

PRODUCTION OF VAPOR GROWN CARBON FIBER
WITH COAL FINES WITHOUT SO₂ EMISSIONS

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

Keywords: SO₂ Control Technologies, Coal Pyrolysis, Vapor Grown Carbon Fibers

ABSTRACT

Each year millions of tons of low-cost hydrocarbons in the form of coal fines are impounded. One potential application would be utilization in a unique process capable of converting the carbon into a highly graphitic vapor-grown carbon fiber (VGCF). This process currently produces vapor-grown carbon fiber from the vapor phase using natural gas, hydrogen sulfide and iron particles. The iron particles initiate the growth of the carbon fibers while the hydrogen sulfide enhances the yield, allowing the process to be economically feasible. Previous demonstrations involving pulverized coal have proven that coal can be used as an alternative source of carbon and sulfur in the production of VGCF. Furthermore, there is evidence that the sulfur from the coal remains with the carbon fiber catalyst during the reaction and does not exhaust as SO₂ into the atmosphere. It is the object of this research to determine if coal fines pulverized to -325 mesh are also a viable source of carbon and sulfur for VGCF production.

INTRODUCTION

Currently, commercial carbon fibers possessing a wide range of properties are formed from precursors of polyacrylonitrile (PAN) or petroleum pitch. Generally, these types of fibers have common methods of synthesis and handling, the latter of which is similar to textiles. Commercial fibers are made by extruding or spinning a continuous filament or thread from a polymer. The continuous filament is subsequently oxidized under tension to 200°C then carbonized by slowly heating it in the absence of air to 1000°C. Additional heating up to 3000°C provides higher degrees of graphitization necessary for ultra-high strength and/or stiffness applications. The cost of multi-step production for commercial carbon fibers limits their application to reinforcements in aerospace composites, golf clubs, fishing poles and other high performance products.

The production method of vapor grown carbon fibers is in sharp contrast to the production method of commercial carbon fiber. The one-step process, shown in Figure 1, has no involved extrusion or spinning operations allowing VGCF to be produced at a significantly lower cost. One type of vapor grown carbon fiber produced in our laboratory, and designated as PYROGRAF III, is initiated with iron particles which catalyze the growth of partially graphitic filaments in the presence of hydrocarbons at 1000-1100°C. Such fibers have diameters on the order of nanometers. Pyrocarbon subsequently deposited on the walls of the filament thickens the diameter of the fiber with the basal planes of the deposited carbon preferentially oriented parallel to the filament surface¹. Recent studies have shown significant enhancement of fiber nucleation efficiency by the addition of sulfur into the reaction². The sulfur reacts with the catalyst and becomes overcoated by the fiber. Although H₂S is beneficial to the efficiency of fiber production, it is used with great reluctance since it is expensive, highly corrosive to rubber seals and metal fittings, flammable, and as toxic as hydrogen cyanide. Therefore, coal fines are being trialed as the source of sulfur to eliminate the hazards and high cost of hydrogen sulfide.

Figures 2 and 3 show scanning electron micrographs of PYROGRAF III and typical continuous commercial carbon fibers. The diameter of PYROGRAF III generally averages 0.2µm as produced while commercial fibers are 8µm in diameter. Unlike commercial fibers, PYROGRAF III are not continuous but are an entangled mass resulting from the

turbulence of their gas phase generation. The length/diameter ratio for PYROGRAF III ranges from 40 to 200. However, due to the purity with which carbon is incorporated into the fiber, VGCF has a highly graphitic structure which results in higher values of physical properties than are realized in commercial carbon fibers, as shown in Figure 4.

Currently, PYROGRAF III production uses iron pentacarbonyl, natural gas and hydrogen sulfide as the sources of iron, carbon, and sulfur respectively. An economic scale-up analysis on the PYROGRAF III process performed by Battelle showed that the VGCF can be produced for under 5 \$/lb using the aforementioned feedstocks. Additional cost reduction would result from using coal fines as shown in Table 1. Reduction in the cost of the feedstocks is vital for allowing PYROGRAF III 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.

EXPERIMENTAL

A reactor used in PYROGRAF III production (Figure 1) was modified to allow the introduction of pulverized coal into the reactor. The reactor normally uses a feedstock mixture of natural gas, iron pentacarbonyl particles transported into the reactor by a helium stream, and 99.3% pure H₂S gas simultaneously injected into the 2000° F reactor. A typical control formulation that would produce a 25% yield is shown in Table 2. The apparatus to feed the coal fines is a Vibra Screw® Mini Feeder driven by a variable speed motor. The hopper is sealed to prevent the influx of oxygen which could cause immediate combustion of any fiber or hydrocarbons at the process temperature. The coal feeder transports the coal dust directly into the main gas feed to be carried into the reactor.

In the coal trials, the hypothesis is that sulfur-bearing coal can replace H₂S as the source of sulfur in the reaction. A combination of coal and methane were used as the hydrocarbon feedstock. The formulation was chosen such that the percentage of sulfur in the reactor derived exclusively from coal is equivalent to the "control" formulation of sulfur in the process when using methane only. Ohio #8 Coal from CONSOL Inc., at 4.71% total sulfur and 46.6% total carbon, was pulverized to less than 63µm. Methane was used as the carrier gas in Trial 1 at the rate required to balance the sulfur/carbon ratio to the control value. To determine the material balance, it was assumed that all the sulfur in the coal exists as hydrogen sulfide. In fact, the compounds of sulfur in coal vary extensively; however, as shown elsewhere², the sulfur level can vary and still produce acceptable vapor grown carbon fiber.

RESULTS

Figure 5 is a micrograph of fiber produced from a mixture of coal and methane in which all of the sulfur was supplied by the coal. It is inferred from this micrograph that the sulfur contained in the coal plays an active role in the catalytic process, similar to the case where H₂S is used. The morphology of the fiber product and the absence of soot in this trial indicates comparable quality to the best material which can be produced by this method. Coal also contributes carbon to the process as can be inferred from Figure 6 in which fiber was produced using coal as the sole source of sulfur and carbon. In this micrograph the presence of soot is evident indicating that the sulfur to carbon ratio is unbalanced.

The degree of graphitic ordering is the crucial property that causes the wide range of strength and conductivity of carbon fibers. To estimate the degree of graphitization of the fiber produced with coal, X-Ray diffraction was used. Table 3 shows that the "as grown" samples using coal has graphitization in a range typical of a low modulus commercial fiber.

In the control process, which relies on H₂S introduced to a pure methane feedstock, periodic analysis has been made of the exhaust

emissions during trials. In the tests to date, sulfur has not been detected in the exhaust. During the present experimentation, the exhaust was sampled using gas chromatography, with a similar result. While the current GC analysis is relatively insensitive with respect to measurements on the control process, the detectability limit implies a sulfur concentration less than 1%.

Since the sulfur content in coal exceeds the control balance, such a result implies an optimistic consequence to a balanced sulfur content. These data taken together offer incontrovertible proof that VGCF can be generated from high sulfur coal. Furthermore, effort to optimize the formulation should result in carbon fiber generated from high sulfur coal with quality and efficiency comparable to processes using other hydrocarbon sources, and at costs enabling economic viability. Although further work is needed to assess the effects of the organics and ash content variation in coal, their presence does not prevent the growth of a carbon fiber with graphitic ordering, and would be acceptable in applications such as reinforcements for cement and rubber.

While these studies indicate the viability of using high sulfur coal as the hydrocarbon feedstock in the 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 particulate in contributing both to the hydrocarbon balance and sulfur balance, is significant in any event.

CONCLUSIONS

It has been demonstrated that coal particulate can be used to produce VGCF, contributing both carbon and sulfur to the reaction. Work is in progress to optimize the process for conversion of coal fines to carbon fiber. Viability of the process will depend on the conversion efficiency, degree of graphitization of the fiber, percentage of ash in the product, and whether the process can be sustained on a continuous basis with an environmentally-benign exhaust. This work suggests an economical and ecologically safe process for the utilization of coal fines as the source material for carbon fiber reinforcements in rubber, cement, as well as composites for automobiles, electronics, and aerospace components.

ACKNOWLEDGEMENT

This research was supported in part by the U.S. Department of Energy under Grant No. DE-FG02-95ER81926. The authors also gratefully acknowledge the contribution Dr. David Anderson from the University of Dayton Research Institute in providing X-ray analysis.

REFERENCES

1. J.L. Kaae, Carbon **23**, 665 (1985).
2. G.G. Tibbetts, C.A. Bernardo, D.W. Gorkiewicz, and R.A. Alig, "Effect of Sulfur on the Production of Carbon Fibers in the Vapor Phase" CARBON, **32**, no. 4, pp.569-576, (1994).

Table 1. PYROGRAF III Material Cost Comparison

	High Purity Methane Only (\$/lb)	Natural Gas Only (\$/lb)	Coal Only @ \$30/ton (\$/lb)	Coal Fines Only @ \$23.50/ton (\$/lb)
Sulfur Source	0.189	0.194	0	0
Carbon Source	69.83	0.44	0.023	0.016

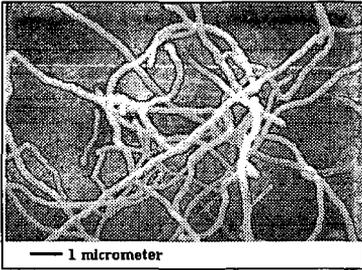


Figure 2. As-grown PYROGRAF III Produced with Methane.

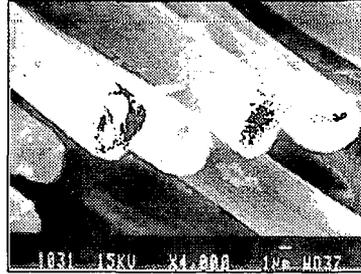


Figure 3. Commercial Carbon Fiber.

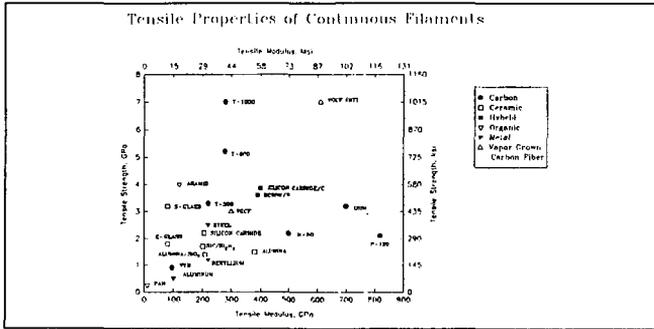


Figure 4. Tensile-Modulus Properties of VGCF.

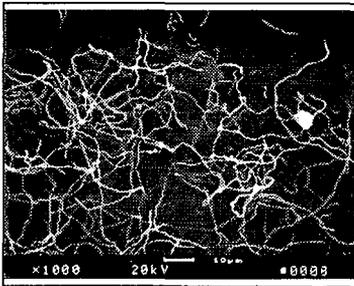


Figure 5. As-grown PYROGRAF III Produced with Coal Replacing H₂S.

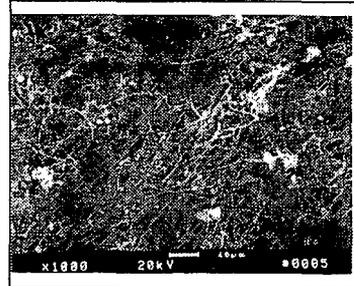


Figure 6. As-grown PYROGRAF III Produced with Coal as Sole Source of Carbon and Sulfur

TABLE 2. Control Formulation for PYROGRAF III Production*

	CONTROL	TRIAL 1
Natural Gas	96.9	87.58
Coal	None	9.33
Sulfur	0.47	0.44
Helium	0.96	0.96
Fe(CO) ₅	1.68	1.69

* Formulations are in per cent by weight

Table 3. X-Ray Diffraction Analysis*

Heat Treat (C)	Fiber	D-spacing (nm)	g_p^* (%)
As-grown	VGCF	.34490	--
1300	ex-PAN	.354	--
As-grown	ATrial (coal)	.3459	--
2200	VGCF	.34206	23
2500	VGCF	.33770	73
2500	ex-PAN	.342	23
2700	VGCF	.33697	82
2800	VGCF	.33663	86
As-grown	PYROGRAF III	.3385	64
--	P-120	.3392	56
--	P-120	.3378	72

* $g_p = (.3440 - D\text{-spacing}) / (.3440 - 3354)$

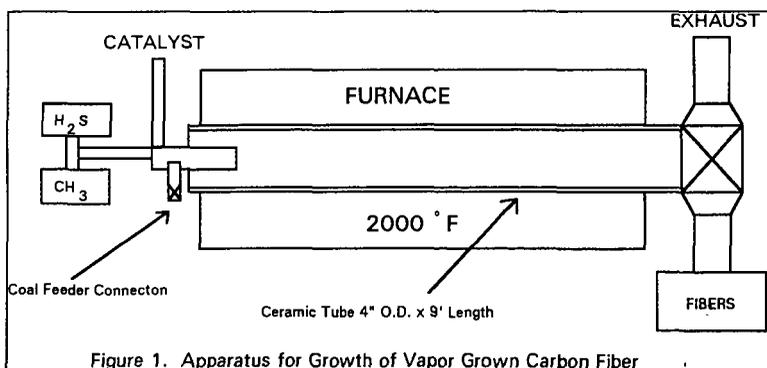


Figure 1. Apparatus for Growth of Vapor Grown Carbon Fiber