Oxygen Corporation (BOC) for testing as molecular sieves. The samples were machined to specific dimensions at ORNL (approx. 2.5 cm diameter x 1.25 cm thick) and activated at CAER The samples were produced to different bum-off, but all have relatively narrow pore size distributions with average pore diameters around 6A.

INTRODUCTION

This report describes the research conducted under Contract #: SC 19X-SN719C, UK-3 over the period 30th March, 1994 - 14th April, 1995. To review the contents of this report in a proper framework, it should be emphasized that there were appreciable delays in formally establishing this contract, such that by 30th March 1994, considerable work had already been conducted under an informal arrangement. A similar situation arose over the nominal reporting period of this report, in that there was a hiatus in funding between 30th September, 1994 and 6th February, 1995. Consequently, the progress that is reported here was, for the most part, achieved through a co-operative effort, and not on a cost reimbursement basis.

The primary intention of this project is to develop, through collaborative research between ORNL and CAER, novel, rigid, monolithic adsorbent carbon fiber Composites that can be produced in single pieces to a given size and shape. The concept has resulted in the filing of a patent application that is held jointly between researchers at the ORNL and the CAER. Because of their potential molecular sieve properties, the composites have been termed carbon fiber composite molecular sieves, or CFCMS. The carbon fiber composites are produced at ORNL and activated at the CAER using steam or CO_2 under different conditions, with the aims of producing a uniform degree of activation through the material, and of closely controlling pore structure and adsorptive properties. The principal focus of the work has been to produce uniformly activated samples with narrow porosity for use in gas separations, although numerous other areas of application are envisaged

The idea for the project originated from work done at ORNL in the 1980s[1]. 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 material was prep& by vacuum molding from water slurries containing chopped carbonized rayon fibers

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(~ 6.5 pm diameter x ~ 0.15 mm) and a phenolic resin. The slurry was vacuum molded into -tubular or plate &&&ration, followed by drying, curing, and carbonization to 1600°C.

The basis for the present project was to use the above technique to produce high surface area carbon fiber composites through the activation-of similar composites, in which porosity is developed in the carbon fibers to produce high surface areas for adsorption. One of the principal changes, compared to the original work, is to utilize lower cost carbon fibers that are produced form isotropic pitches (other types of fiber will also be included in the studies). In recent years, a great interest has developed in the activated forms of such isotropic carbon fibers, where high surface areas can be produced by partial gasification in steam or other oxidizing gas[2,3]. 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 the development of an extensive pore structure. It was also assumed that the ease and kinetics of activation should be much more favorable than with high performance fibers which, in addition to possessing different structure, have been subjected to elevated temperatures. Early results confirmed this supposition, in that it was found that isotropic fibers that had been heat treated to 1600°C were much more difficult to activate than fibers that had been heat treated to 1100°C.

The interest in activated carbon fibers as adsorbents is that they have novel properties that make them more attractive than conventional forms of activated carbons (powder or granular) for certain application& Among their possible uses, activated carbon fibers are of interest for the adsorption and recovery of organic vapors; in environmental protection; the removal of SO_x and NO, from flue gas; and the improvement of air quality; and water treatment[3-8]. 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. Hence, the interest in producing rigid adsorbent composites.

This report provides an account of studies of composite activation, the measurement of physical properties (dimensional change during activation, gas permeability), and the results of experiments to evaluate their effectiveness for the separation of gas mixtures.

OBJECTIVES

The specific objectives of this research program are listed underneath by Task number.

Task

UK-1A	Prepare and supply activated rayon fibers to ORNL for the production of mesoporous CFCMS material
UK-1B	Investigate the steam activation of CFCMS from ORNL. Determine the relationships between activation conditions and the uniformity of the product, and between burnoff and porosity and shrinkage.
UK-1C	Supply fibers synthesized at CAER to ORNL for incorporation into cFcM.s material.
UK-1D	Develop methods to assess the potential of activated CFCMS for gas Separation.

Current Status: Task 1A is completed; Task 1C will be done in the future; and Tasks 1B and 1D are ongoing.

TECHNICAL PROGRESS

Material Preparation

Carbon fiber composites are prepared at ORNL by vacuum molding from water slurries containing phenolic resin and chopped isotropic petroleum pitch fibers, (P-200, ~ 17.5 μm diameter, average length 380μm, supplied by courtesy of John Newman, 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. To date, twenty-one samples of material, consisting of plates approximately 28 x 12 x 1.5 cm have been supplied by ORNL. In addition, ten discs (approx. 2.5 cm diameter x 1.25 cm thick) have been provided for the production of activated samples for gas separation testing by the British Oxygen Corporation.

Activation

The carbon fiber composites are activated at the CAER in steam or CO_2, using samples of dimensions up to 1.5 x 4 x 12 cm that are cut from the original plates. The composites are activated in a Lindberg tube furnace at temperatures between 800 and 950°C and for reaction times from OS-4 hours. Surface areas and pore size distributions are determined for samples taken from selected

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areas of the activates, using a 10 port automated surface area analyzer, OMNISORB 610. The high efficiency of this instrument allows the measurement of surface area and the characterization of pore sizes down to 4 A, using nitrogen at 77K and CO_2 at 298K as'adsorbents.

Activated carbon fibers produced from isotropic petroleum pitch have been reported to develop high surface areas (in some cases up to 2000 m^2g^{-1}), with almost all of the pore volume present in micropores (< 2nm diameter pores)[3]. These properties are retained by the composites, as illustrated in Table 1, where the nitrogen BET surface area is shown as a function of burn-off in steam (percent weight loss during activation). It can be seen that high surface areas can be attained in the composites at moderate burn-off.

The pore size distribution is narrow, although it broadens with increasing activation: the average pore width increases from 0.58 to 0.83 nm as the burn-off with steam increases from 16 to 31%. The sample at 16% burn-off has the narrowest pore size distribution with almost all pores less than 6 nm in diameter, while the more activated samples have significant proportions of pores from 6-8 nm in diameter. Depending on the application, a compromise may be required between pore size distribution and total surface area. Samples activated in CO_2 show the same trend in surface area development as the steam activated samples. At comparable levels of burnoff the BET surface area is 566 m^2g^{-1} for steam and 527 m^2g^{-1} for CO_2 while the pore widths are similar, 0.58 nm vs 0.62nm, Table 1. The plot of BET surface area against burnoff in Figure 1 illustrates a similar correlation for both activants.

Table1: Surface area and average pore size for CFCMS at different levels of burnoff in steam and CO_2

Burnoff	BET(m^2g^{-1})	Average pore size(nm)
Steam (concentration: 97 vol %)		
16	566	0.58
20	936	0.75
31	1240	0.83
CO_2 (concentration: 100 vol %)		
13	512	0.60
18	527	0.62
36	800	0.76

Uniformity of Composites and Activated Composites

One of the main concerns in this work is the ability to uniformly activate the composites: this will become especially critical when attempting to active large monoliths, where the diffusion of activating gas to the center of the artifacts could present a limiting factor. Consequently, a great deal of effort has been taken to ensure uniform activation., Since the start of the project, the activation procedure has been progressively modified in order to establish furnace conditions that will help to realize this objective. One factor that cannot be controlled through the activation however, is the uniformity of the composite blocks as they are received from ORNL. Before discussing further the activation process, the uniformity of the as-received composites will be addressed.

Uniformity of as-received composites

A sample of composite, 28 x 12 x 1.5 cm, supplied **by ORNL (UK-10-2) was examined for** consistency of density, thickness and permeability by removing 18 nominally 1" cores and measuring them individually.

The results showed that density was the least variable parameter. Even so, the variation was 0.347 to 0.382 g/cc. The thickness of the block was extremely variable with a range of 13.4 to 17.8 mm. The thicker areas did not seem to be directly linked to the higher density areas. Similarly, no correlation was obvious between density and permeability (for measurement details see later section), i.e there is far from equal resistance to flow over the whole area, which could obviously affect the distribution of the activating gas, and the removal of the products of the gasification reactions. These variations in the physical parameters must result from the forming technique and are expected to exert some influence on the rate and extent of reaction and surface area development

Uniformity of Activation

The principal parameters that can be varied in the activation process are, the reactor &sign and configuration, the partial pressure of the activating gas, total flow rate, temperature and reaction time.

Two different reactor arrangements have been investigated. In the first configuration (reactor 1), steam is introduced at several points along the length of the composite. In the second (reactor 2), the steam is introduced at one end only and passes downstream over the composite. The uniformity of activation was tested by measuring BET surface areas on sub-samples taken from different

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positions (A, B, and C) in the composite (dimensions 1.5 x 4 x 12 cm). The results of these measurements are shown in Table 2 for several series of experiments, and illustrated in Figure 2 for one of the sets of data from reactor 1.

In the initial experiments, essentially pure steam (95 vol%) was used as the activating agent. Water at a flow rate of 60cc/hr was mixed with nitrogen at 80cc/min in reactor 1. These conditions resulted in non-uniform surface area development throughout the sample, which was attributed to the high concentration of steam. When the steam concentration was reduced to 61vol% (sample 106, Table 2) and 44 vol% (sample 109, Table 2), the uniformity improved significantly. The standard deviation in surface area along the 12cm length of sample came down to 7 and 2% respectively. In future studies a concentration of 44 vol% H_2O in N_2 or less will be used to achieve uniform activation.

As can be seen in the Table, reactor 2 did not provide uniform activation even at low steam concentrations: the BET surface area varied by a factor of about three. The reason is believed to be the depletion of the activating agent downstream due to the reactions that take place in the part of the sample closest to the steam inlet

Activation with CO_2 is found to give more uniform surface area development than steam, Table 2. Reactor 1 gave an 8% variation in BET surface area, while reactor 2 still gave 20%. CO_2 activation gives a slightly different pore size distribution than steam activation[9]. There is a significantly slower reaction rate than with steam, since the larger dimension of the CO_2 molecule results in a slower diffusion into the porous system and is more restricted in its access to the micropores. The CC&activation runs were therefore carried out at higher temperatures (850-950°C), for 1-3 hours, and at a rate of 2l/min.

Table 2: Uniformity of BET Surface Area

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Dimensional Changes

There is an overall **shrinkage** of the composites during activation. The changes have been measured in all three directions of the composite. A direct correlation is found between dimensional shrinkage and **burnoff,** Figure 3, and is similar for CO_2 and steam activation.

It has been reported that carbon shrinkage can be caused by **direct** reaction between O_2 and C, as carbon is directly removed from exterior surfaces. At **temperatures** above **800°C,** oxygen is known to react more than 100 times faster with carbon than steam and CO_2, which leads to a **diffusion-controlled** reaction involving a **shrinking** core type of mechanism, and there is minimal contribution **to** porosity development. In the present studies, there should only be **low** concentrations of oxygen present, and the causes of the shrinkage ate not clear. External bum-off in the **activant** gas could **make some contribution, but this is expected** to be **small.** Another factor might be degradation of the binder. In any event., at high levels of **burnoff,** above about **40%,** the extent of contraction produces stresses in the **composites that result** in fracture **in a** plane parallel to the plane of deposition when the composite was first formed by **filtration.**

Permeability and Adsorptive Properties

The permeability of the composites and activates has been measured by a simple apparatus where the sample under test is sealed in a plastic funnel using foam rubber. Air is passed through the sample at a rate of 15-60 **l/min,** and the differential pressure over the sample is measured using a water manometer. Results of the permeability measurements are shown in Figure 4. For a composite of thickness **13mm,** an air **flow of 15 l/min through a** disc **of diameter** 25mm (i.e. **30m³/min** per **m²**) generates a pressure differential less than **0.5psi.** This permeability is comparable to that of **an** equivalent bed depth of 2 mm sized granules, and much higher than for a similar bed of 14 micron sized powder. The high permeabiity is due to the very open structure of the composites.

The rate of gas adsorption on CFCMS has been compared with that on other carbons by **thermogravimetric analysis** using NO as the test ad&bate. The rate of adsorption on activated carbon fiber composites is found to be much higher than on a granular commercial coconutshell derived **carbon,** Figure **5, due** to the **essential** absence **of diffusion** limitations in the carbon fiber composite. Only when the granular carbon is reduced to a comparable particle size (average diam 14 microns vs 12-15 microns **fiber** diameter) do the rates begin to correspond. The high **adsorption** rate is another benefit of the open architecture of the composite since the **fibers** within are almost as accessible as **free** fibers. The materials Gill therefore have+ high potential for processes requiring rapid adsorption and desorption **rates,e.g.** gas separation,solvent recovery etc.

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Gas Separation

The unique properties of the activated composites - narrow, unimodal pore structure, high surface area, rapid rat& of adsorption and desorption, 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 CH_4-CO_2 was selected as the model mixture, following studies of the adsorption of these gases by TGA which showed that the carbons have high capacity for adsorbing CO_2 (up to 10 wt%) while much less methane is adsorbed, Figure 6.

An apparatus was then constructed to examine the effectiveness of CFCMS for gas separation, Figure 7. Samples have been tested using a mixture of 75% CH_4 and 25% CO_2 . The composition and flow rate of the emergent gases are detected as a function of time using a mass spectrometer and a mass flow meter. The sample is sealed in place using a rubber seal. Helium is first purged through the system and when the gas analysis indicates that virtually pure helium is emerging at the outlet, the valve is switched and the 75%CH_4/ 25% CO_2 mixture is introduced at a fixed controlled flow rate (usually 50 ml/min). The outlet flow rate and composition is 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 CH_4 and CO_2 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% CH_4, 25% CO_2. The volumes of gas produced per gram of composite with 95%, 90% and-85% CH_4 concentration are then calculated.

Results of the gas separation experiments are shown in Table 3. Samples activated to low burnoff (5-7% wt loss) and low surface areas (from 300-500m^2/g) show excellent separation of CO_2 and CH_4, compared to samples produced at higher burnoff (10-30% wt. loss, surface area 500-1000m^2/g). The volumes of effluent gas produced at 95 and 90% methane concentration are shown in Figure 8 as a function of burn-off. The most effective carbons are produced at low bum-off, and there appears to be no benefit in producing composites at burnoffs higher than 10%. The same trend is reflected in the equivalent plot against micropore volume in Figure 9, from which it appears that the ideal micropore volume should be less 0.15 cc/g.

These results are rather unexpected. The greater separation efficiency obtained at low burn-off means that the most effective CFCMS can be produced at relatively low cost. However, there remain the questions of defining the parameters that influence this gas separation, and whether these are applicable to other gas mixtures.
The influence of average pore diameter on the separation 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. However, other parameters such as surface chemistry cannot be neglected. Future work will be directed to further elucidating the CFCMS parameters that are most important to the separation process.

Table 3: Volume of CH_4 produced at 9585% concentration from a mixture of 75% CH_4/25% CO_2

Sample	Cumul. vol of CH4 out			Burn-off (%)	Activation			BETsa (m2/g)	pore vol (cc/g)	diam. (A)
	95%	90%	85%		med	temp(°C)	time(hr)			
SA 124	-	47	90	24	CO_2	900	3	632	0.2	5.8
SA 139	33	69	127	8	H_2O	850	1/4	444	0.26	12.0
SA 132	35	67	112	8	CO_2	850	2	424	0.19	7.6
SA 135	39	78	133	12	CO_2	850	4	548	0.23	5.9
SA 136	44	80	146	7	CO_2	1000	1/60	291	0.11	11.0
SA 137	53	87	146	7	CO_2	950	1/6	397	0.13	8.8

Samples. for Commercial Evaluation

Five samples of CFCMS have been recently prepared for shipment to British Oxygen Corporation (BOC) for testing as molecular sieves. The samples were machined to specific dimensions at ORNL (approx. 2.5 cm diameter x 1.25 cm thick) and activated at CAER. The samples were produced with different burn-offs, but all with relatively narrow pore size distributions with average diameters around 6A. The surface areas ranged from 300-900m2/g. Activation conditions and the resulting BET-surface areas and pore widths of the samples are listed in Table 4.

Table 4 : Surface Area and Pore Size of Carbon Fiber Composite Molecular Sieves' Prepared for BOC

Run #	Position	Activation			burnoff (%)	BET surface area (m²/g)	Pore width(A)
		temp(°C)	rx.time	agent			
160	A	800	30 min	H_2O	7	434	6.0
	B					271	5.9
161	A	950	10 min	CO_2	6	372	11.0
	B					304	13.4
166=168	A	800	3 hr	H_2O	17	529	6.8
	B					572	6.1
	C					534	
167=169	A	800	6 hr	H_2O	28	657	6.4
	B					847	6.9
	C					806	8.6
170=171	A	950	3 hr	CO_2	32	836	6.1
	B					879	6.9
	C					830	6.9

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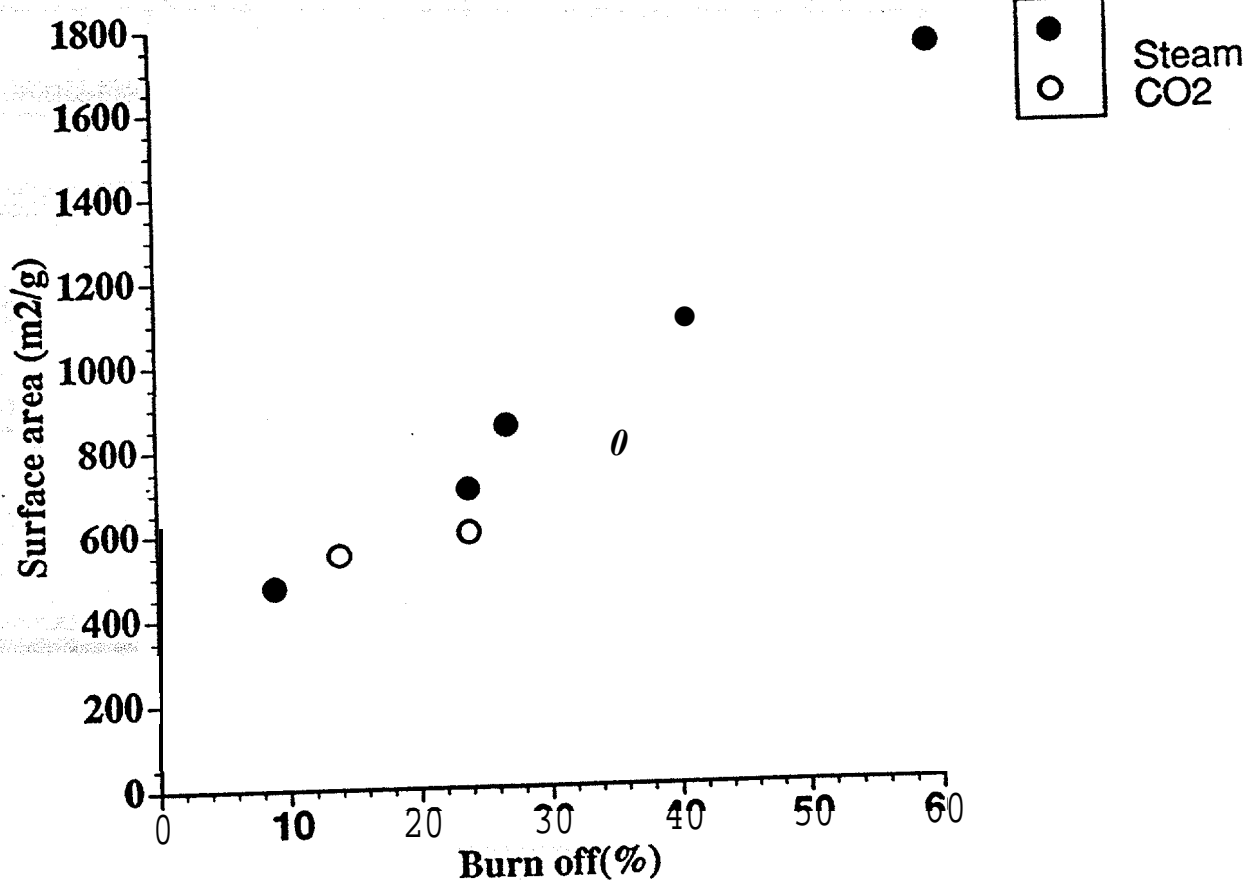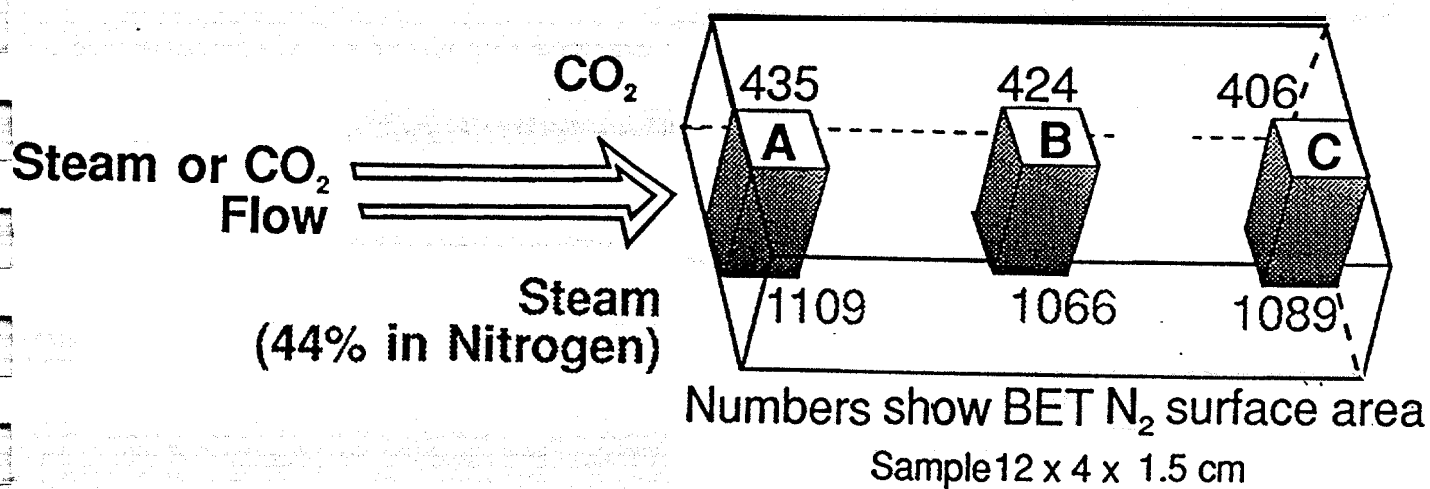
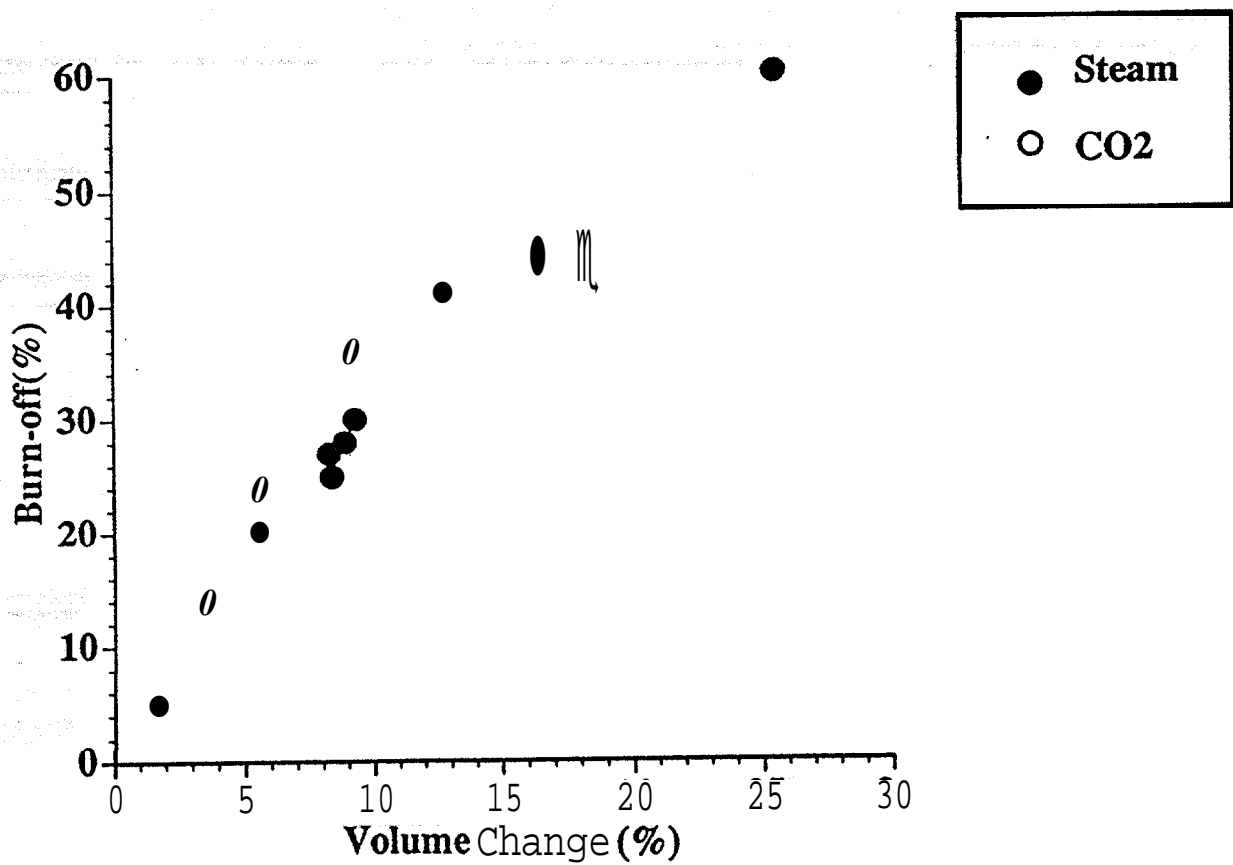9.   T. Wigmans, Carbon Vol. 27. No. 1. pp. 13-22 (1989).

Figure 1: Relationship between Surface Area and Burnoff for CFCMS (Concentration of steam: 44 **vol %,** concentration of CO_2 : 100 **vol %,** reaction temperatures 800-950°C)

CO₂

Steam or CO₂
Flow

435   424   406

A   B   C

Steam
(44% in Nitrogen)

1109   1066   1089

Numbers show BET N₂ surface area
Sample 12 x 4 x 1.5 cm

Reactor configuration 1

Figure 2:   **Uniformity of activation of CFCMS**
(Concentration of steam: 44 vol %, concentration of CO₂: 100 vol
%, reaction temperatures 877 and 850°C respectively)

Figure 3: Relationship between Dimensional Change and Burnoff for CFCMS
(Concentration of steam: **44 vol %,** concentration of CO_2 : 100 **vol %,**
eaction temperatures **800-950°C)**
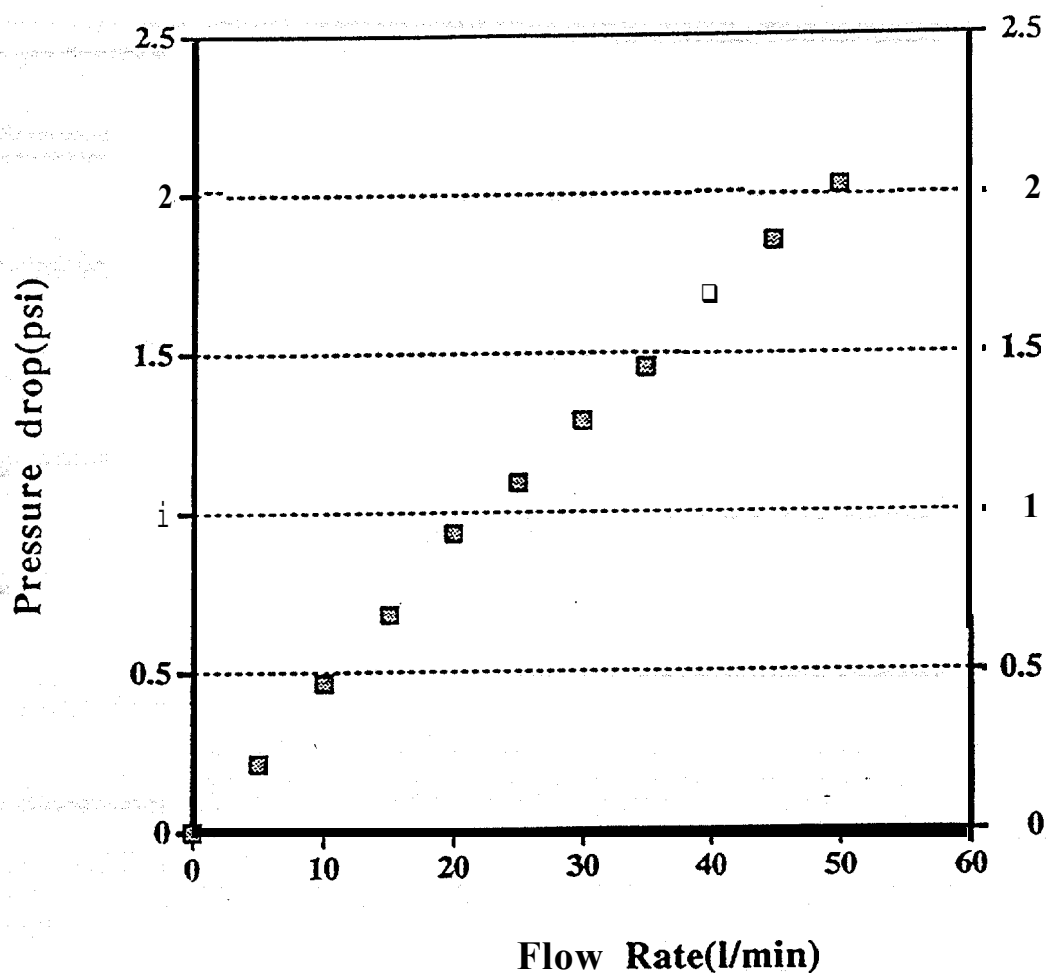
Figure 4: Permeability of CFCMS materials measured by air flow through a circular composite disk.
(Sample. UK 19-1, Density 0.365g, length 1.3cm, diameter 2.5 cm)

Adsorption Rate is Strongly Influenced by Carbon Diameter
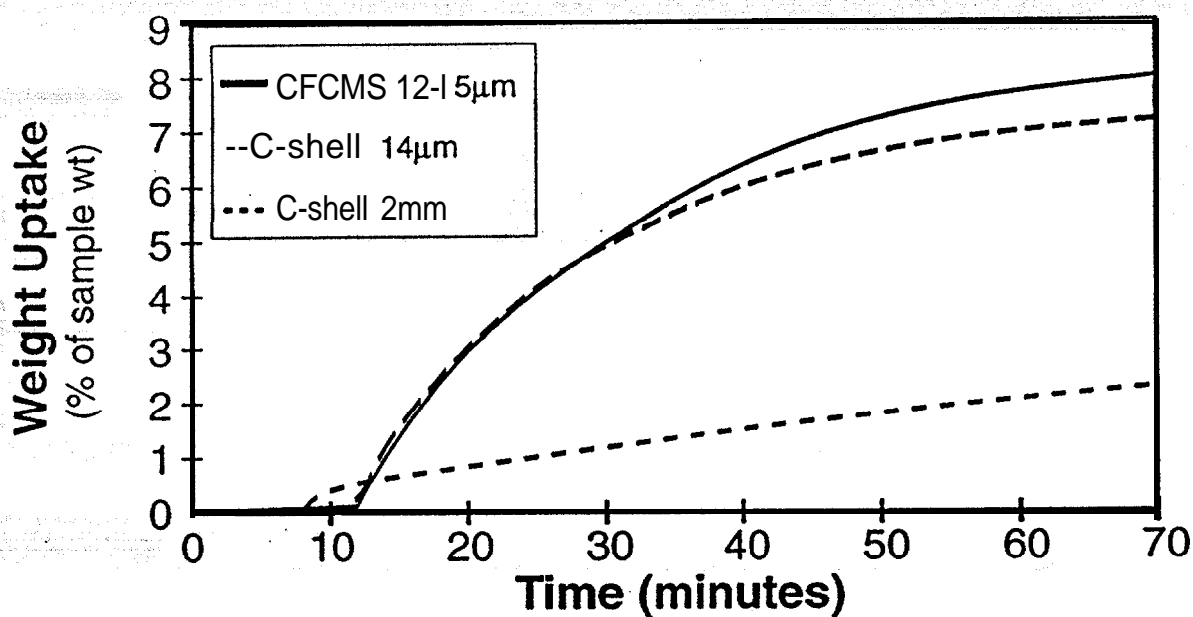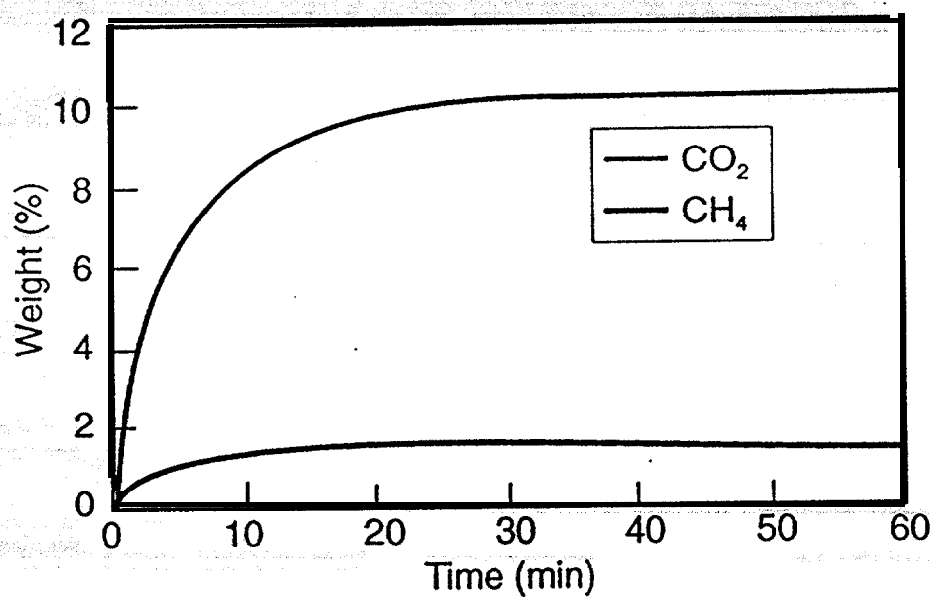
(NO Adsorption at 28°C, no oxygen;
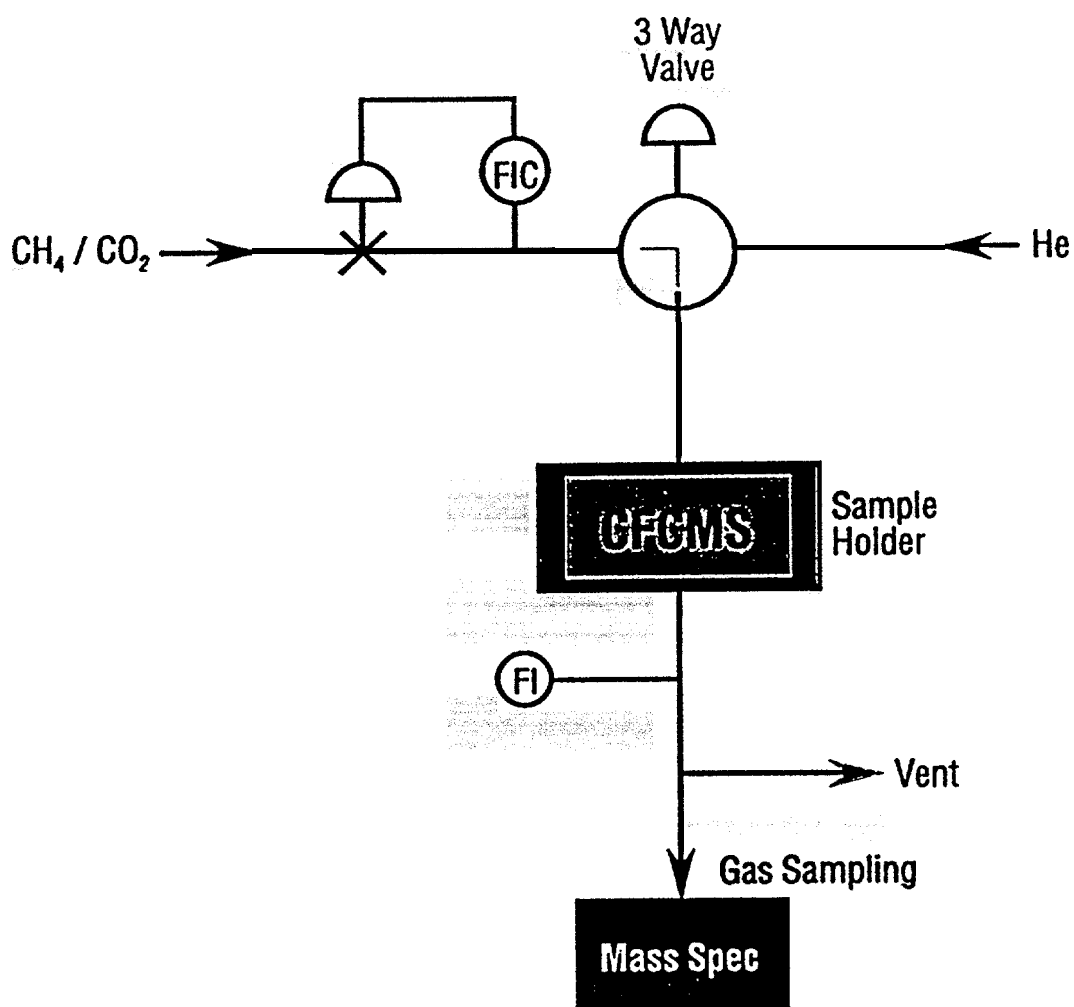C-shell = Commercial coconut shell carbon)

Figure 5: **Adsorption rates of CFCMS compared** with a **commecial** granular activated carbon at two **particie** sizes, **granulars** at 2mm and finely **ground** to 14μm.
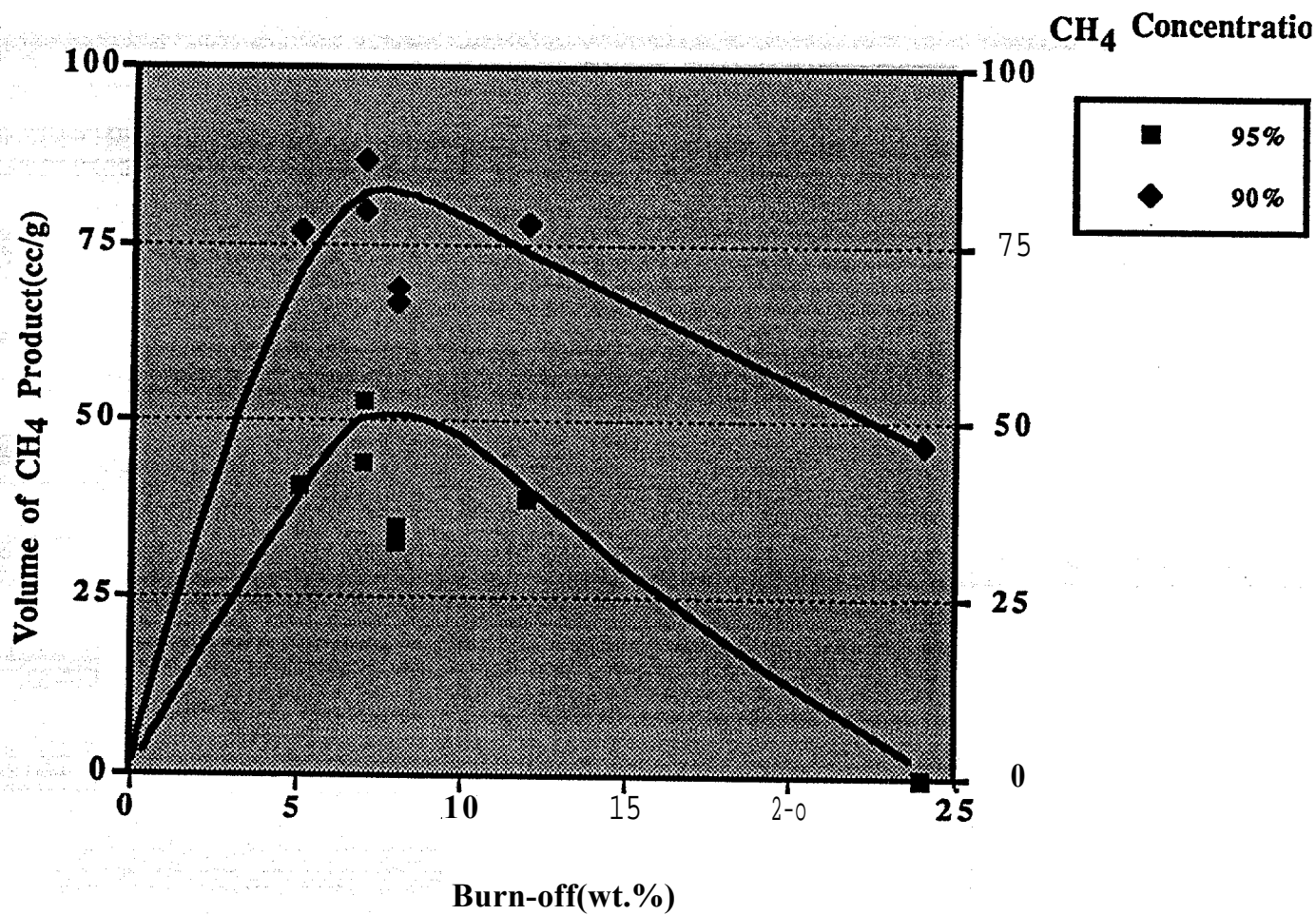
Average pore width, L = 0.74 nm
BET surface area = $822 m^2/g$

Figure 6: Adsorption of CH_4 and CO_2 on CFCMS using TGA (STP).

3 Way Valve

CH₄ / CO₂ →

FIC

← **He**

GFGMS Sample Holder

FI

→ **Vent**

Gas Sampling

Mass Spec

Fig& 7: Schematic Arrangement of Apparatus for testing Gas Separation.

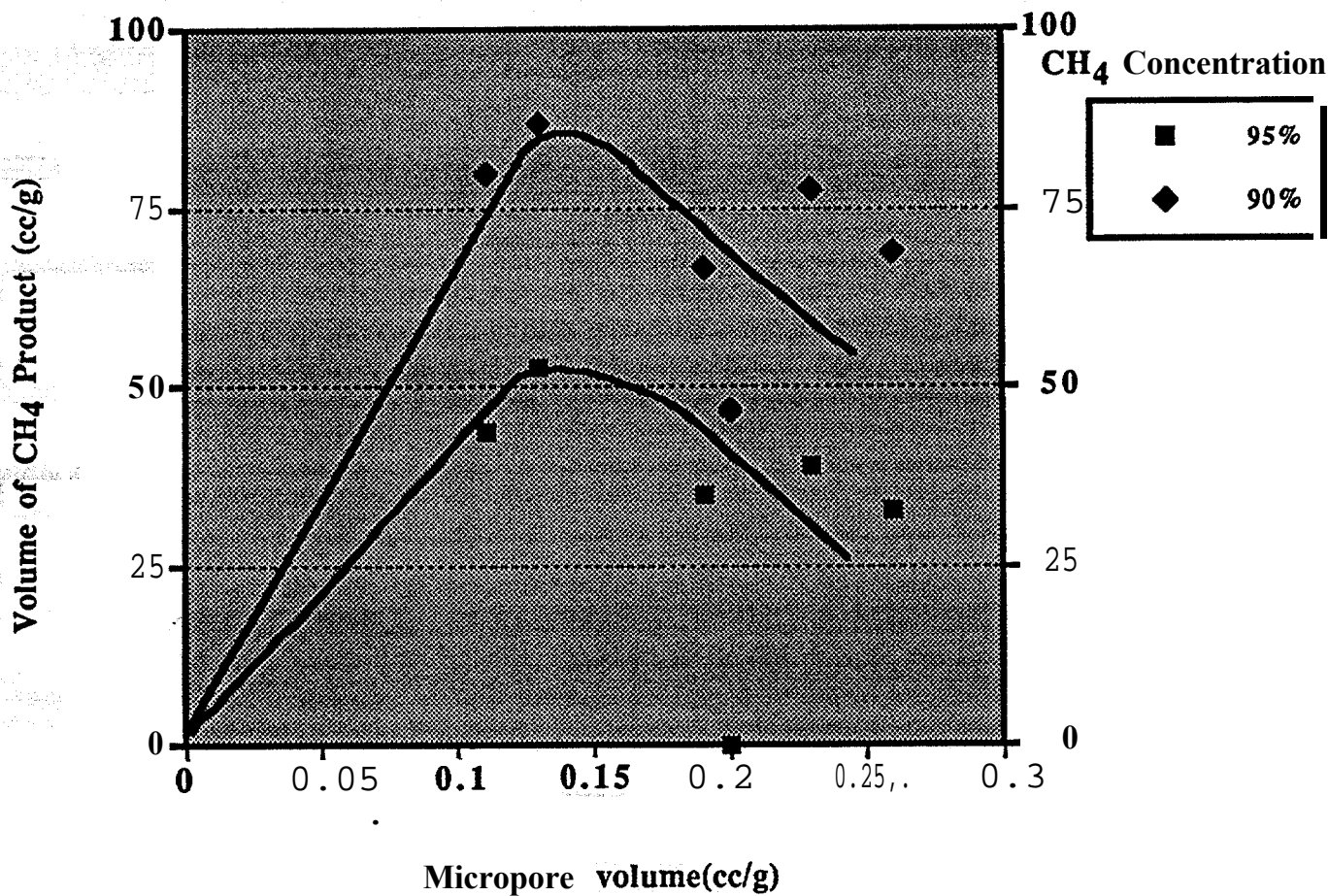, **Figure 8:** Influence of degree of activation on volume of effluent gas produced with high CH₄ purity.

Figure 9: Relation of CFCMS micropore volume to volume of effluent-gas produced with high CH$_4$ purity.
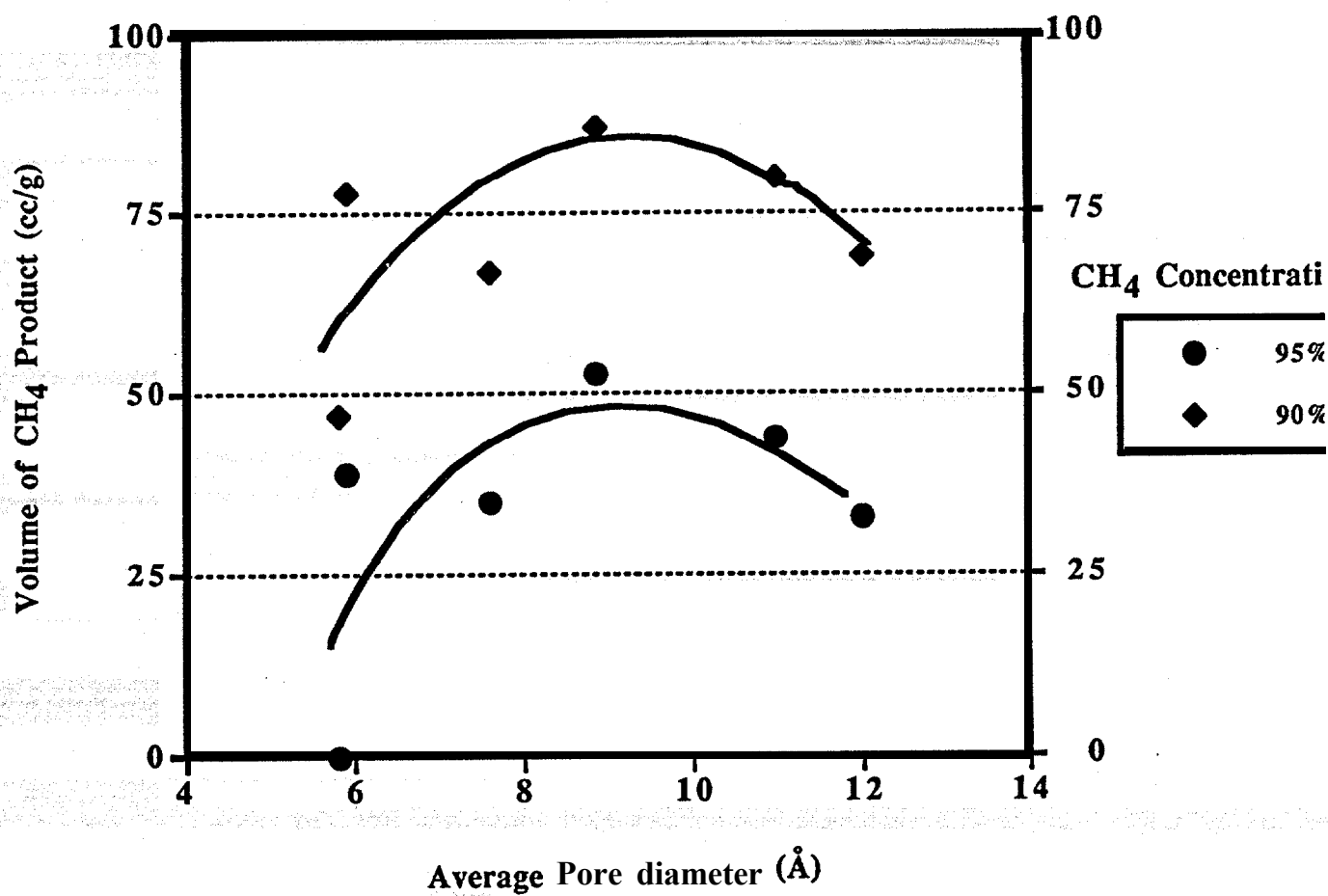
Figure 10: Relationship of average pore diameter to volume of effluent gas produced with high CH_4 purity.