JAN 19 1996

ORNL/Sub/94-SN719/01

June 28, 1995

Report Prepared by

University of Kentucky Center for Applied Energy Research,
3572 Iron Works Pike, Lexington KY 405 1 1-8433, USA

under

Subcontract Number: SC 19X-SN719C, UK-3

for

OAK RIDGE NATIONAL LABORATORY

Oak Ridge, Tennessee 3783 1

managed by

MARTIN MARIETTA ENERGY SYSTEMS, INC.

for the

U.S. Department of Energy

under Contract No. DE-AC05-84OR2 1400

SUB00068

TOPICAL REPORT

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

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

b y :

Marit JAGTOYEN, Frank DERBYSHIRE, Geoff KIMBER, You Qing FEI

May 19, 1995

**Research sponsored by the U.S. Department of Energy,
Fossil Energy
Advanced Research and Technology Development Materials Program**

Report Prepared by

**University of Kentucky Center for Applied Energy Research,
3572 Iron Works Pike, Lexington KY 40511-8433, USA**

under

Subcontract Number: SC 19X-SN719C, UK-3

for

**OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. Department of Energy
under Contract No. DE-AC05-84OR21400**

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 **CO₂** 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 for 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 **CO₂**, 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 improved the uniformity of surface area distribution. Activation with **CO₂** 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 **CO₂** 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 **CH₄-CO₂** 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 **CO₂** and **CH₄**, 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 burn-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 **CO₂** 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

(~ 6.5 μ m diameter x ~0.15 mm) and a phenolic resin. The slurry was vacuum molded into tubular or plate form, 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 from 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 applications. 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 treatment³⁻⁸. 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 **380 μm** , 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 CO₂**, 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

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 Å, using nitrogen at 77K and CO₂ 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 m²g⁻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 CO₂ show the same trend in surface area development as the steam activated samples. At comparable levels of **burnoff** the BET surface area is 566 m²g⁻¹ for steam and 527 m²g⁻¹ for CO₂ 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 CO₂

Burnoff	BET(m ² g ⁻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)**, **ie** 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

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% H₂O** in **N₂** 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 **CO₂** 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%. **CO₂** 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 **CO₂** 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

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 **CO₂** and steam activation.

It has been reported that carbon shrinkage can be caused by **direct** reaction between **O₂** 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 **CO₂**, 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 are not clear. External burn-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 permeability 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 adsorbate. 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.

Gas Separation

The unique properties of the activated composites - narrow, unimodal pore structure, high surface area, rapid rate 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 $\text{CH}_4\text{-CO}_2$ 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 300-500 m^2/g) show excellent separation of CO_2 and CH_4 , compared to samples produced at higher burnoff (10-30% wt. loss, surface area 500-1000 m^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 burn-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 CH₄ produced at 9585% concentration from a mixture of 75% CH₄/25% CO₂

Sample	Cumul. vol of CH ₄ out			Burn-off (%)	Activation			BETsa pore vol diam.		
	95%	90%	85%		med	temp(°C)	time(hr)	(m ² /g)	(cc/g)	(Å)
SA 124	-	47	90	24	CO ₂	900	3	632	0.2	5.8
SA 139	33	69	127	8	H ₂ O	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 6Å. 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 (m ² /g)	Pore width(A)
		temp(°C)	rx.time	agent			
160	A	800	30 min	H ₂ O	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 ₂ O	17	529	6.8
	B					572	6.1
	C					534	
167=169	A	800	6 hr	H ₂ O	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

REFERENCES

1. G. C. **Wei**, and J. M. **Robbins**, Ceramic Bull., **64(5)** (1985)691
2. M. W. Thwaites, M. L. Stewart, **B. E. McNeese**, and M. Sumner, Fuel **Proc.Tech.**, 34, 137-145 (1993).
3. **M.Suzuki**, **Proc. Biennial Carbon Conference**, Buffalo (1993).
4. L Mochida, Y-N. Sun, H. Fijitsu, S. Kisamori, and S. Kawano, Nippon Kagaku Kaishi (**J.Chemical Society of Japan**), **6**, 885-890 (1991).
5. L Mochida, T. **Hirayama**, S. Kisamori, S. Kawano, and **H. Fijitsu**, Langmuir, 8 (**9**), 2290-94 (1992).
6. **K. L. Foster**, R. G. Fuerman, J. Economy, S. M. **Larson**, and **M. J.Rood**, Chem. Mater., 4, 1068-1073 (1992).
7. **J. Economy**, **K. Foster**, A. **Andreopoulos**, and **H. Jung**, Chemtech, **597-603**, October (1992).
8. **M. Suzuki**, Water Science technology, **23**, 1649 (1991).
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 CO₂ : 100 vol %, reaction temperatures 800-950°C)

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 CO₂ : 100 vol %, reaction 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 commercial granular activated carbon at two particle sizes, granulars at 2mm and finely ground to 14µm.

Average pore width, $L = 0.74 \text{ nm}$
BET surface area = $822 \text{ m}^2/\text{g}$

Figure 6: Adsorption of CH₄ and CO₂ on CFCMS using TGA (STP).

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 CH₄ purity.

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