

**PRODUCING VAPOR GROWN CARBON FIBERS WITH
HIGH SULFUR COAL WITHOUT SO₂ EMISSIONS**

R. Alig, M. Lake, J. Guth, and D. Burton
Applied Sciences, Inc.
P.O. Box 579
Cedarville, OH 45314

Keywords: SO₂ Control Technologies, Coal Pyrolysis, Organic Sulfur Removal

ABSTRACT

This paper describes the development of a unique process that produces a highly graphitic, vapor grown carbon fiber (VGCF) from the gas phase in pound quantities. Past vapor grown carbon fiber progress has stagnated because the iron catalyst did not grow filaments profusely enough to make a practical continuous reactor. It has been found that adding H₂S at an equimolar level with the iron catalyst, the filament formation vastly increases. Coal is desirable as a sulfur source, for it eliminates the need for handling toxic H₂S, and it is a very low cost hydrocarbon supply for the process. We show that Ohio, high-sulfur coal containing 2.5 to 4.6% sulfur accomplishes both tasks. There is also evidence that sulfur from the coal remains with the carbon fiber catalyst during the reaction and does not exhaust as SO₂ into the atmosphere.

INTRODUCTION

Carbon fibers have been of practical interest within the industrial community for over a century; Thomas Edison tried them as filaments for light bulbs. The Air Force started carbon fiber development for aerospace in the 1950's because of their mechanical and electrical shielding properties. These fibers were found to be stronger than steel, stiffer than titanium, and yet lighter than aluminum. Today, golf clubs, fishing poles, and tennis rackets are typical uses in the commercial sector.

A. Commercial fibers

Commercial carbon fiber uses are limited because they are more expensive than competing metals for engineering applications. Furthermore, their diameter is 8 μ , which is larger than normal fillers, such as carbon black, for reinforcement. This imposes expensive and limited processing techniques into composite applications. Hand lay-ups and slow pultrusion techniques are the norm; straight injection molding is out of the question. The total U.S. market for carbon fibers in 1990 was 6 million lb, of which 0.8 million lb were for the recreational market at an average cost of 23 \$/lb for the carbon fiber¹. For comparison: 3 billion lb of carbon black were shipped to rubber manufacturers in 1992² at an average cost of 0.25 \$/lb.

Commercial carbon fibers are formed from polymer precursors such as polyacrylonitrile (PAN) or petroleum pitch. The precursor is extruded or spun similar to textiles into a continuous filament or thread, oxidized under tension to 200^o C, and followed by slow heating in the absence of air to 1000^o C to carbonize the fiber. Sometimes, the carbon fiber is given additional heating up to 3000^o C to develop higher degrees of graphitization, which is needed for expensive ultra-high strength (2000 \$/lb range) applications.

B. Vapor grown carbon fiber

This paper is based upon a unique form of carbon fiber requiring no precursor filament. It is called vapor grown carbon fiber (VGCF), known as PYROGRAF IIITM. From initial inventions at General Motors, the patents were licensed to Applied Sciences, Inc. in 1992 for further development and manufacture. The process began by early workers, exposing vapor phase metals, generally iron, supported on inert substrates while exposed to hydrocarbons and hydrogen³ at a temperature in the 1000 - 1150^o C. range. This catalyzed the growth of long, slender, partially graphitic filaments⁴ as

shown in Figure 1. Although these methods remained essentially batch processes and too inefficient for mass production, this VGCF when subsequently heat-treated has a thermal conductivity of 1950 W/m-K (highest value found in nature except for diamond) and is sold as a carbon/carbon composite for aerospace thermal management materials. This was followed by attempts at a continuous process by injecting and dispersing the iron catalyst particles directly into the gas stream, and eliminating the use of a substrate for growth^{6,7}. This was still non-productive; the iron catalyst did not grow filaments profusely enough to make a practical continuous reactor. A breakthrough occurred when it was found and confirmed from early work in the 1950's by Kauffman and Griffiths⁸ that sulfur was vital to fiber formation. Adding hydrogen sulfide (H₂S) at an equimolar level with the iron catalyst, vastly increase^{9,10} the filament formation making a continuous reactor practical (Figure 2). We believe that the sulfur is incorporated in the fiber by being adsorbed onto the catalyst, and subsequently overcoated with graphite.

Figure 3 shows scanning electron micrographs of vapor grown carbon fibers grown by a gas phase process in comparison with typical continuous commercial carbon fibers. The diameter of PYROGRAF III generally averages 0.2 μ as produced, while commercial fibers are 8 μ in diameter. Due to the nature of the gas phase generation, the fibers become entangled during growth and are not continuous like commercial fibers. The length/diameter ratio for PYROGRAF III ranges from 40 to 200. Due to the process and purity with which carbon is formed into the fiber, VGCF is highly graphitized (Table 2) and the stress/strain properties for 7.5 μ VGCF (Figure 4) results in similar or higher property ranges than commercial carbon fibers. The smaller diameter and entanglements of the PYROGRAF III defy measurement.

C. Coal

Most of the VGCF made to date used laboratory grade methane, benzene, acetylene, etc. as a hydrocarbon source as a step toward reproducible results. Since we have developed one product line that can produce almost a pound per hour, natural gas is frequently used for high volume trials. Although the addition of H₂S was instrumental in achieving this improvement, it is used with great reluctance. Hydrogen sulfide is expensive, highly corrosive to rubber seals and metal fittings, flammable, and its toxicity is on a par with hydrogen cyanide.

This suggests that a fossil fuel such as Ohio high sulfur coal may be especially apropos for this problem since Ohio coal production has gone from 55 million tons in 1970 to 33 million tons in 1990. Ohio coal's high sulfur content is most responsible for this decline, which is projected to go lower due to the 1990 Clean Air Act Amendment. Furthermore, coal would have a tremendous effect on the eventual price of the fiber. The hydrocarbon is the most expensive cost item, followed by the electric oven energy and the catalyst. Although the energy consumption and output capabilities are not yet optimized for a total cost picture, the formulations that will be discussed later show that coal at 30 \$/ton not only drastically reduces the cost of the carbon source, but totally eliminates the price of the sulfur:

PYROGRAF III MATERIAL COST COMPARISON

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

EXPERIMENTAL

In this experiment, a reactor that normally uses a feedstock mixture of 99.9% pure methane was converted to enable use of coal as the hydrocarbon feedstock (Figure 3). Helium is bubbled through liquid iron pentacarbonyl to provide Fe catalyst particles, and 99.3% pure H₂S gas is simultaneously injected into the 1100° C reactor. A typical control formulation that produces a 25% yield is shown in Table I. A screw type apparatus was assembled to feed the coal and driven by a variable speed motor. It is similar to commercial equipment except the feed box is sealed from the air; otherwise, it may cause combustion as the coal enters the reactor. A carrier gas is used to transport the coal dust from the screw feed into the reactor hot zone.

Two trials using coal are shown in Table 1. In Trial 1, the hypothesis is that sulfur-bearing coal can replace H₂S as the source of sulfur in the reaction. Coal and methane were used as the hydrocarbon feedstock. The formulation was developed so that the sulfur content in the coal was equivalent (1.6 H₂S/Fe(CO), molar ratio) to the sulfur in the "control" formulation using methane and hydrogen sulfide. Ohio #8 Coal from CONSOL Inc., at 4.71% total sulfur and 46.6% total carbon, was pulverized to less than 63 μ . Methane was the carrier gas at a rate calculated to maintain a similar 1.6 molar sulfur/carbon ratio as the "control". It was assumed that all the sulfur in the coal was converted to hydrogen sulfide.

Trial 2 was to test the hypothesis that coal could serve as the only supply of the hydrocarbon and sulfur, and produce vapor grown carbon fiber. The pulverized coal was carried into the reactor with a non-hydrocarbon carrier (hydrogen). Upper Freeport Seam coal was obtained from Kaiser Engrs. with 2.5 % total sulfur and an estimated 65% carbon content. In this case without methane dilution, the molar sulfur/catalyst ratio is 4.5, which is considerably higher than the minimum 1/1 ratio for good filament formation.

RESULTS AND DISCUSSION

Carbon yield is here defined as the fraction of fiber harvested to the total carbon introduced into the reaction from all hydrocarbon sources. In the "control", vapor grown carbon is routinely produced with a yield of 25% with a 2% standard deviation. In Trial 1, with coal, methane, and no H₂S, the carbon yield is 19%. The photomicrograph in Figure 6 shows very good growth and confirms that the sulfur contained in the coal plays an active role in the catalytic process, and can potentially replace the need for using H₂S in the reaction.

The sulfur content in coal is well beyond the optimum amount for the formation of carbon fibers. Figure 6, reproduced from one of our prior papers¹⁰, shows SEM photomicrographs of carbon fiber produced with H₂S/Fe(CO), ratios of 0, 1.4/1 and 17/1. The sparse fiber in the photo without sulfur clearly illustrates the need for sulfur. However, the photo at the very high 17/1 ratio still produces very good carbon fiber; the fiber length is shorter, and tends to be more jagged and the soot content increases. Nevertheless, this leads to the possibility that high sulfur coal in spite of its problems for other uses may be a unique asset for the production of acceptable vapor grown carbon fiber.

In Trial 2, coal is the only source of both hydrocarbon and sulfur; a yield of 47% was obtained and a SEM photomicrograph is shown in Figure 5. There is good, but shorter fiber formation with a fair amount of soot and perhaps some ash. From past experience, the high carbon yield is anticipated, for we know that at extremely high sulfur levels, only soot will be formed. Nevertheless, these results support the conclusion that the inherent carbon in coal is actively pyrolyzed to products which participate in the catalytic fiber nucleation and growth process.

Photomicrographs are the basic estimate of fiber formation. However, X-ray diffraction can estimate the graphitic ordering and is the crucial property for assuring the quality of the fiber's strength and conductivity. Samples from the trials were analyzed by X-ray diffraction; Table 2 shows that the fiber samples from coal Trials 1 and 2 have a graphitization index that is typical for low modulus commercial fiber.

In earlier trials that rely on introducing H₂S into a pure methane feedstock at equivalent ratios with the catalyst, periodic analysis has been made of the exhaust. To date, sulfur has not been detected in the exhaust. This could be explained by the proposal¹⁰ that the sulfur dissolves in such large amounts that it melts the iron catalyst and thus stays with the catalyst at the base of the fiber. How much sulfur can be dissolved as the sulfur increases is unknown; there is a limit where fiber is no longer formed. A packed column gas chromatograph (GC) with thermal conductivity detector was used to estimate the composition of the exhaust gases of a series of coal trials when the sulfur was running at 4.5 times the usual amount (Trial 2) and the presence of sulfur was not detected. This instrument does not have the sensitivity to measure nitrogen or sulfur compounds below about 0.1-1 percent. Gastec detection tubes capable of detecting sulfur dioxide concentrations of 0.25 ppm and above were also used and no SO₂ was detected. Future work is needed with a capillary column GC with dedicated nitrogen and sulfur detectors.

Nevertheless, the data does support the theory that the sulfur does unite with the catalyst during fiber formation and would eliminate or reduce the release of harmful sulfur compounds into the atmosphere. Future work should also address the sulfur content, if any, in the residual ash over a wide range of sulfur/catalyst ratios. Although further work is needed to assess the effects of the organic and ash content variation in coal, their presence does not prevent the growth of a carbon fiber with graphitic ordering. For some applications such as rubber reinforcement, it is possible that the sulfur content in the fiber may be uniquely desirable and enhance the bonding during the rubber vulcanization process.

While these studies indicate the viability of using high sulfur coal as the hydrocarbon feedstock in production of VGCF, in practice, the high percentage of sulfur in various coals, as well as the variability of the percentage of sulfur in coal, will most likely mandate a combination of hydrocarbon feedstocks in order to maintain the process balance needed for optimum production. The role of coal in contributing to the hydrocarbon balance, as well as the sulfur balance, has significant implications.

CONCLUSIONS

It has been demonstrated that high sulfur coal can be used to make VGCF, contributing both carbon and sulfur to the reaction. This work suggests an ecologically safe process for utilization of high sulfur coal. If future trials continue to confirm these conclusions, the economic impact of coal on the price of carbon fiber will open new applications for carbon fiber in rubber reinforcements, cement, composites for automobiles, electronics, and aerospace components.

ACKNOWLEDGEMENT

This research was supported in part by the Ohio Coal Development Office/Ohio Department of Development under Grant Number CDO/R-922-8. The authors also gratefully acknowledge the contribution of Dr. Gary Tibbetts, General Motors NAO Research & Development, for his assistance and pioneering work that has made vapor grown carbon fibers a commercial reality, Dr. David Anderson from the University of Dayton Research Institute in providing X-ray analysis, and much assistance from the OCDO staff in performance of this work.

REFERENCES

1. C. Petersen, **ADVANCED COMPOSITES**, March/April 1994, pp 20.
2. **CARBON LINES** Vol. 4, No. 1, March 1993, Newsletter by Huber engineered Carbons Division.
3. G.G. Tibbetts, **Carbon** 30, 399 (1992).
4. J.L. Kaee, **Carbon** 23, 665 (1985).
5. M. Endo and T. Koyama, Japanese patent 1983-180615, Oct 22 (1983).
6. Y. Komatsu and J. Endo, Japanese patent 60-32818, Feb 22 (1985).
7. K. Arakawa, U.S. Patent 4,572,813, Feb. 25 (1986).
8. H.F. Kauffman and D.J. Griffiths, U. S. patent 2,796,331, June 18 (1957).
9. G.G. Tibbetts, D.W. Gorkiewicz, and R.L. Alig, **CARBON** 31, 809 (1993).
10. 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).

TABLE 1. TRIAL FORMULATIONS*

	<u>CONTROL</u>	<u>TRIAL 1</u>	<u>TRIAL 2</u>
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

TABLE 2. X-RAY DIFFRACTION ANALYSIS

HEAT TREAT (°C)	FIBER TYPE	D-Spacing (nm)	g _D * (%)
AS-GROWN	VGCF	.34490	--
1300	ex-PAN	.354	--
AS-GROWN	COAL & METHANE	.3459	--
AS-GROWN	COAL ONLY	.3451	--
2500	ex-PAN	.342	23
2500	VGCF	.3377	73
as-grown	PYROGRAF III	.3385	64
--	P-120	.3378	72

*g_D = (0.3340 - D-Spacing)/(0.3440 - 0.3354)

Fiber Nucleation and Growth Model

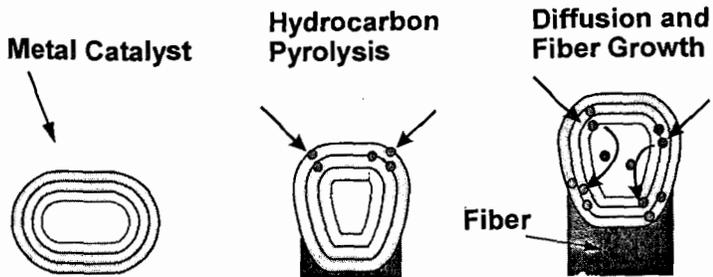


Figure 1. Fiber Nucleation and Growth Model

Carbon Fiber Process

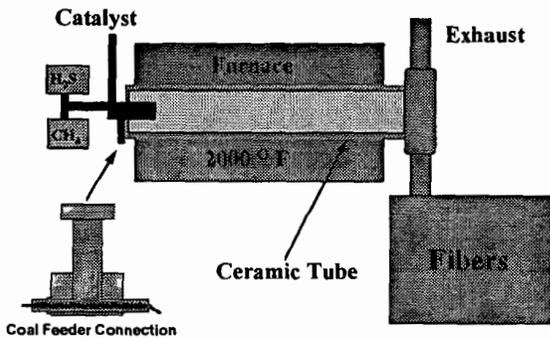


Figure 2. Carbon Fiber Processing

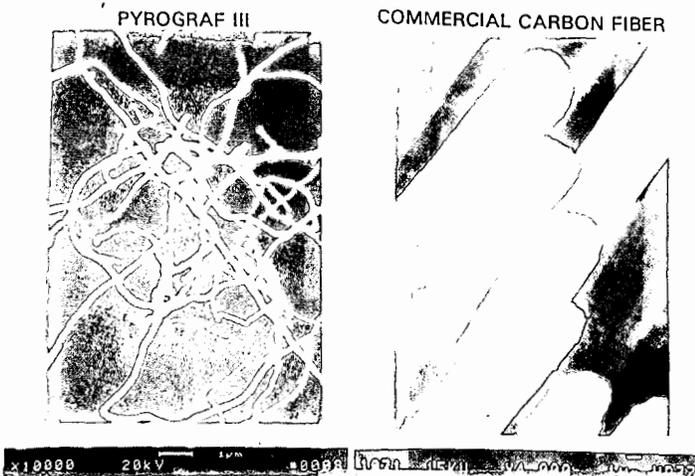


Figure 3. Scanning Electron Micrographs Comparing Vapor Grown Carbon Fiber with Commercial Carbon Fiber

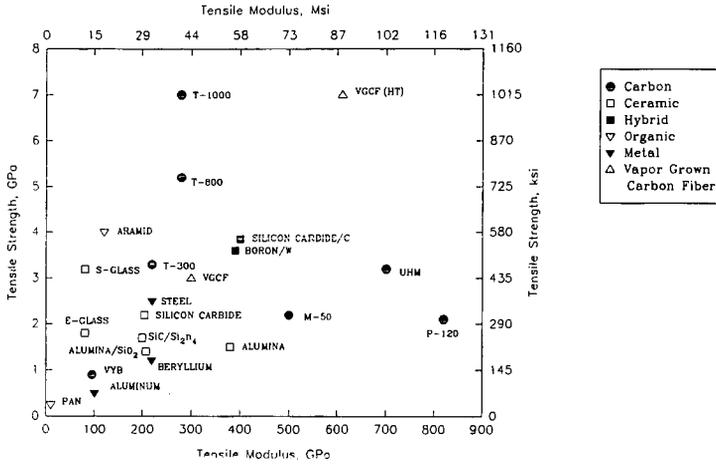


Figure 4. Tensile-Modulus Properties

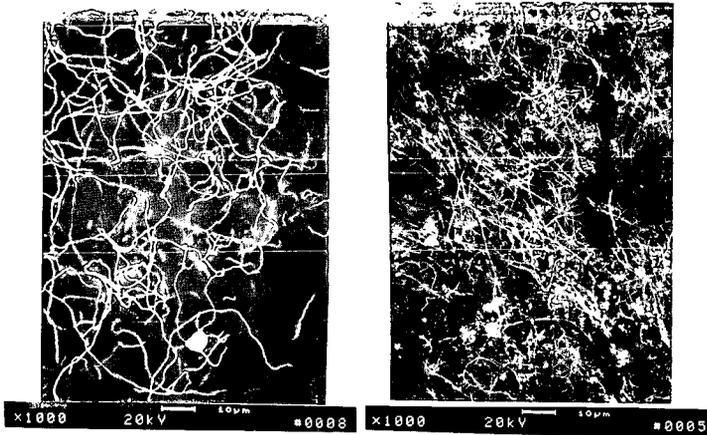


Figure 5. Coal Derived Fiber

Effect of H₂S on Fiber Growth

SEM Photomicrographs

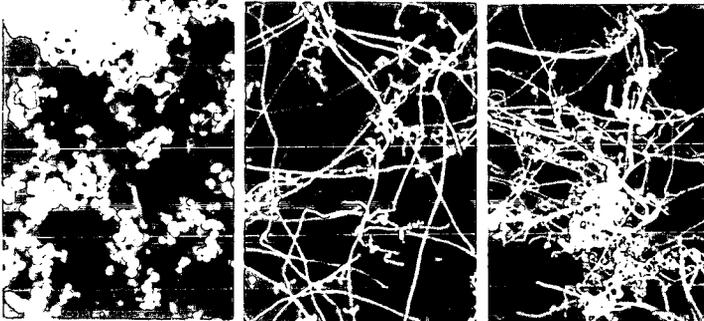


Figure 6.

No H₂S Flow

H₂S/Fe.(CO)₅=1.4/1

H₂S/Fe (CO)₅=17/1