OCDO--95004423

Utilization of High Sulfur Coal in Carbon Fiber Production

FINAL REPORT

Grantee:
Applied Sciences, Inc.
141 W. Xenia Ave.
P.O. Box 579
Cedarville, OH 45314
(513) 766-2020

Project Manager:
Mr. Robert L. Alig
Senior Research Scientist
(513) 766-2020

Reporting Period:
April 1993 - August 1994

RECEIVED
DEC 19 1994
DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

Employee Investigators
Mr. David J. Burton
Dr. Jason R. Guth

Contributors
Dr. David Anderson, Univ. Dayton Research Institute
Dr. Gary Tibbetts, NAO General Motors Research

This project was funded in part by the Ohio Coal Development Office, Department of Development, State of Ohio.

Project Number: OCDO/R-922-8
Date of Submission: December 12, 1994

TABLE OF CONTENTS

TABLES

FIGURES

EXECUTIVE SUMMARY

PYROGRAF-III™ is a highly graphitic vapor grown carbon fiber (VGCF) produced by the chemical vapor deposition of carbon on metallic catalysts in the temperature range of 1100° C. This is entirely different from commercial carbon fiber, which is made by first forming a filament and then graphitizing it in a high temperature oven. For PYROGRAF-III™ small amounts of sulfur in the form of hydrogen sulfide are added to the process to enhance the yield. This method of supplying the necessary sulfur is both expensive and hazardous since hydrogen sulfide is flammable, toxic, and corrosive. To supply the sulfur more economically and safely, high sulfur coal was proposed as a replacement for the hydrogen sulfide gas. Applied Sciences, Inc. is the sole producer of this material in pound quantities.

The primary objective of research grant OCDO-922-8 was to demonstrate that Ohio's high sulfur coal can replace the expensive, toxic hydrogen sulfide in the production of vapor grown carbon fiber as well as become a partial or complete source of carbon. The secondary objective was to analyze the exhaust for the release of harmful sulfur compounds and to project the economic potential of the use of coal. These objectives were completed in two Tasks.

Task I trials were performed using Ohio No. 8 coal with 4.71% sulfur as the only source of sulfur. This Task grew from earlier work[1] where it was established that sulfur bonds with the metal catalyst when added in equimolar amounts and assists the growth and formations of the carbon fiber. It has not been ascertained and beyond the scope of this Task to analyze if both the organic and pyritic sulfur in coal partake in the bonding with the catalyst. Methane was added to maintain optimum ratios of sulfur, catalyst, and carbon developed earlier without coal. The fibers produced were of good quality with no visible defects such as imbedded ash and soot particles. Thus Task I proved that high sulfur coal can replace hydrogen sulfide as a sulfur source in the production of PYROGRAF-III™ vapor grown carbon fiber without diminishing the quality of the fiber.

Task II trials were performed to determine whether coal could be used as the exclusive feedstock in the production of PYROGRAF-III™. To make this determination, trials were performed using Upper Freeport Seam (2.5% sulfur) and Clarion 4A Seam (3.6% sulfur) coal as the sole source of carbon and sulfur. Micrographs of the fibers produced in these trials showed the presence of good quality carbon fiber intermixed with particulate. This particulate matter is anticipated as a result of feeding five (5) times the optimum sulfur/catalyst ratio. From previous work with high purity methane and hydrogen sulfide, carbon fiber can still be produced with sulfur levels as high as seventeen (17) times the optimum sulfur level[1].

The exhaust gases were analyzed by gas chromatography for a qualitative estimate of the emissions. Methane, hydrogen, ethane, and propane were found in the exhaust. This indicates that the exhaust could be recirculated and combusted to supply a tremendous source of energy for the PYROGRAF-III™ process, thereby reducing production costs as well as serving as a carrier gas to move the pulverized coal into the reactor. Gas detection tubes with a 0.25 ppm sulfur dioxide detection limit were also used to check the exhaust gases during Task II coal trials; the presence of SO_2 was not detected in any of the samples. This is an indication, but not conclusive evidence that high sulfur coal can produce carbon fiber without generating environmental pollution. The sulfur in the reaction certainly affects and improves the formation, and excessive sulfur changes the length and linearity of the formed fiber[1]. However, more data are needed before a claim can be made that this will always be the case.

From 15 years of development, coal seems to be a logical candidate and these results were anticipated, however, there was one concern that needed demonstration. It was expected that the carbon and sulfur would react as predicted; the unknown factor in this project was the possibility that an ingredient in the ash or nitrogen compounds in coal could also enter the fiber growth reaction and affect the fiber. In subsequent analysis, the fiber made with coal was of good quality. Although the role of ash needs further study, it did not hamper the fiber's nucleation and growth.

The project proceeded in a timely manner, except developing a coal feed system at a nominal cost consumed more effort than anticipated. Improvements and further work is still needed in this area, however, the feeder was sufficient to accomplish the tasks.

Commercialization Timetable

This project laid the foundation for future scale-up considerations for the production of PYROGRAF-III™ carbon fiber from high sulfur coal. Applied Sciences is anticipating manufacturing 400 lb in 1995 and 4000 lb in 1996. More important than the schedule, is the need to resolve the scale-up issues through pilot line development in order to be in a position to be in the million lb or above by 1998 or 1999. This project indicated that coal with its inherent sulfur and competitive cost are desirable assets and should be pursued further for eventual incorporation into the scale-up for the production of vapor grown carbon fiber.

If funding, process, and application development can proceed "hand-in hand", the impact upon Ohio coal consumption could reach several million tons per year to satisfy the demand of PYROGRAF-III™ carbon fiber within 5 years. If funding were not an issue, this projection could be reduced to three years. The use of coal in the production of PYROGRAF-III™ has tremendous economic impact on the goal of getting the cost under $3/pound. The coal would supply a cheap source of carbon and sulfur which are essential to the PYROGRAF-III™ process as well as provide a tremendous amount of energy through recycled exhaust gases. By producing a low-cost carbon fiber, closer in price to fiberglass and carbon black, many applications would be opened which currently are closed due to the cost of carbon fiber, which is in the 15 to 2500 $/lb range.

Markets

The markets available for the immediate utilization of PYROGRAF-III™ carbon fiber are the rubber, plastic, composite, and the concrete industries. Currently a rubber manufacturer is testing large samples of PYROGRAF-III™ as a reinforcement for partial replacement of carbon black. PYROGRAF-III™ carbon fiber increases the stiffness of rubber by a factor 2.5 times that of carbon black.

The market for the entire plastics industry in the U.S. is forecasted to be 87 billion dollars in 1996 which translates into 39 billion pounds[2] of plastics. Of the entire market, Ohio is the second largest plastic manufacturer in the nation with 8.28 billion dollars forecasted for 1996. However, the composites industry (2.9 billion pounds) is only 7.5% of the entire industry. This is a strong indicator that even though carbon fibers, especially commercial carbon fibers, may have desirable properties, their growth has been stagnated by their inherent high price. However, if PYROGRAF III can substantially undercut this price through the use of high sulfur coal, many markets will open that presently do not even consider the use of carbon fibers. At present, Applied Sciences has a three year grant from the Edison Materials Technology Center for the development of low-cost carbon fiber reinforced composites. Sheet molded composites are also under development with Ashland Chemical.

The concrete industry used 68.7 million short tons of Portland type and 2.6 million short tons of masonry type cement in 1990.[3] To reduce cracking over large temperature changes, concrete needs better reinforcement and better thermal transfer properties. Therefore, PYROGRAF-III^{TM} which has been used as a reinforcement in other materials and has a thermal conductivity approaching that of diamond, would be a potential additive for concrete. Furthermore the presence of ash would not be a detriment to the product.

This is a partial list of potential markets. Others could include aerospace, brake linings, electronics, and batteries. However, if coal were used to produce carbon fiber at a rate of 6 lb per 1 lb of fiber produced and attained various penetrations into the above targeted markets, the following table estimates the implications for coal and could eventually surpass Ohio's coal present production (33 million tons/year):

TABLE 1. POTENTIAL MARKET IMPLICATIONS

POTENTIAL MARKET	MARKET CONSUMPTION (MILLION TONS/YEAR)	MARKET PENETRATION(PERCENT)	PYROGRAF III^{TM} (MILLION TONS/YEAR)	COAL REQUIRED: (MILLION TONS/YEAR
CARBON BLACK	1.5	20	0.3	1.8
PLASTICS	19.5	10	1.95	11.7
CONCRETE	71.3	5	3.6	21.9

Future Plans:

This project demonstrates that Ohio high sulfur coal is capable of producing PYROGRAF-III^{TM} carbon fiber potentially at a much lower cost with good fiber quality without environmentally harmful exhaust gases. However, there are areas that need further investigation:

1. Available commercial coal feeders feed coal consistently over a range of outputs. Such a unit is needed to improve the limitations of the unit assembled for this project. From this, meaningful studies and statistical analysis could begin on various grades of coal, % Yield, flow rate optimization, ash build-up, residence times, energy losses, exhaust gas recirculation, coal particle size, and material/energy balances for cost optimization.

2. Although sulfur and nitrogen oxides have not been observed to date in the exhaust, this area needs thorough examination with precise equipment for recycling and environmental control. Process variations such as temperature (currently 1150°C), flow rates, etc. need to be monitored and correlated with precise exhaust analysis.

3. The ash residue and its disposition needs study with coal grades at different ash, organic sulfur, pyritic sulfur, and organic levels. Some collects in the cooler sections of the exhaust tubes and some may stay with the fiber and may need to be filtered out while adding the sizing treatment.

4. While coal-derived fibers are expected to perform equally well as methane-derived fibers, they need to be surface treated with a sizing and compared by application trials in rubber and plastics. Note: All commercial carbon black, carbon and glass fibers are routinely coated with a sizing material for densification and wet-out properties.

Utilization of High Sulfur Coal in Carbon Fiber Production

Introduction

Carbon fibers are highly valued for their high strength, stiffness, and low weight properties, but are too expensive to be considered for many applications. A new type of carbon fiber has been developed which has demonstrated applications in rubber, plastics, and composites. This new type of carbon fiber is PYROGRAF-III™. It is a vapor grown carbon fiber produced in a one-step, semi-continuous process. It is produced from the decomposition of hydrocarbon gases on metallic particles inside a reactor. Sulfur is added to the reaction mixture in the form of hydrogen sulfide to increase the yield[1]. This method of supplying the necessary sulfur is both expensive and hazardous since hydrogen sulfide in flammable, toxic, and corrosive. Concerns over raw material costs and safety have led to the use of high sulfur coal as an inexpensive and safe feedstock in the production of PYROGRAF-III™.

The primary objective of this research grant was to demonstrate, through Task I, that high sulfur Ohio coal can replace hydrogen sulfide in the production of PYROGRAF-III™ carbon fiber. In these trials, the coal was supplemented with methane in order to attain the same sulfur/carbon level as the as the standard, methane-only formulations. This Task also entailed the development of a feed apparatus to inject the pulverized coal into the reactor. The objective of Task II was to demonstrate conclusively that the inherent hydrocarbon content of Ohio coal alone can produce PYROGRAF-III™ without using other hydrocarbons such as methane as a carrier gas for the pulverized coal. Secondary Task II objectives were:

1. analyze the exhaust from the process to ascertain if coal as a feedstock is an ecologically safe fuel with little or no release of SO_x compounds into the atmosphere,
2. ascertain the quality of the coal derived fiber,
3. develop preliminary mass and energy balances for the conversion of coal to fiber based upon available trial exhaust analysis data,
4. Estimate the economic potential of using coal in the production of PYROGRAF-III™.

There were no other co-sponsors for this project.

Technical Discussion

Carbon fibers have been of practical interest within the industrial community for over a century, as can be recalled from Thomas Edison's application of the fibers as filaments for light bulbs. Today, a class of carbon fibers exist which are valued primarily for their mechanical properties and are the reinforcements in composites used in aerospace applications, golf clubs, fishing poles, and similar consumer products. These fibers possess physical properties which are of great interest to engineers in that carbon fibers can be synthesized which are stronger than steel, stiffer than titanium, and yet lighter than aluminum. A negative attribute of commercial carbon fibers is that they are more expensive than the competing metals for engineering applications.

The commercial carbon fibers of today are formed from precursors of polyacrylonitrile

(PAN) or petroleum pitch, and have widely ranging values for the properties cited above, but generally have in common the methods of synthesis and handling, the latter of which is similar to textiles. These fibers are made by initially extruding or spinning a continuous filament or thread from a polymer. The continuous fiber is oxidized under tension to 200°C; then slowly heated in the absence of air to 1000°C to carbonize the fiber. Additional heating up to 3000°C provides higher degrees of graphitization used for expensive ultra-high strength and/or stiffness applications.

In 1992, Applied Sciences Inc. was licensed[4] by General Motors to develop and manufacture a vapor grown carbon fiber known as PYROGRAF-III™. This unique type of carbon fiber proposed for utilizing coal as a feedstock is synthesized in a simple CVD process. The process has no involved extrusion or spinning operations, and thus has the potential of significantly reducing the cost of production. This new type of fiber, known as vapor grown carbon fiber (VGCF), has mechanical properties which compare favorably to current commercial fibers, as well as having electrical and thermal properties which are significantly higher than other carbon fibers. Finally, because of the simplicity of synthesis and the potential to be produced from low cost hydrocarbons, VGCF may be produced at a fraction of the cost of current commercial carbon fibers with comparable properties.

The production of vapor grown carbon fiber begins with metallic particles, generally iron, which, upon exposure to a hydrocarbon gas at a temperature in the 1000 - 1100^0 C. range, catalyze the growth of long, slender, partially graphitic filaments, initially only a few nanometers in diameter. A fraction of these filaments grow to macroscopic lengths when exposed to a gas of low carburizing potential, while still retaining the outside diameter of the initial catalytic particle. Pyrocarbon subsequently deposited on the walls of the filament thicken the fiber to larger diameters, with the basal planes of the deposited carbon preferentially oriented parallel to the filament surface[5], thus producing partially graphitic properties in the resulting fiber. Figure 1 shows scanning electron micrographs of vapor grown carbon fibers grown by a gas phase process, designated as PYROGRAF III, contrasted to typical continuous commercial carbon fibers. The diameter of PYROGRAF III generally averages 0.2μ as produced, while commercial fibers are 8μ in diameter. Resulting from turbulence in the gas phase generation of the fibers, the fibers become entangled during the production process. Unlike commercial fibers, as shown in Figure 2, PYROGRAF III fibers are not continuous. The length/diameter ratio for PYROGRAF III ranges from 40 to 200. Due to the process and purity with which carbon is incorporated into the fiber, VGCF has a highly graphitic structure, which results in higher physical property values than are realized in commercial carbon fibers, as shown in Figures 3 and 4.

Initial development of VGCF used selected laboratory grade hydrocarbon gases (e.g., 99.9% pure) such as methane, benzene, or acetylene, to ensure reproducibility of scientific results. However, to achieve economic success, it is necessary to use the least expensive feedstock possible. Any number of fossil fuels, including natural gas, oil or coal products would be much more economical than using high-purity laboratory grade gases as are currently used. Reduction of feedstock cost would allow the fiber product to be considered for automotive applications, such as in sheet molding compounds and numerous low strength components such as motor housings, interior panels, and other low-cost applications.

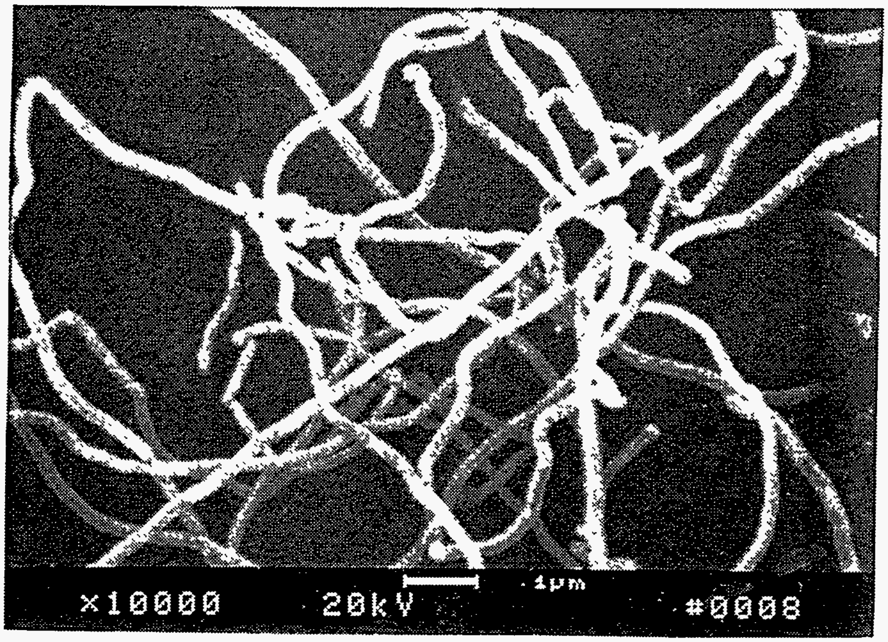

Figure 1. Vapor-grown Carbon Fiber.

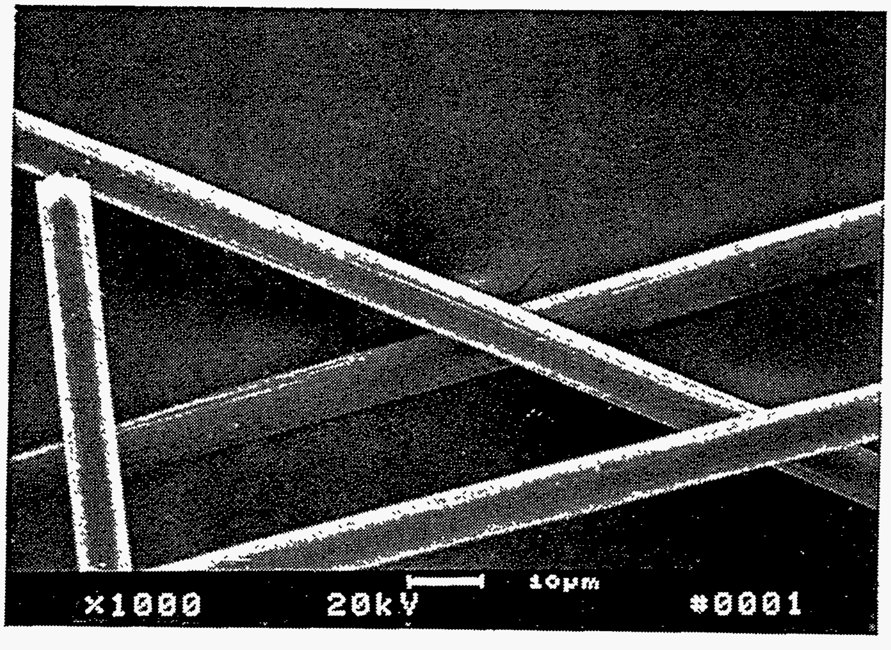

Figure 2. Commercial PAN Fiber.

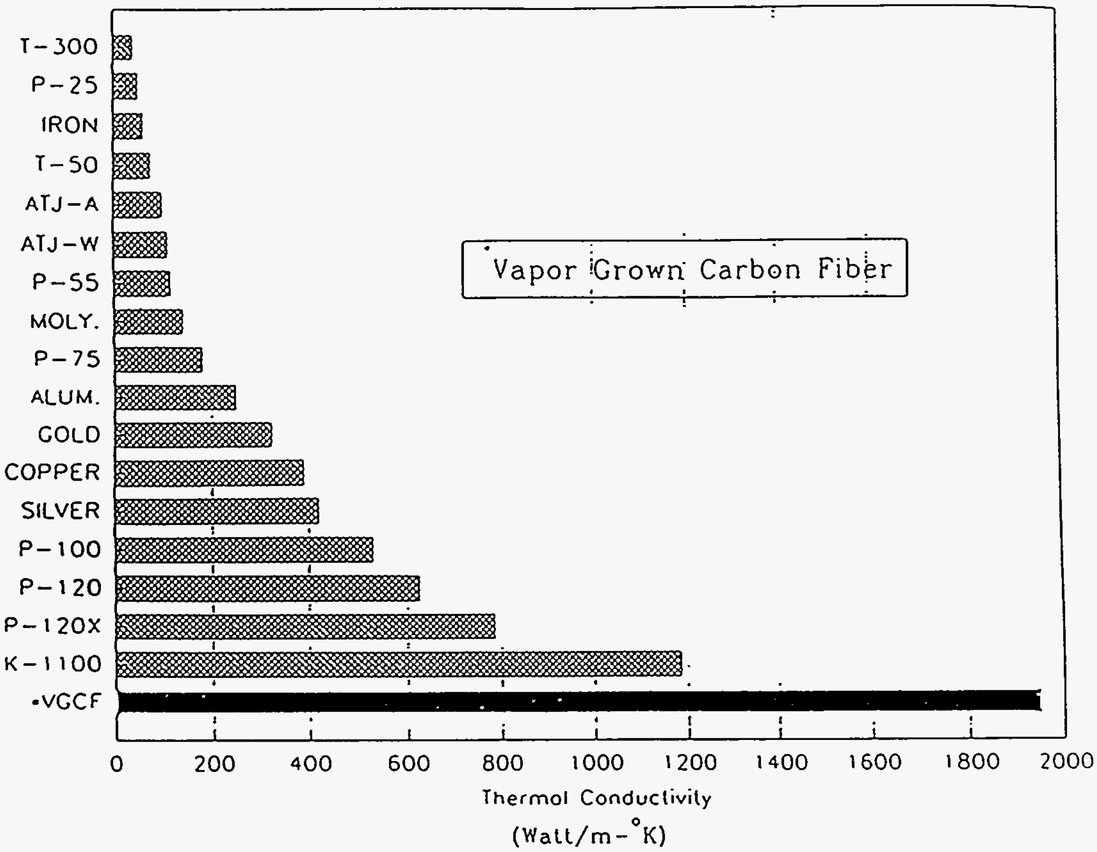

Figure 3. Thermal Conductivity

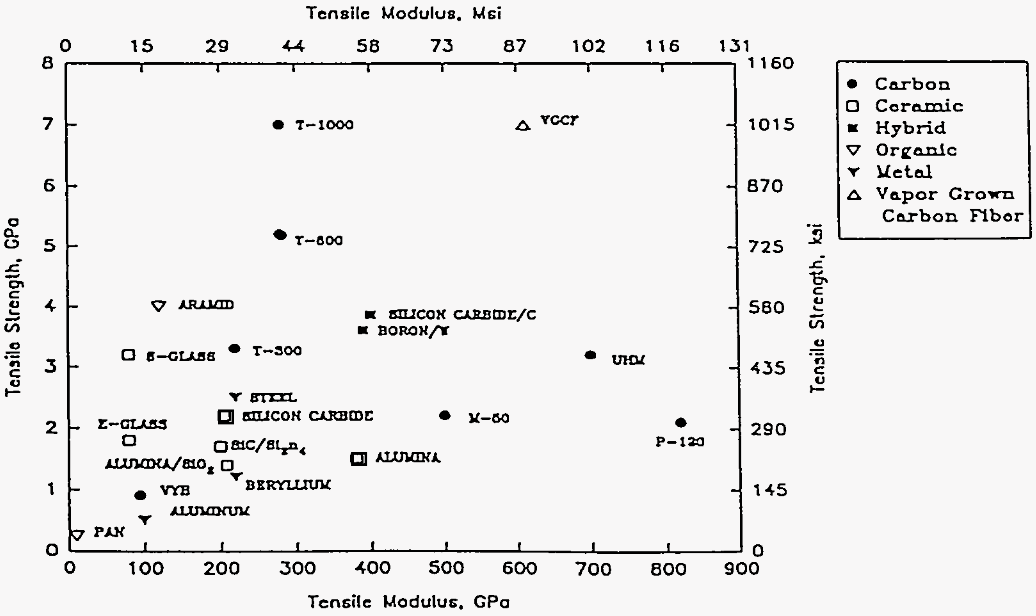

Figure 4. Tensile-Modulus Properties

Recent studies have shown significant enhancement of fiber nucleation efficiency by the addition of quantities of sulfur into the reaction.[1] Furthermore, the sulfur introduced becomes incorporated into the fiber by being adsorbed onto the catalyst, and subsequently overcoated with graphite. Although the addition of H_2S was found to be beneficial to the efficiency of fiber production, it was used with great reluctance since H_2S is expensive, highly corrosive to rubber seals and metal fittings, flammable, and as toxic as hydrogen cyanide. These findings suggest that substitution of inexpensive high sulfur coal for purified methane as the hydrocarbon feedstock could be accomplished, and have tremendous impact on the economics of fiber production.

Process Description

The production of vapor grown carbon fiber grew from work initiated by Dr. Gary Tibbetts at the General Motors Research Laboratories in 1979[6]. The concept underlying the production of carbon fiber by this method begins with metal particles, generally iron, catalyzing the growth of long slender partially graphitic filaments when hydrocarbon gases decompose on the catalyst surface in the 1000 - 1100°C range. When the hydrocarbons decompose, they deposit carbon atoms which diffuse through the catalyst particle and initiate carbon fiber growth. It is also known that the addition of sulfur to the reaction in amounts equimolar to the catalyst greatly enhances the yield and quality of the fiber by liquefying the metal catalyst[1]. In the PYROGRAF-III™ process, all the feed materials are injected into a horizontal furnace in the gaseous phase through a 3/8" injection tube. The reactant gases enter the furnace well mixed and fiber formation is initiated once the temperature of the reactants are above 1000°C. The newly grown fibers are then removed from the furnace while maintaining the furnace at temperature.

Since PYROGRAF-III™ has always been produced from gaseous feedstocks, modifications were necessary to introduce the pulverized coal into the furnace. An auger feeder system was developed and mounted to the furnace to convey the coal into the main gas injection tube. Once in the 3/8" gas injection tube, the coal becomes entrained in the feed gases and subsequently transported into the oven. A diagram of the process is presented in Figure 5. This process line is capable of producing several grams of fiber and removing it in cycles every few minutes.

Approach, Procedures, and Problems

Achieving the objectives of this project required substitution of solid coal for gaseous hydrocarbon feedstocks. Heretofore, only gases and occasionally liquids have been injected into the reactor. An apparatus was developed to feed the pulverized coal into the reactor. The coal feeder consisted of a 1/4" drill bit used as an auger, housed in a stainless steel block with a hopper positioned directly above the drill bit. The drill bit was attached to a variable speed motor and calibrated to establish the flow rate. The auger system was used to transport the pulverized coal into injection tube where the feed gases would then convey the coal powder into the furnace. See Fig. 6 for details.

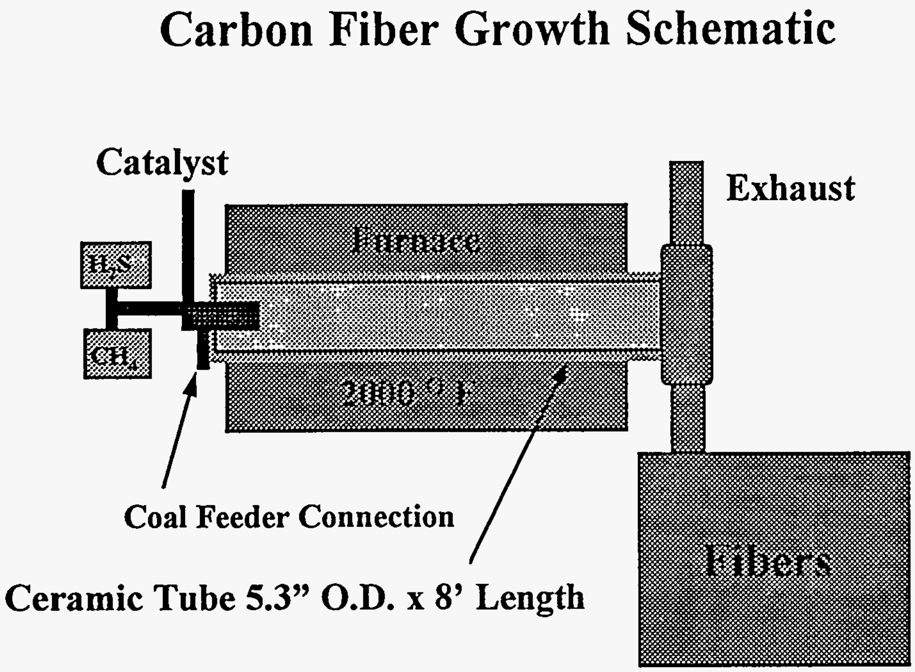
Carbon Fiber Growth Schematic

Figure 5. Diagram of the PYROGRAF-III™ process using coal.

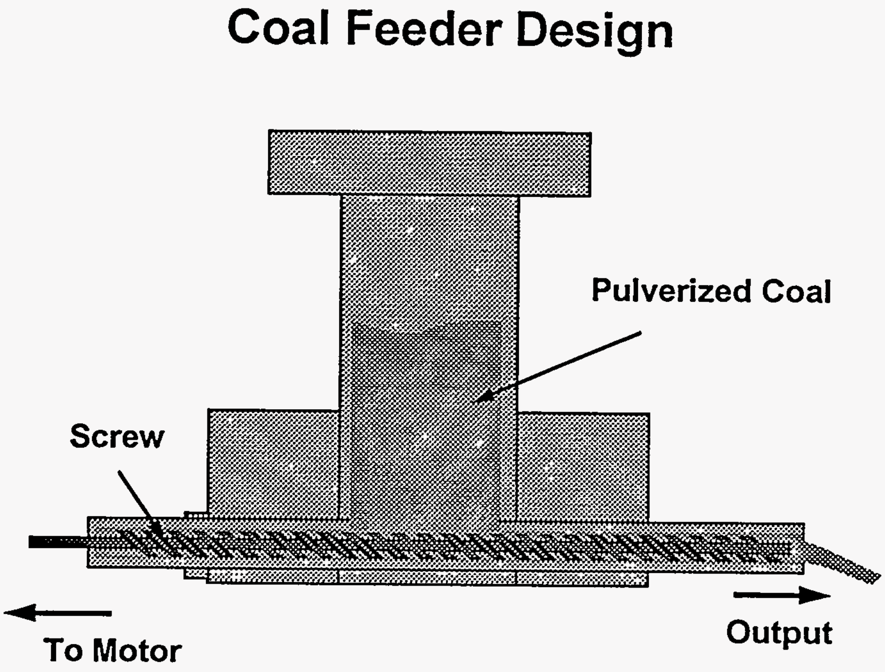
Coal Feeder Design

Fig. 6. Coal Feeder Apparatus

Once the coal feeder was completed, process variables were determined for trials using pulverized Ohio coal as the sole source of sulfur. Calculations assumed that all the sulfur in the coal was being utilized in the reaction process. The injection rate of the coal was chosen to input a sulfur/carbon ratio equal to the sulfur carbon ratio used in normal PYROGRAF-III^{TM} trials using methane and no coal. In order to achieve this optimum sulfur/carbon ratio and still use coal, methane was added as a supplemental source of carbon. A new reaction furnace had been assembled for the coal trials and was tested using control runs made without coal to assure proper functioning of the furnace and controllers. After the reaction furnace and controllers were approved, coal trials using Ohio (No. 8) coal were initiated. During these preliminary coal trials, the disadvantages of using an auger system became evident. Reactant gases from the furnace would escape through the coal feeder emitting harmful gases into the lab area when the fiber was purged from the reactor at the end of its growth period. Other problems included the stoppage of coal flow due to the formation of bridges and arches in the hopper. To remedy these problems, tighter seals were added to the coal feeder, a funnel made from a teflon/fiberglass weave was inserted into hopper, and a vibrator was attached to the feeder during the trials. These improvements solved the problems of renegade emissions and coal flow stoppages. The results from these initial trials performed in Task I and the results of additional trials performed in Task II are detailed in the following sections.

Project Results

Task I.

The objective of this Task was to demonstrate that high sulfur Ohio coal can produce PYROGRAF-III^{TM} carbon fiber and eliminate the need for using hydrogen sulfide gas. The reactor control formula uses a feedstock mixture of 99.9% pure methane, 99.3% pure H_2S, and $Fe(CO)_5$ catalyst (in a helium carrier) is simultaneously injected into the 1100^0 C reactor. A typical control formulation that would produce a 25% yield is shown in Table 2, and the flow rate formulations are outlined in Table 3. In the coal trials, methane is used to carry the pulverized coal into the reactor at the same sulfur/carbon level as the "control" formulation, which produces PYROGRAF-III^{TM} using high purity methane and hydrogen sulfide on a daily basis. In these trials, the coal was supplemented with methane in order to attain the same hydrocarbon level as the "control" formulation. The coal used for Task I was Ohio (No. 8) coal pulverized to less than 63μ with a total sulfur content of 4.71% and a fixed carbon content of 46.6% (approximate total carbon content of 57%). The ratio of sulfur/carbon in this coal was above the optimum sulfur/carbon ratio and therefore additional carbon was supplied in the form of methane to balance the ratio.

TABLE 2. CONTROL AND BASIC FORMULATIONS*

	Control	Task I	Task II
Methane	96.90	87.58	None
Coal	None	9.33	80.68
Sulfur	0.47	0.44	2.02
Hydrogen	None	None	13.30
Helium	0.96	0.96	1.45
$Fe(CO)_5$	1.68	1.69	2.55

* Formulations are in per cent by weight

The flow rate formulations, fiber output, and the growth time in the reactor before removal for the Task I trials with Ohio (No. 8) coal are shown in Table 3.

TABLE 3. COAL TRIALS PERFORMED DURING TASK I*

Phase I Coal Trials	Methane (cc/min)	Helium (cc/min)	Coal* (g/min)	Fiber Output (grams)	Growth Time (min)
9/1/93 Runs 3-5	4300	220	0.35	10.9	4
9/2/93					
Runs 4-5	4300	220	0.68	24.2	4
Runs 6-11	4900	220	0.68	15.4	4

* The coal flow rates are rough approximations due to the inaccuracy of the coal feeder.

The yields for these fibers were not calculated due to the inaccuracy of the coal feeder. However, the fibers were examined under the scanning electron microscope (SEM) and the fibers were straight with no visible defects such as imbedded ash and soot particles. Thus Task I proved that high sulfur coal can replace hydrogen sulfide as a sulfur source in the production of PYROGRAF-III^{TM} without visually changing the quality of the fiber. Figure 7 shows the visual quality of the fibers produced from high sulfur coal and the absence of surface defects on the fiber.

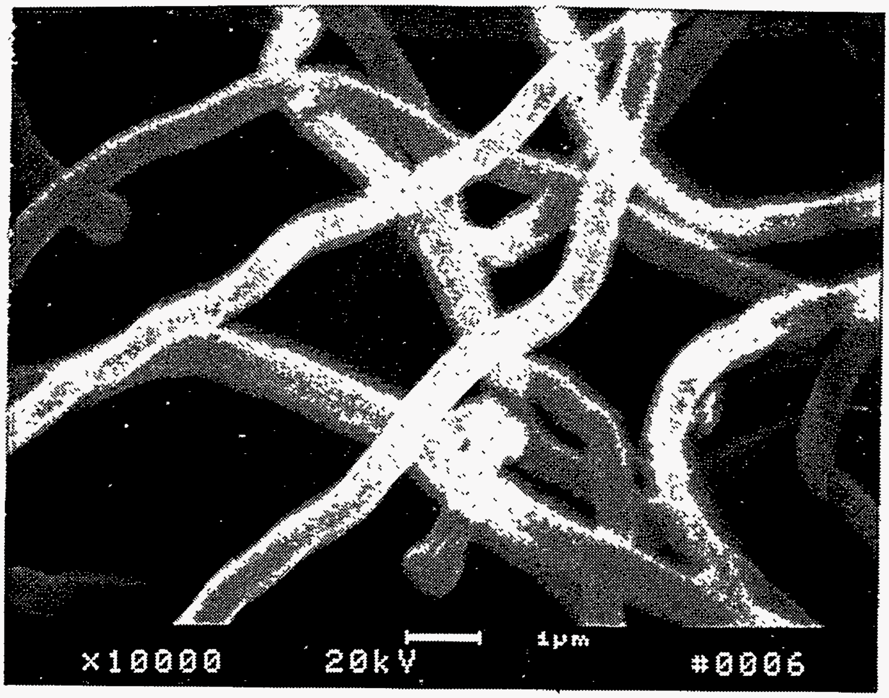

Figure 7. Task 1, SEM of PYROGRAF-III™ produced from coal.

Task II.

In Task II, the main objective was to prove that the inherent carbon content of the coal was being utilized in the formation of the carbon fiber. This objective was achieved by performing trials where the coal was the only source of carbon. This entailed carrying the pulverized coal into the reactor with hydrogen gas as a carrier instead of methane. Hydrogen was chosen because cylinders and the flow control hardware were available. Furthermore, hydrogen is one of the known exhaust gases that will eventually be recirculated. Thus unlike Task I, Task II did not supplement the coal with additional carbons sources to balance the carbon/sulfur ratio. It was found earlier that the sulfur to carbon ratio can be twelve times the control sulfur/carbon ratio and still produce good quality fiber[1]. The coal used for the initial trials of Task II was from the Upper Freeport Seam with a 2.5 wt% sulfur content and an estimated 65 wt% total carbon content pulverized to 74 μ particle size. The basic formulation is shown in Table 2. Carrier gas flow was varied in order to assure that the pulverized coal and the catalyst were thoroughly mixed upon entering the reactor. Many trials were performed using Upper Freeport Seam in which the hydrogen gas was used to transport the pulverized coal into the reaction furnace. Carbon fiber was produced in every trial. Figure 8 is a micrograph of fiber made from coal, hydrogen, and helium containing the $Fe(CO)_5$.

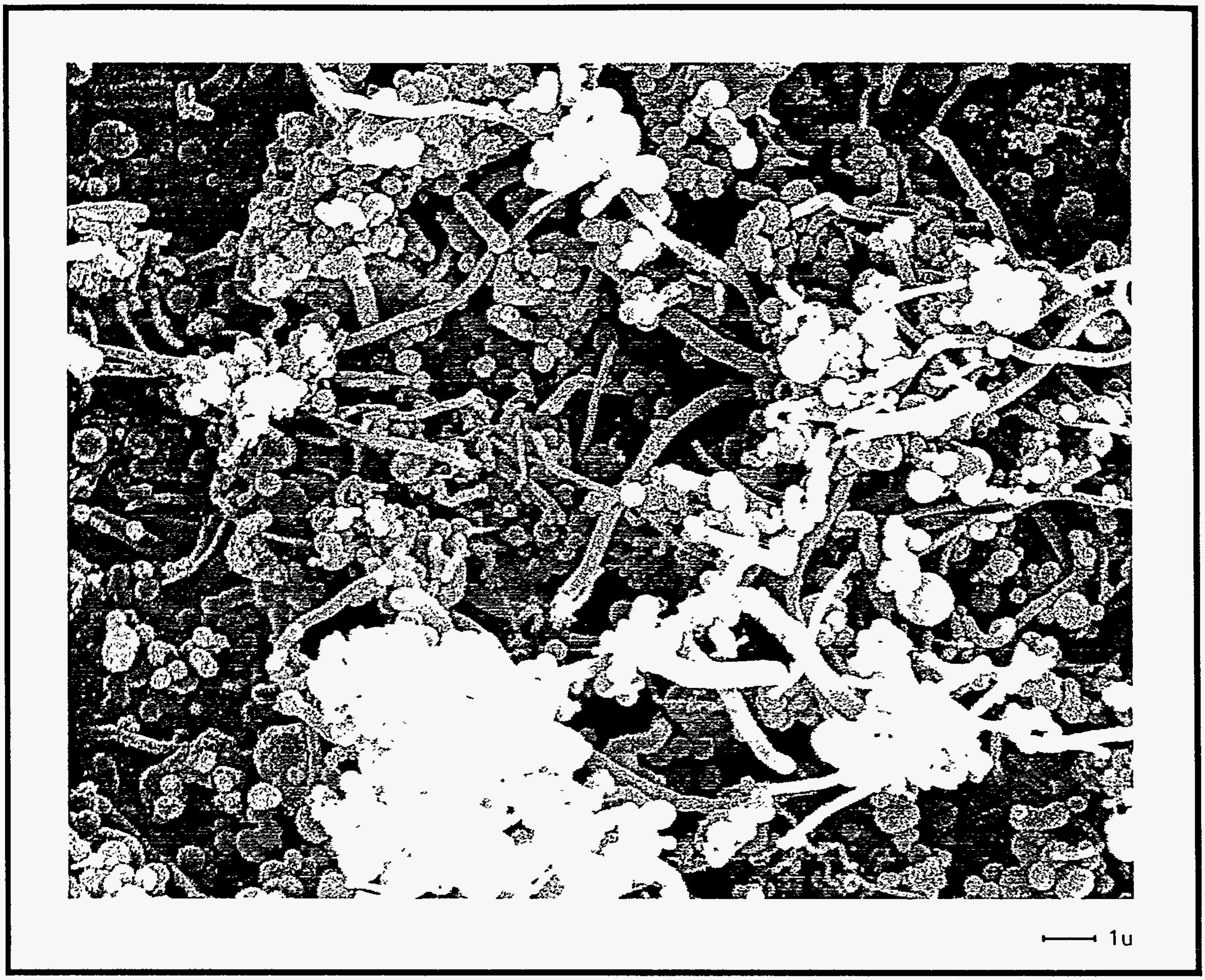

Figure 8. Task II, SEM of PYROGRAF-III™ produced from coal as the only carbon source.

The micrograph above shows the presence of good fiber, intermixed with particulate, made directly from coal with no additional carbon or sulfur sources. The size and shape of these particles are very similar to particles in micrographs of very early PYROGRAF-III™ trials before the importance of the sulfur concentration on the VGCF process was determined. In the past, these particles have been analyzed as primarily carbon (soot) and iron from excess catalyst. Ash from the coal is probably also present. In summary, this micrograph shows conclusively that the carbon content of coal is utilized in the formation of PYROGRAF-III™. The trails performed for Task II are outlined in the Table 4.

TABLE 4. COAL TRIALS PERFORMED DURING TASK II*

Phase II Coal Trials	Methane (cc/min)	Helium (cc/min)	Hydrogen (cc/min)	Coal* (g/min)	Fiber Output (grams)	Growth Time (min)
02/03/94						
Run 1	0	220	4000	0.2	1.1	1
Runs 2-3	0	220	4000	0.2	0.5	1
02/11/94						
Runs 1-3	0	220	4000	0.2	1.8	1
Runs 4-9	0	220	4000	0.2	4.6	1
03/15/94						
Ru 13-14	0	220	6000	0.6	0.5	1
03/29/94						
Ru 10-12	1200	225	4000	0.6	Trace	1
04/04/94						
Runs 1-3	1200	75	4000	0.6	0.7	1
04/07/94						
Runs 1-3	2000	85	4000	0.73	0.7	1
Runs 4-6	3000	85	3000	0.73	0.3	1
Runs 7-9	1000	85	5000	0.73	0.1	1
Ru 10-12	2000	200	4000	0.73	0.3	1
Ru 13-15	2000	150	4000	0.73	Trace	1
Ru 16-18	2000	250	4000	0.73	Trace	1
04/11/94						
Runs 1-3	2000	85	4000	0.73	Trace	1
04/12/94						
Runs 2-6	0	220	6000	0.73	0.7	1
06/07/94						
Runs 4-7	1700	100	0	0.4	0.5	2
Runs 8-10	3500	100	0	0.4	0.1	2
Ru 14-15	0	100	4500	0.4	0.1	1
06/16/94						
Runs 3-5	2800	125	0	0.4	0.1	2
Runs 6-8	2800	100	0	0.4	0.2	2
Runs 9-11	1700	125	0	0.4	0.1	2
Ru 12-13	0	125	4500	0.4	0.1	1

06/17/94						
Runs 1-5	2800	125	0	0.4	Trace	2.2
Run 6	1700	100	0	0.4	Trace	3
Ru 12-14	1188	100	0	0.4	0.2	1
Ru 17-19	0	100	4500	0.4	0.1	1
07/06/94						
Run 1	1700	100	0	0.4	Trace	2
Runs 2-8	1700	100	0	0.4	0.1	3.7
Runs 9-11	5100	300	0	0.4	1.0	2
Ru 12-14	5100	300	0	0.4	4.6	2

For more conclusive evidence that graphitic fiber was truly formed, Dr. David Anderson of the Univ. of Dayton Research Institute assisted with X-ray diffraction analysis. The degree of graphitic ordering is the crucial property that causes the wide range of strength and conductivity shown earlier. To estimate the degree of graphitization, samples from each Task were examined by X-ray diffraction. The following Table shows that the "as-grown" samples derived from coal have a graphitization index in a range typical with that of a low-modulus commercial fiber.

TABLE 5. X-RAY DIFFRACTION ANALYSIS

HEAT TREAT (^{0}C)	FIBER TYPE	D-Spacing (nm)	g_p* (%)
AS-GROWN	VGCF	.34490	--
1300	ex-PAN	.354	--
AS-GROWN	COAL & METHANE Task I	.3459	--
AS-GROWN	COAL Task II	.3451	--
2500	ex-PAN	.342	23
2500	VGCF	.3377	73
as-grown	PYROGRAF III	.3385	64
--	P-120	.3378	72

*g^p = (0.3340 - D-Spacing)/(0.3440 - 0.3354)

The development of the mass and energy balances for the conversion of coal into PYROGRAF-III™ were projected from the qualitative analysis of the exhaust gases. Initially, Applied Sciences Inc. did not have the capability to analyze the exhaust. However, a Perkin Elmer Sigma 3B gas chromatograph (GC) and an integrator unit were obtained in December from General Motors Research in Detroit as partial fulfillment of their support for this project. The separating columns accompanying the units were not capable of separating differing hydrocarbons and new columns were ordered. The gas chromatograph is currently capable of separating O_2, N_2, CO, CO_2, H_2S, NH_3, H_2O, and C-C hydrocarbons. Hydrocarbon concentrations as low as 100 ppm can be detected, but the other gases are limited to about 1000 ppm. The GC was used to analyze trials over a span of several days where high sulfur coal was used to produce PYROGRAF-III™ carbon fiber. No harmful sulfur compounds were detected in any of these analyses. Figure 9 is a GC readout in from a typical coal plus catalyst run without additional hydrocarbons. This particular analysis was made using a new ceramic reaction tube; it provided an opportunity to run trials knowing with certainty that there was no contamination from residual hydrocarbons from earlier trials. In this case, the usual procedure of checking the equipment by starting the day with a "control" trial with methane was dispensed with and the trials began using coal as the only hydrocarbon source.

The by-products in the exhaust of the coal to fiber process are methane, carbon dioxide, and water as shown in the chart above. This chart represents the relative amounts of each component and not their quantitative values. The large peaks of oxygen and nitrogen are from the air remaining at the end of the furnace from the previous removal stage and from the loose tolerances inherent in the coal feeder.

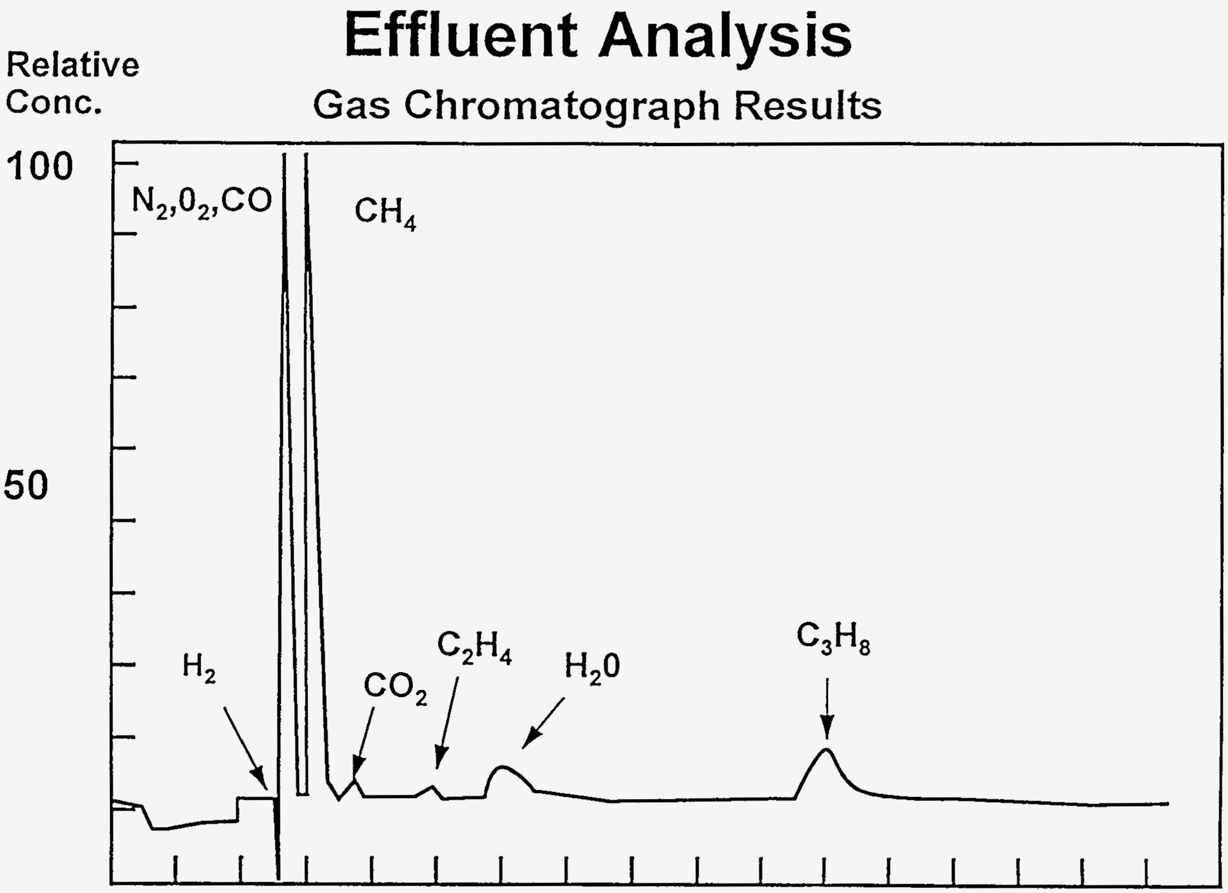

Figure 9. Gas Chromatograph Analysis of the exhaust from ANC-09 Shots 14-15 using Clarion 4A Seam.

In addition to the gas chromatograph, Gastec 5L SO_2 gas detection tubes with a lower sulfur dioxide detection limit of 0.25 ppm were used to analyze the exhaust gases of several different coal trials; the presence of SO_2 was not detected in any of the samples. This is a good indication, but not conclusive evidence that high sulfur coal can produce carbon fiber without generating environmental pollution. The sulfur in the reaction certainly affects and improves the formation, and excessive sulfur changes the length and linearity of the formed fiber. This is consistent with prior examinations of the exhaust in trials using hydrogen sulfide gas as the sulfur source. It has been shown prior to working with coal that sulfur in the PYROGRAF-III™ process becomes part of the catalyst and remains encapsulated in the fiber[1]. However, more data are needed before a claim can be made that this will always be the case. These results indicate that the exhaust, in addition to the possibility of being free of polluting chemical species, is also energy-rich, and could be recirculated to supply a significant fraction of the energy required for the PYROGRAF-III™ process.

The conversion efficiency or yield of using coal to produce VGCF requires further data. The yields have been inconsistent due to variation on the coal feeder. However, there have been some yields in the 20-30% range which indicate that coal may be able to completely replace the need for hydrogen sulfide with no reduction in yield. These results are preliminary; more work is needed to provide accurate statistical data for future precise material and energy balances for scale-up considerations.

It is estimated from these laboratory scale trials that 5.7 pounds of Upper Freeport Seam coal with a 2.5 wt.% sulfur content and a 69.3 wt.% carbon content would be required to produce one (1) pound of PYROGRAF-III™ carbon fiber assuming a 25% conversion efficiency. From the tentative inputs into the reactor and using the GC exhaust analysis as a qualitative guide, stoichiometric calculations in Appendix A indicate that 0.2 lbs. of water, 1.1 lbs. of carbon dioxide, 2.9 lbs. of methane, and 0.5 lbs. of hydrogen are generated and released in the exhaust for every pound of fiber produced. More work, such as quantitative exhaust data is needed for comparison with the predicted material balances developed in Appendix A.

A large portion of the energy involved in the formation of VGCF from coal is consumed in fiber nucleation and growth. The activation energy required to nucleate and grow one mole of methane to VGCF is 272 kJ or 65.0 kilocalories. This is approximately 30% of the total energy required to raise the reactants to 1100°C, initiate fiber nucleation and complete fiber growth assuming a 25% yield. It has been observed that methane has the highest nucleation and growth energy requirement for all hydrocarbons[7]. Therefore, by using coal, different hydrocarbons would be used in the fiber formation and the energy of nucleation and growth would be reduced.

Another area of cost reduction along with using coal would be to recycle the exhaust gases and burn the combustibles. From the GC estimate, material inputs,and literature heat data, estimates for the amount methane and hydrogen have been calculated. The material balance indicates that 2.9 lbs. of methane and 0.5 lbs. of hydrogen are generated for every pound of fiber produced. If these gases were recycled and combusted, they would generate approximately 85,000 calories per minute which is almost three times the energy required to produce the fiber. The energy analysis for the formation of PYROGRAF-III™ from Upper Freeport Seam coal is detailed in Appendix B.

Marketing/ Commercialization Discussion

There are many various applications for PYROGRAF-III™ in the commercial market. These applications include uses in rubber, composites, concrete, and plastic products where the fiber's unique characteristics would be very beneficial. The potential markets for coal derived fiber are discussed in more detail below.

Rubber Products

In 1992 carbon black shipments to rubber manufacturers were almost 3.0 billion pounds[8]. If PYROGRAF-III™ were to capture 20% of this market and use Upper Freeport Seam coal with a 2.5 wt.% sulfur content and a 69.3 wt.% carbon content, it would consume 1,800,000 tons of coal/year. This is approximately 5.5% of the 33.1 million tons of coal produced in Ohio[9] in 1990. The benefits of using PYROGRAF-III™ in rubber compounds are:

1. Reinforcement - Work has been underway for several years to make rubber products with PYROGRAF-III™ and the progress has been quite successful. Natural rubber formulations have been mixed with PYROGRAF-III™ as the reinforcement material in place of carbon black and the modulus increased by a factor of 2.5. These results are quite different from commercial carbon fibers which have performed poorly in the past as a rubber reinforcement due to their large diameter of 8 microns and small surface/volume ratio. Conversely PYROGRAF-III™ fiber has a 0.2 micron diameter and 40 times the surface/volume ratio of commercial fibers. A rubber company has been evaluating PYROGRAF-III™ in increasing quantities and substantiates its reinforcement capabilities. None of this fiber used coal as a feed material as it is in the early development stages and not enough material was available.

2. Sulfur Content - Coal in the 2.5 wt.% sulfur range is 5 times higher (2.0 grams/min of coal and 220cc/min of He) than the usual equimolar sulfur/catalyst ratio that has been used for producing most of the PYROGRAF-III™ to date. However, good fiber can still be produced from higher sulfur/catalyst ratios as shown in previous work[1]. It has a shorter length and we speculate that the sulfur content on the surface will be higher but the fiber will still perform well as a reinforcement. The excess sulfur may be very desirable for rubber applications since sulfur and its derivatives are the backbone for cross-linking the rubber molecules, which is essential for rubber reinforcement. For illustration, the following is a generalized recipe with specific ratios typical for a tire tread. The figures in parenthesis show the ranges of variations for these ingredients as they are adjusted to produce the variety of properties needed for the rubber industry:[10]

Rubber	100 - parts by weight	
Sulfur	3	(0.5-50)
Accelerator	1	(0.3-3)
Zinc Oxide	5	(2-10)
Stearic Acid	1	(0-4)
Antioxidant	1	(0-3)
Wax and Oil	5	(2-50)
Carbon Black & Fillers	50	(20-300)

This shows that the excess sulfur is not a detriment for rubber products; it could uniquely enhance not only the degree of bonding of the rubber, but also the interfacial bond strength of the rubber and fiber.

3. Ash Content - It was beyond the scope of this grant to characterize the ash content and determine where the residue settles. About the only thing known about the ash is that it did not become imbedded in the graphitic fiber structure during growth. This was shown through X-Ray and scanning electron microscope evaluations. If the ash had embedded itself in the fiber structure, coal would not be a feasible alternative hydrocarbon without a prior distillation procedure. Nevertheless, if ash is present, it could become one of the non-black fillers used in the rubber recipe as shown above. Coal dust, per se, was used as a filler in rubber 25 years ago; its major obstacle was cost for it could not compete with limestone, which was under a penny a pound.

4. Cost - The cheaper grades of commercial carbon fiber start at 15 $/lb and move into the 2500 $/lb and up depending upon the degree of graphitization desired. As a result, many markets do not even consider using carbon fiber because of the cost, even if the properties may be very desirable. Although the process is not fully developed for a total cost picture, the goal is to get PYROGRAF III^{TM} under 3 $/lb. However, a partial costing of the formulations in Table 6 shows that coal at 30 $/ton not only drastically reduces the cost of the carbon source, but totally eliminates the price of the sulfur:

TABLE 6. PYROGRAF-III^{TM} MATERIAL COST COMPARISON

	Control Methane Only ($/lb)	Control Natural gas only ($/lb)	Task 1 94% N. g. 6% Coal ($/lb	Task 2 100% Coal ($/lb
Sulfur Source	0.189	0.194	0	0
Carbon Source	69.83	0.44	0.419	0.067

Plastic Composites

U.S. shipments of thermoset and thermoplastic composites will grow to 2.9 billion pounds in 1994[11]. Of this, ½ billion pounds consists of pultruded composites which require fibers with continuous length; this excludes the non-continuous, entangled PYROGRAF-III™. This leaves an existing market of 2.4 billion pounds. If the average composite uses 20% by weight fiber and if PYROGRAF-III™ were used in 20% of the market, this would require 260,000 tons of coal per year.

Applied Sciences is also involved in a three year project with the Edison Materials Technology Center (EMTEC) concerning the development of low-cost, high performance composites using PYROGRAF-III™ carbon fiber. This project is in its incipient stages and includes the participation of many organizations such as Delco Chassis, General Motor Research Center, Goodyear Tire and Rubber Co., Ohio University, Performance Plastic Inc., University of Dayton, and Wright Laboratory. The main goal of this project is to develop a low-cost carbon fiber reinforced composite (CFCR) which could be used in auto-body panels. Currently, the major barrier to using CFCRs in the automotive industry is cost. Presently, at the urging of General Motors, initial trials are underway with Ashland Chemical to mold vinyl ester sheet molding compounds (SMC) panels using PYROGRAF-III™ for use as auto-body panels. This program is in the initial stages of applying sizings to the fiber to build an interfacial bond between the fiber and the vinyl ester when mixed and molded.

Plastics Industry

The market for the entire plastics industry in the U.S. is forecasted to be 87 billion dollars in 1996 which translates into 39 billion pounds[12] of plastics. Twenty-six percent (26%) of this market is consumed by the electronics industry and 5.1% is used by the auto industry. Of the entire market, Ohio is the second largest plastic manufacturer in the nation with 8.28 billion dollars forecasted for 1996.

In comparison, the above composites industry (2.9 billion pounds) is only 7.5% of the entire industry. This shows that even though fibers, especially commercial carbon fibers, may have desirable properties, their growth has been stagnated by their inherent high price. However, if PYROGRAF III can substantially undercut this price through the use of high sulfur coal, many new markets will open that presently do not even consider for the use of carbon fibers. For example, the electronics industry needs materials with better thermal and electrical conductivity to dissipate heat and static electricity, PYROGRAF-III™ has these properties in addition to reinforcement capabilities.

Concrete Industry

The concrete industry used 68.7 million short tons of Portland type and 2.6 million short tons of masonry type cement in 1990.[13] To reduce cracking over large temperature changes, concrete needs better reinforcement and better thermal transfer properties. Therefore, PYROGRAF-III™ which has been used as a reinforcement in other materials and has a thermal conductivity of 1950 W/mK, second only to diamond, would be an ideal additive for concrete.

Also, the high electrical conductivity of PYROGRAF-III™ would be a desirable property for concrete bridges using steel reinforcements. The carbon fiber would make allow the introduction of a reverse electrical current which would counteract the galvanic corrosion of the steel which forms iron oxides that expand and eventually crack the concrete[14].

If PYROGRAF III were to achieve 5% of this market, it would annually consume 3.6 million tons of fiber, which translates into using an additional 21.9 million tons of high sulfur coal (66% of Ohio's coal production). Cost is the major obstacle and little development has been done in this area. At present, trials are underway to develop a sizing to bond the fiber and concrete.

Future Work

This project has proven that Ohio high sulfur coal is capable of producing PYROGRAF-III™ carbon fiber. However, there are still some areas that need further investigation:

1. A better system of feeding the coal is needed. The present variation makes statistical control impossible, which is crucial for any manufacturing process. From this, meaningful studies could begin on various grades of coal, % Yield, flow rate optimization, ash build-up, residence times, energy losses, exhaust gas recirculation, coal particle size, and material/energy balances for cost optimization.
2. Although Sulfur and nitrogen oxides have not been observed to date in the exhaust, this area needs thorough examination with precise equipment for recycling and environmental control. Process variations such as temperature (currently 1150°C), flow rates, etc. need to be monitored and correlated with precise exhaust analysis.
3. The ash residue and its disposition needs study. Some collects in the cooler sections of the exhaust tubes and some may stay with the fiber and may need to be filtered out while adding the sizing treatment.
4. While coal derived fibers are expected to perform equally well as methane derived fibers, they need to be surface treated with a sizing and compared by application trials in rubber and plastics. Note: All commercial carbon black, carbon and glass fibers are routinely coated with a sizing material for densification and wet- out properties.

Ideally, these issues would be resolved through low-volume applications development with high volume potential with the development and demand of the fiber progressing together. Currently, PYROGRAF-III™ is being evaluated in low-cost, high performance composites through a development project involving Edison Materials Technology Center. This project involves the participation of Delco Chassis, General Motor Research Center, Goodyear Tire and Rubber Co., Ohio University, Performance Plastic Inc., University of Dayton, and Wright Laboratory.

References:

1. G.G. Tibbetts, C.A. Bernardo, D.W. Gorkiewicz, and R.L. Alig, "Effect of Sulfur on the Production of Carbon Fibers in the Vapor Phase", **CARBON, 32,** No. 4, pp. 569-576, (1994).

2. Advanced composites Plastic Site Selector pp 2, (1993).

3. Statistical Abstract of the United States, U.S. Department of Commerce, 113 Edition, Table 1185, pp 696, (1993).

4. U. S. Patents, No. 4,391,787, No. 4,491,569, No. 4,497,788, No. 4,565,684, No. 4,749,557, No. 5,024,818, and pending patents.

5. J.L. Kaae, Carbon 23, 665 (1985).

6. G.G. Tibbetts, "Carbon Fibers Produced by Pyrolysis of Natural Gas in Stainless Steel Tubes", **Extended Abstracts,** 16th Biennial Conference on Carbon, San Diego, pp. 531, (1983).

7. P.A. Tesner, *The Formation of Carbon from Hydrocarbons of a Gaseous Phase,* Khimiya, Moscow, (1972). or **Chemistry and Physics of Carbon,** edited by Peter A. Thrower, Vol. **19**, pp 154-155.

8. *CARBON LINES* Vol. 4, No. 1, March 1993, Newsletter by Huber engineered Carbons Division.

9. J.F. Bird, N. S. Tostenson, **OHIO COAL DEVELOPMENT AGENDA,** p. 5, (1992).

10. M. Morton, " Introduction to Rubber Technology", Reinhold Publishing Corp. New York, pp. 30 (1959).

11. *PLASTICS TECHNOLOGY*, pp 175, May (1994).

12. Advanced composites Plastic Site Selector pp 2, (1993).

13. Statistical Abstract of the United States, U.S. Department of Commerce, 113 Edition, Table 1185, pp 696, (1993).

14. Mechanical Engineering, September, pp 40 (1985).

PROJECT BUDGET

(deleted)

APPENDIX A

Complete Material Balance for Coal + Catalyst

Coal Type : Upper Freeport Seam

Basis : 2600.0 gms of coal
5.7 lb coal

	weight. %	grams	pounds
Total Sulfur	2.5	65.0	0.1
Organic	?	0.0	0.0
Sulfate	?	0.0	0.0
Pyritic	1.4	36.4	0.1
Carbon	69.3	1801.8	4.0
Ash	8.1	210.6	0.5
Nitrogen	1.5	39.0	0.1
Oxygen	13.2	343.2	0.8
Hydrogen	5.4	140.4	0.3
Sums	100.0	2600.0	5.7
Input Total		10330.9	22.8 lb

Gas Flows

	cubic cm	grams	pounds
Helium	286000.0	47.5	0.1
with Catalyst		21.8	0.0
Hydrogen	5200000.0	434.7	1.0
Air :	5987520.0	7226.9	15.9
Nitrogen		5550.3	12.2
Oxygen		1676.6	3.7
Carbon from Catalyst		6.7	0.0
Oxygen from Catalyst		8.9	0.0
	Total =	7730.9	17.0

Outputs

	grams	pounds
Fiber (25% yield)	452.1	1.0
Carbon Dioxide	484.1	1.1
Methane	1304.6	2.9
Water	99.0	
Ash	210.6	0.5
Hydrogen	234.6	0.5
Oxygen	1588.6	3.5
Nitrogen	5589.3	12.3
Helium	47.5	0.1
Soot	244.6	0.5
Total	10255.1	22.4

Therefore, an estimated 5.7 pounds of coal are used to produce 1 pound of PYROGRAF-III carbon fiber.

APPENDIX B

ENERGY CALCULATIONS FOR THE CONVERSION OF COAL TO PYROGRAF III

SENSIBLE HEAT CHANGE

	Flow Rates (cc/min)	Flow Rates (g/min)	Temp 1 (Kelvin)	Temp 2 (Kelvin)	Energy Required (cal/min)		
Hydrogen	20000.0	1.7	298.0	1373.0	6371		Ref. Watson
Helium	1100.0	0.2	298.0	1373.0	244		Ref. Perry's
Catalyst-Negligible							
Coal		10.0	298.0	1373.0	2795.0	low	Ref. Watson
					3977.5	high	
Air:	33000.0						
Oxygen	6930.0	9.2	298.0	1373.0	2483.5		Ref. Watson
Nitrogen	26070.0	30.6	298.0	1373.0	8890.6		Ref. Watson

LATENT HEAT OF REACTION

Fiber nucleation and growth = 65000.0 cal/mol of reactant Ref. Tesner

---

TOTAL ENERGY REQUIREMENTS

	(g/min)	(mol/min)	(cal/min)
Total Carbon Input	6.9	0.6	
Yield of	25%		
Fiber Produced =	1.7	0.1	9375.8

(Most that can be blown out consistently to this date.)

Total cal. required for 10.0 grams of coal per minute for one minute growth periods= 31342 cal/min
2.19 kW

18091 cal/g of fiber
32578 BTU/lb of fiber
9.55 kW-hrs/lb of fiber

EXHAUST ANALYSIS

SENSIBLE HEAT CHANGE

	Flow Rates (g/min)	Temp 1 (Kelvin)	Temp 2 (Kelvin)	Energy Exhausted (cal/min)
Methane	5.0	1373.0	298.0	4854.9
Hydrogen	0.9	1373.0	298.0	3508.7
CO2	2.0	1373.0	298.0	576.7
Nitrogen	30.7	1373.0	298.0	8859.8
Oxygen	8.9	1373.0	298.0	2369.1
Water (gas)	0.4	1373.0	298.0	223.7
Water Condensation - Negligible			TOTAL	20392.9

HEAT OF COMBUSTION

	(g/min)		(cal/min)
Methane	5.0		59307.8
Hydrogen	0.9		26184.9
		TOTAL	85492.7

TOTAL CALORIES/MINUTE 105886 cal/min

Therefore, three times the amount energy to produce the fiber can be recouped from the exhaust.

Watson, Hougen, Regatz: Chemical Process Principles, Wiley & Sons, N.Y., 1954
Perry's Chemical Handbook, 6th Ed., McGraw Hill, N.Y., 1984
Tesner: Kinetics of Pyrolytic Carbon Formation; Chemistry and Physics of Carbon, Peter A. Thrower, Vol 19, pgs. 83-157