Enhanced Sulfur Removal of Coal Via Carbon Fiber Production

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ENHANCED SULFUR REMOVAL OF COAL VIA CARBON FIBER PRODUCTION

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ABSTRACT

The characterization of highly graphitic vapor-grown carbon fiber (VGCF) produced by the floating catalyst method was determined to evaluate the effect of processing changes on the VGCF properties. Properties examined were bulk density, bulk resistivity of compressed fiber bundles, UV absorption of acetone extractables, graphitic index, pH value, and ASTM dibutyl phthalate absorption number. The data show the properties do not vary significantly from three different reactor tubes used to produce the fibers. Of the properties examined, only graphitic index, density and UV absorption of acetone extractables appear to be independent of sampling handling. Resistivity is directly correlated to the pressure exerted to from the fiber pellet due to the layering of the fiber bundles. The pH of fiber samples suspended in water does not vary significantly. The dibutyl phthalate absorption number is strongly affected by the compression of the material. Thus, only the graphitic index, the UV absorption of acetone extractables, and the apparent density will be used to aid in process quality control and to determine the process conditions required to produce carbon fiber with properties optimized for specific conditions using high sulfur coal dust.

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EXECUTIVE SUMMARY

The project objective is to develop a unique process in which coal is desulfurized with concurrent production of a highly graphitized carbon fiber and a hydrogen rich hydrocarbon mixture that can be used as an energy source for commercial power. Currently methane is the carbon source for the fibers, but coal will be substituted for the methane. Before coal can be used to replace the methane in the reaction, two points needed to be addressed. The first is the reproducibility of the three reactors used to form the fibers. It is very important to determine that each of the three reactors is producing comparable material, and that the reactors themselves have no bearing on the outcome of carbon fiber production. The second is to determine which parameters best characterize the material. Once the parameters are chosen, data modeling of the reaction can be performed. A number of properties were studied (graphitic index, apparent density, absorption of acetone, absorption of dibutylphthalate, UV absorption of acetone extractables, pH, wettability by water, and electrical resistivity), but only three of the measured parameters appear to be independent of sample handling. These three are graphitic index, density and UV absorption of acetone extractables. The next step is to study the effects of the variation of reaction conditions on the properties of the vapor-grown carbon fibers. Once these changes are understood, methane will be replaced with coal dust and the reaction optimized.

INTRODUCTION

A catalytic process using methane or natural gas, hydrogen sulfide and ammonia at 1100 °C produces a highly graphitized carbon fiber. The catalyst, formed from iron pentacarbonyl, functions as a nucleation point for the carbon fiber growth and is bonded securely to the fiber. The fiber grows through graphitic bonds, but rather than forming a plane, the graphitic sheet wraps around itself to form a cylindrical sheath. The sheaths wrap around each other to yield an onion-like cross section to the fiber. The dimensions of the fibers are ~200 nanometers in diameter, but several millimeters in length. The sulfur is added to the hydrogen mix to enhance fiber growth, and is believed to assist the iron catalyst. The sulfur is believed to be strongly scavenged and locked into the fiber. This is confirmed by failing to detect sulfur in the exhaust analyzed by gas chromatography. Our intent is to replace the methane and hydrogen sulfide with high-sulfur coal. As a result of this reaction, the sulfur content of the coal will be locked into valuable carbon fibers that can be used as an additive for rubbers, plastics, composites, epoxies and even concrete. In addition to the fibers, a hydrogen rich hydrocarbon mix is left over which can be used as a combustion heat source for commercial power or industrial chemical processes.

EXPERIMENTAL

The initial approach is to characterize carbon fibers produced by heating mixtures of methane, hydrogen sulfide and ammonia with an iron catalyst at approximately 1100 °C. Samples of the carbon fibers are analyzed at two points in the process. A diagram of the process is shown in Figure 1. Samples are taken from the material as it is stored in the Collector after separation, and samples are taken from the material after it has been processed and bagged for shipping. The raw carbon fiber samples taken from the collector are produced from one of the three reactors used in this process and give information on the initial fibers coming out of the reaction as well as the productivity of each individual reactor. Whereas the samples taken after bagging are mixtures of the material from all three reactors that have been washed with aqueous surfactant and then tumbled dried. Measurements from these samples yield data on the final product and the effect that processing has on the fibers.

Both sample sets are characterized by measuring the following properties:

graphitic index, apparent density, absorption of acetone, absorption of dibutylphthalate, UV absorption of acetone extractables, pH, wettability by water, and electrical resistivity.

PYROGRAF III PROCESS FLOW DIAGRAM

The data from these measurements are tabulated in Tables 1-4. For all measurements, a sample size of ~0.100 g was used.

DISCUSSION

Before coal can be used to replace the methane in the reaction, two points needed to be addressed. The first is the reproducibility of the three reactors used to form the fibers. It is very important to determine that each of the three reactors is producing comparable material, and that the reactors themselves have no bearing on the outcome of carbon fiber production. The second is to determine which parameters best characterize the material. Once the parameters are chosen, data modeling of the reaction can be performed. A number of different properties of the fibers were studied to see which were independent of handling. Most of the assays were chosen because of their use in analyzing carbon black, a common carbon additive that the carbon fibers are meant to replace in various products. Table 1 shows the data of several assays on the raw fibers coming out of each reactor. Samples from three to four different runs were analyzed to assess the reproducibility of the carbon fiber production in these reactors and to determine which characterization methods were best for analyzing the fibrous material.

TABLE 1. Results of the absorption number of acetone and dibutylphthalate (DBP), UV-absorption of acetone extractables, pH, and water wettability measurements on raw carbon fibers. Samples from three to four different runs in each of the three reactors were used for each assay.

Sample	Absorption Number (ml/g)		UV Absorption of Acetone Extractables at 400 nm	pH	Wettability in Water
	Acetone	DBP			
Reactor 1 mean	72	64	0.82	5.5	None
std. dev.	16	15	0.58	0.3	
Reactor 2 mean	68	69	0.28	5.7	None
std. dev.	18	18	0.16	0.4	
Reactor 3 mean	65	59	0.42	5.3	None
std. dev.	4	8	0.21	0.2	

The dibutylphthalate (DBP) absorption number is related to the ease of incorporation of carbon black into rubber and rubber-like compounds. A similar significance for the carbon fibers is anticipated. Both the acetone and DBP numbers are highly correlated. The absorbed molecules are probably filling cavities produced by the tangle of fibers as well as being adsorbed onto the carbon surface itself. The filling of cavities may account for the smaller absorption number seen for the DBP. DBP is a larger molecule than acetone and would be more difficult to diffuse into these cavities. Pelletized samples of the fibers yield significantly smaller absorption numbers which support the notion of cavity absorption. Pressing fibers into a pellet would diminish the void spaces within the material and lead to lower absorption numbers.

When the fibers are exposed to acetone, a yellow colored solution forms. This solution contains impurities extracted from the carbon fibers. The acetone extractables have a maximum absorbance in the range of 400 to 700 nm, and UV spectroscopy can be used to estimate the quantity. The data seen in Table 1 suggest that there is some variability from reaction tube to reaction tube in the amount of impurities produced. However, the amount of these impurities in the raw fibers is small. Evaporation of acetone leaves a residue that is only 0.4 - 0.7% by weight of the starting fibrous sample. The identity of the impurities is not yet fully determined, but these extractables are not very volatile. Even when samples are heated for two days at 235 °C, no weight loss is detected.

The pH of water/acetone washes is only slightly acidic, and occur in a very narrow range (5.3 - 5.7). This is very comparable with carbon black which also yields slightly acidic solutions. Pure water cannot be used in this assay because of the lack of wettability of the carbon fibers. The carbon fibers are highly hydrophobic, and do not wet with water even after extended exposures. To get any pH reading other than neutral requires that there be some organic solvent present (in this case acetone).

The carbon fibers are pelletized in order to examine the resistivity of the material. Since pressure is required to form the pellets, the effects of pressure on resistivity and density were measured. Samples from three to four different runs were analyzed from each reactor, and pressed into pellets under different pressures. The dimensions of the pellets were measured as was the resistance using simple current voltage measurements. From this data, the resistivity and density were calculated, and Table 2 shows the results. As is readily apparent, the density of the pelletized sample increases as the pressure to create it is increased. This is expected since the compression of the material shrinks the void spaces created by the entangled fibers. The compression is not totally

permanent since the pellets expand slightly after the pressure is released. What is surprising is the apparent increase in resistivity. By pressing the fibers closer together, the electrical conductivity of the material should increase (the resistance should decrease), but this is not the case. The amount of error associated with the measurements makes any true trends obscure, but a definite increase is detected. The error in the pellets is due to the considerable non-homogeneity in the

TABLE 2. The effects on density and resistivity with relation to the pressure exerted to form the pelletized sample.

Sample	Pressure (psi)	Density (g/cc) mean	Std. Dev.	Resistivity (Ω -cm) mean	Std. Dev.
Reactor 1	5,093	0.131	0.022	16.35	4.71
	7,639	0.151	0.031	18.61	1.91
	10,186	0.153	0.046	15.45	6.51
	12,732	0.158	0.028	17.20	6.09
	15,279	0.168	0.034	17.08	3.03
	25,465	0.202	0.050	22.60	4.09
Reactor 2	5,093	0.126	0.034	15.91	8.41
	7,639	0.147	0.016	20.23	7.66
	10,186	0.144	0.016	23.11	12.97
	12,732	0.180	0.032	30.62	11.29
	15,279	0.199	0.047	34.48	11.56
	25,465	0.214	0.047	37.24	24.74
Reactor 3	5,093	0.144	0.006	21.63	6.63

	7,639	0.165	0.018	22.72	2.40
	10,186	0.177	0.017	20.10	4.64
	12,732	0.182	0.014	24.12	8.40
	15,279	0.191	0.017	21.71	10.07
	25,465	0.216	0.012	22.98	10.92

samples as is evidenced by the fact that pelletizing a number of samples from the same production run using the same pressure yielded resistivities between 29.65 Ω -cm to 65.00 Ω -cm with a mean of 45.53 Ω -cm and a standard deviation of 12.62 Ω -cm. Part of this variance can be attributed to the fact that there appears to be three types of fibrous material produced by the reaction. There is a high, medium and low density mix of bulk fiber. The various densities are a function of the degree of entanglement of the fibers, the degree of nonfibrous material and the handling of the material at the Collector. Since a different pellet was used at each pressure and the ratio of these three density types varied from pellet to pellet, no accurate trend in resistivity versus pressure could be established.

To alleviate the sampling variability, repeated pressings with increasing pressures were applied to the same pellet, and data was taken after each application of pressure. Several pellets were studied in this manner, and the data is tabulated in Table 3.

TABLE 3. Effects of increasing pressure on the resistivity and density of a pelletized carbon fiber sample. A number of pellets were studied and the mean and standard deviation of the results are recorded.

Pressure (psi)	Density (g/cc) mean	Std. dev.	Resistivity (Ω -cm) mean	Std. dev.
5,093	0.125	0.018	30.53	10.39
7,639	0.178	0.025	37.73	6.91
10,186	0.222	0.016	45.59	8.95
12,732	0.253	0.033	43.35	7.87
15,279	0.284	0.017	44.98	5.93
25,465	0.305	0.042	51.84	12.28

As the data in Table 3 suggests, both the density and the resistivity of the fibrous material definitely increases as pressure is increasingly applied to form the pellet. This is expected for the density, but is not for the resistivity. However, this trend is not uniform for the resistivity. As can be seen, the resistivity increases until 12,732 psi at which point there is a noticeable decrease, but then the trend begins increasing again. Two possible explanations have been examined for this trend. The first is that the pressure is causing the fibers to break. Fiber breakage would be detrimental to electrical conduction since the number of gaps the electrons would have to jump would increase, and the dip in the trend could be a point where the compression of the fibers overshadows the breakage. The second explanation is the entangled fibers are being forced from a three dimensional matrix to a planar state. The gap between the planes would also be detrimental to electrical conduction. There is evidence for this idea from the physical state of the pellet as increasing pressure is repeatedly applied. Examination shows that the pellet becomes very much less resilient after repeated pressings, and that it easily breaks into flakes.

To examine these two hypotheses, Scanning Electron Microscopy was used in conjunction with the other measurements. The data from the SEM showed no fiber breakage even after repressing the pellet at the highest pressure. Nonetheless, the pellet showed the same increasing density and resistivity as seen in the other samples after they were repeatedly repressed at increasing pressures. Thus, fiber breakage was not the explanation for the increase in the resistivity. To test the second explanation, the pellet was dissected and reformed so that the carbon planes were set parallel with respect to the electrodes used to measure the resistance. In other words, the carbon fiber planes were rotated 90° from where they had been. The resistivity of the reformed pellet was substantially smaller than the initial pellet, and this strongly supported the planar concept. It should be also noted that increasing pressure after each repressing is not required to see this trend. Repeated pressings using identical pressures produced similar results, though to a smaller degree. Thus, the act of applying pressure (either using identical or increasing pressure) repeatedly to a pellet causes carbon fiber layers to form, and that in turn increases the electrical resistivity of the pellet.

The data so far examined was collected on the raw fibers. One of the tasks of this work is to alter the reaction conditions including the conversion from methane to coal, and thus the characteristics of the raw fibers needed to be examined in detail to

see which parameters were most convenient and reliable for study since these would be examined in tandem with condition alterations. However, the processed fibers were also briefly examined to see the effect that washing the fibers in aqueous surfactant and drying had on them. It should be noted that the processing combined the product from all three reactors, and a leveling effect should be seen. The data from a number of assays on the processed fibers is shown in Table 4. Compared to the raw fibrous material, the processed material is considerably different. First, the acetone and DBP absorption numbers are much smaller. During the processing the material is mixed with a blending device with the aqueous surfactant, rinsed and dried. During all the handling, the material undergoes compression, and with the decrease in void space, a decrease in the amount of absorbed material, either acetone or DBP is detected. The UV-absorption of acetone extractables also shows a decrease after fiber processing, but that is to be expected. The washing with the aqueous surfactant is meant to remove most of the impurities within the fibers, and indeed that is occurring. Interestingly, the pH increases because of the processing. The material yields a basic instead of an acidic pH. The reason for this is unknown, but it could not be due to incomplete removal of the surfactant during the processing. The pH of the surfactant solution is 5.9. Both the density and the resistivity of the samples seem to be leveled. However, as was seen with the raw fibers, the pressure used to form the pellets has a strong effect on the resistivity and density of this material, and a similar effect would be expected for the processed fibers.

TABLE 4. Results of the Absorption number of acetone, UV Absorption of acetone extractables, pH, Density of pelletized samples, and Resistivity of pelletized samples on a number of processed fiber samples.

Sample	Absorption number (ml/g) of Acetone	UV-absorption of acetone extractables at 400 nm	pH	Density (g/cc) pelletized sample at 15,279 psi	Resistivity (Ω -cm) pelletized sample at 15,279 psi
P1-21	24	0.492	6.6	0.2461	71.54
P1-22	25	0.285		0.3541	
P1-23	19	0.262	8.5	0.3767	30.67
P1-24	32	0.407	8.5	0.2461	26.33
P1-30	23	0.300			
P1-31	25	0.270	8.4	0.2461	41.82
P1-32	25	0.199	9.1	0.2461	30.67

P1-33	21	0.397	7.8	0.2436	14.03
P1-34	31	0.330	6.8	0.2587	22.37
P1-35	26	0.289	7.5	0.2486	40.41
Mean	25 ± 3	0.323 ± 0.067	7.9	0.2740 ± 0.052	34.73 ± 17.41

CONCLUSIONS

As was stated at the beginning of the discussion, two points needed to be addressed. The first was the reproducibility of the three reactors, and second was the determination of which parameters best characterized the raw fibrous material. From the data presented, it can clearly be seen that the three reactors are producing comparable raw fibers. As for the second point, a number of assays were examined to see what type of method best characterized the raw fibers. Although there are a few more that need to be examined such as infrared spectroscopy, enough has been accomplished to show which of the examined assays are significant to the product. Only three appear to be independent of sample handling. These are the graphitic index, density, and UV absorbance of acetone extractables. The graphitic index yields data on the degree of crystallinity of the fibers, density yields information of the packing of the fibers, and UV-absorbance yields information of the degree of impurities present. The absorption number and pH may also yield some information about the product.

NEXT STEPS

In the statement of work, there are three objectives to be accomplished. The first is to use coal as the carbon source for vapor-grown carbon fibers. The second is to verify the removed of all sulfur from the effluent gases from the coal, and that the hydrocarbon rich exhaust is an ecologically safe fuel. The third is characterize the carbon fibers formed from methane and how the reaction conditions affect the properties. Once the affect of reaction conditions on the properties of the fibers is understood, this knowledge is to be applied to the fibers produced from coal.

The first and third objectives have been partly addressed and summarized in this semi-annual report. To complete these tasks, the reaction conditions (temperature and reactant flow rates) will be changed, and the raw fiber product will be analyzed to see what affects, if any, the various changes have on the fibers. Initially, methane will be

used as the carbon source. Once these alterations are understood for the production of carbon fibers from methane using data modeling, coal dust will be substituted as the carbon source with and without the use of hydrogen sulfide. The production of carbon fibers from the coal dust will then be optimized by data modeling the reaction.