PRODUCING VAPOR GROWN CARBON FIBERS WITH HIGH SULFUR COAL

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Introduction

Early methods of producing vapor-grown carbon fiber (VGCF) with iron catalysts did not grow filaments profusely enough to make a low-cost product. Kauffman and Griffiths[1] and later Tibbetts et al[2] found that adding hydrogen sulfide (H_2S) vastly increases filament formation. However, H_2S is expensive, highly corrosive, flammable, and nearly as toxic as hydrogen cyanide. These properties led to the consideration of high-sulfur coal as an alternative sulfur source. In addition to the sulfur, the carbon in coal can also contribute to fiber formation at a much lower cost than other carbon sources. Since VGCF is made in a reducing instead of a combustion environment, the by-products, gaseous hydrocarbons and hydrogen, should be free of sulfur dioxide. This paper discusses the effects of ash-laden, high-sulfur coal on the production of VGCF.

Experimental

A ceramic tube reactor, 5.3" diameter by 96" long, was used in all the trials. On one end of the reactor, shown in Figure 1, is an injection manifold for the reactants. The reactants include H_2S, 200 mesh (73μm) coal, natural gas, and the catalyst, ironpentacarbonyl, and inert gases. The other end is connected to the fiber separation and collection unit.

Table 1 compares the relative feed compositions of the control formulation and two formulations using coal. The control uses H_2S and no coal with a sulfur to iron, S:Fe, molar ratio of 1.9. Trial 1 uses coal as full replacement of H_2S with a S:Fe molar ratio of 1.9. In Trial 2, the coal was the sole source of carbon and sulfur S:Fe molar ratio of 4.0. Trial 2 was to test the hypothesis that VGCF could be made with coal as the only supply of carbon.

Results and Discussion

Fiber Quality - The control formulation has a fiber yield of 25% and an apparent density ranging from 0.0010 - 0.0015 g/cc. The control formulation produces fiber with moderate amounts of surface residuals and a bulk resistivity between 5-10 W-cm.

In Trial 1, the yield was 17% and the apparent density varied greatly within fiber product. To separate these different grades of product, the fiber was filtered using screens with 1" and ¼" square openings into three portions. 40% of the fiber mass from Trial 1 had an apparent density of 0.0011 g/cc. This low density material, shown in Figure 2, contains very low ash levels and is very similar to fiber produced under control conditions (not shown). This material also has low surface residual contamination as indicated by acetone washings. The bulk resistivity of this portion of the fiber is approximately 8 W-cm. The medium density portion has an apparent density of 0.0027 g/cc indicating higher levels of particulate. The medium portion, shown in Figure 3, contains 30% of the product mass. This portion of the product also has higher levels of surface residuals and formed a yellow acetone extract. The bulk resistivity is approximately 17 W-cm resistivity. The high density portion has an apparent density of 0.0095 g/cc, indicating that it contains the majority of the ash. This portion, shown in Figure 4, is 30% of the product mass and has the highest amount of surface residuals. The bulk resistivity is approximately 22 W-cm.

In Trial 2, the yield was 47% and the apparent density was greater than 0.03 g/cc. Despite having a higher S:Fe ratio, Trial 2 still produced good fiber as shown in Figure 5.

X-ray Diffraction - The d-spacing of the fiber made with the control formulation typically range between 0.3405-0.3374 nm. The d-spacing for Trial 2 was 0.3451 nm which is typical for low modulus commercial fiber. X-ray analysis of the fiber grades from Trial 1 is not complete.

Process Exhaust - The sulfur dioxide levels of the exhaust were all below 0.0004 lb. of SO_2/MBtu. This is well below the allowable limits for new coal based power plants is 0.12 lb. of SO_2/MBtu. The H_2S levels in the exhaust were below 0.013 lb. of H_2S/MBtu. These levels are too high for H_2S but could be converted to SO_2 upon combustion of the recycled exhaust. This would produce 0.024 lb. of SO_2/MBtu and still be under the allowable limit.

Conclusions

High sulfur coal can produce VGCF, contributing both carbon and sulfur to the reaction. The low-density portion of the coal-derived VGCF is believed to be suitable for electrical applications while the ash-laden, high density portion may be suitable as an anti-static filler. The VGCF process provides an unique alternative to the combustion of high-sulfur coal without the environmental impact of SO_x. Finally, high-sulfur coal provides a less expensive starting material.

Acknowledgment

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Table 1. Control and Coal Modified Formulations [a]

	Control	Trial 1	Trial 2
Natural Gas	87.6	79.2	None
Coal	None	8.4 [b]	78.8 [c]
Hydrogen Sulfide	0.4	None	None
Inert Gases [d]	10.8	11.6	18.2
Catalyst	1.2	0.8	3.0

a. All values are in weight percent.
b. Eastern Kentucky coal fines containing 3% sulfur, 12% ash, 70.3% carbon, 4.6% hydrogen, 1.3% nitrogen, and 7.1% oxygen by weight.
c. Ohio Upper Freeport Seam from Kaiser Engineers with 2.5 % sulfur, 21% ash, and a 65% carbon by weight.
d. Inert Gases: H_2, He

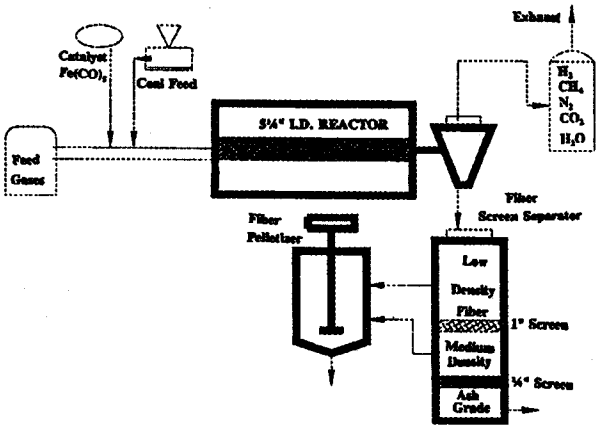

Figure 1. VGCF Process Schematic

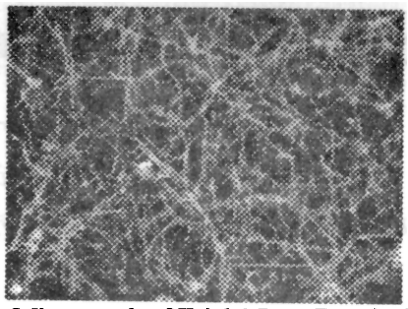

Figure 2. Micrograph of Trial 1 Low-Density Fiber

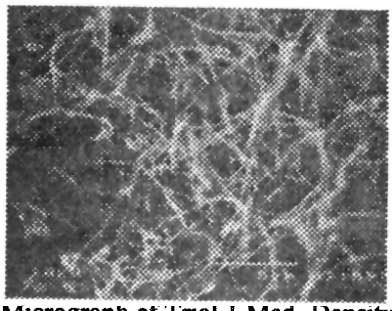

Figure 3. Micrograph of Trial 1 Med.-Density Fiber

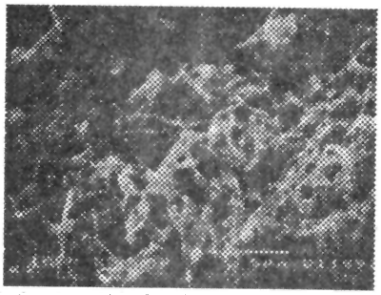

Figure 4. Micrograph of Trial 1 - High-Density Fiber

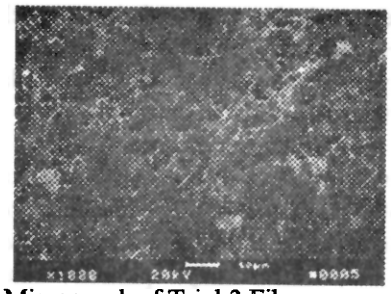

Figure 5. Micrograph of Trial 2 Fiber.

References

1. 1. H. F. Kauffman and D. J. Griffiths, U. S. patent 2,796,331, June 18 (1957).
2. 2. G. G. Tibbetts, C. A. Bernardo, D. W. Gorkiewicz, and R. L. Alig, *Carbon*, 1994, 32(4), 569