Carbon Black Produced by the Pyrolysis of Coal

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Carbon black equivalent to commercial grade has been produced by the pyrolysis of coal at 1250° to 1350° C. at the U. S. Bureau of Mines, Pittsburgh, Pa. The maximum yield of black obtained from Pittsburgh seam coal (hvab rank) is about 20% by weight based on the raw coal fed. The work has been done on a bench-scale electrically heated unit with a maximum coal feed rate (70% − 200 mesh) of 3 pounds per hour. By-products are a coal char which could be burned for power generation and by-product gas (8 to 9 cu. feet per pound of coal) containing 80% hydrogen. The carbon black product has been evaluated in chemical and rubber compounding tests by industrial companies and found to be equivalent in quality to fine thermal (FT) grade of commercial blacks. A patent has been granted to the U. S. Government. Cost studies indicate that carbon black could economically be produced from coal.

In 1968 the total production of carbon black in the United States was 2,838,000,000 pounds, a 12.5% increase over 1967 (U. S. Bureau of Mines, 1969). Production has increased steadily since 1942, at an average rate of more than 5% annually (Figure 1). The growth of the carbon black industry has closely paralleled that of the automotive industry.

The largest user of carbon black is the rubber industry, which accounts for about 94% of domestic use; the remainder is divided principally among the ink, paint, paper, and plastic industries. Of the carbon black used by the rubber industry, roughly 90% is used for motor vehicle tires and the rest for mechanical goods. Increasing ratios of carbon black to rubber in tire treads—currently about 50 parts of black to 100 parts of rubber—account for some of the increased carbon black demand. Much of the increased demand for black has resulted from the increased number of motor vehicles.

Until 1945 almost all carbon black was made by the channel, gas-furnace, and thermal processes from natural gas (U. S. Bureau of Mines, 1965). Since the introduction of the oil-furnace process in 1945, three fourths of the carbon black has been made from liquid hydrocarbons.

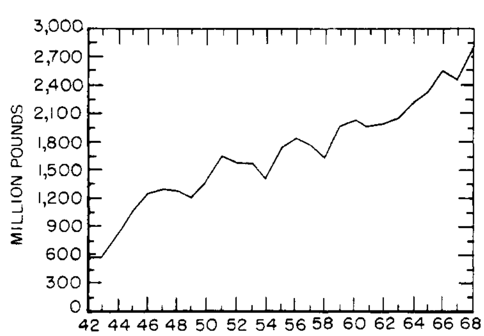


Figure 1. United States production of carbon black 1942 to 1968

Although the channel process has been almost replaced by the more efficient oil-furnace process as the principal source of rubber grades of carbon black, it remains the principal source of the premium grades of blacks used in the paint and lacquer and printing ink industries. The oil-furnace process involving partial combustion of an oil feedstock produces a wide particle size range of carbon blacks, accounting in part for its wide usage.

The thermal process produces coarser blacks, in contrast to the narrow range of fine particle blacks produced by the channel process. Thermal blacks blend to give softer rubber stocks more desirable for tire carcasses. In the thermal process natural gas is heated to 1350° to 1650° C., where it decomposes to hydrogen and carbon.

Currently furnace black plants account for about 85% of domestic carbon black capacity, channel plants about 5%, and thermal plants 10%. Of the three types, use of thermal black is increasing most rapidly; its sales rose an average of 8.1% per year from 1956 to 1966.

The U. S. Bureau of Mines in its search for new uses for coal has been investigating the production of carbon black from coal. A thermal-type black has been produced by pyrolysis of coal at 1250° to 1350° C. This paper describes recent results from this investigation in which a larger diameter reactor is used than in earlier reported studies (Johnson *et al.*, 1967).

Description of Equipment

A flowsheet of the experimental unit is shown in Figure 2. Coal sized to 70% minus 200 mesh is dropped free fall through a preheat zone (850° C.) and then through

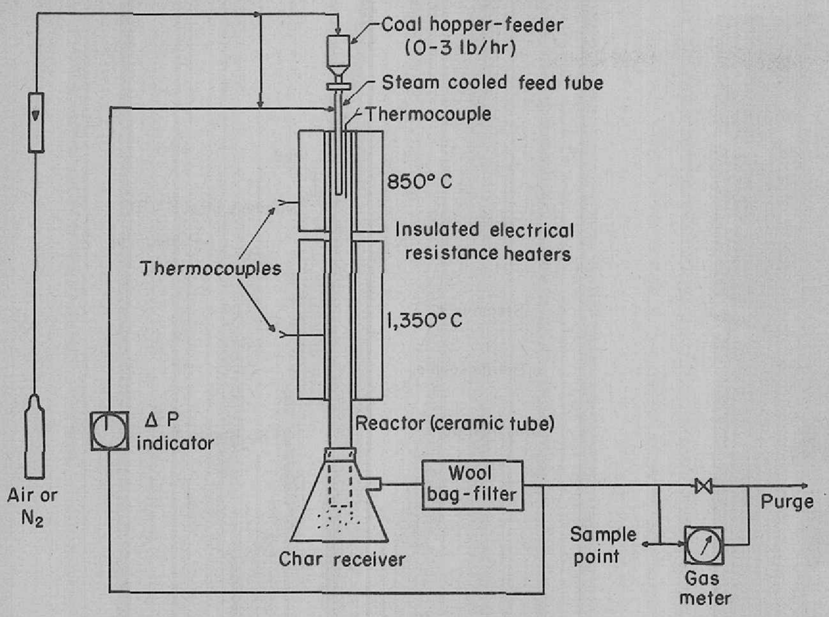


Figure 2. Flowsheet of experimental unit for producing carbon black from coal

the reaction zone in the presence of a carrier gas, generally bottled nitrogen.

Partial decomposition of the coal occurs at the elevated reactor temperature (1250° to 1350° C.), forming char, carbon black, and gaseous pyrolysis products. The coal used in testing (unless otherwise noted) was high-volatile A bituminous (hvab) Pittsburgh seam from Bruceton, Pa., containing about 37% volatile matter.

Part of the carrier gas enters the reactor with the coal, increasing the velocity of the falling coal. The remainder enters the top of the reactor adjacent to the cooled feed tube, where it flushes away tar vapors which could adhere to walls and cause plugging.

The reactor (Figure 3), a 4-foot length of vitreous refractory mullite (3¼-inch i.d., 3½-inch o.d.) is jacketed with two electrical resistance heaters. The top heater serves as a preheater for the coal and gas (maximum temperature 850° C.), is 12 inches long, and is wound with Nichrome wire. A Kanthal heater (Al-Cr-Co-Fe alloy) with a maximum temperature rating of 1350° C. encloses the middle 20 inches of the tube or the reaction zone.

The bottom section of the reactor tube, exposed to the atmosphere for rapid cooling of the products, fits into a side arm flask or char receiver in which the heavier solids are collected. The light, fluffy solids (carbon black) are carried by the product gas stream to a wool-felt bag filter, where they are collected. Clean product gas is then metered, sampled, and flared. Since the unit was originally designed for making hydrogen cyanide from coal and ammonia, the piping and vessels are of stainless steel and glass, and the unit is completely enclosed and ventilated to prevent accumulation of escaped gases. Figure 4 is a view of the panel board and external structure. A special coal-feed system (Figure 5) was designed to prevent agglomeration and possible plugging of the reactor by heating the coal rapidly through its plastic stage of about 400° C.

The finely ground coal is fed through a steam-jacketed tube (1-inch o.d.) which extends into the preheat zone of the reactor. The coal leaves the end of the feed tube, which is at the temperature of the steam (about 200° C.), to enter the preheat zone. The temperature rise of the coal to 850° C. is very sudden because of the high heat-transfer rate to the small particles in low concentration in the carrier gas. The gas fed with the coal keeps the particles in motion and helps prevent agglomeration as the coal rapidly passes through its plastic stage.

Chromatographic analyses were made of spot samples of the product gas. Proximate and ultimate analyses (Am. Soc. Testing Materials, 1966; Fieldner and Selvig, 1951) were made of the char and heavier solids collected in the char receiver and the carbon black collected in the bag filter. Oil absorption values and BET surface areas

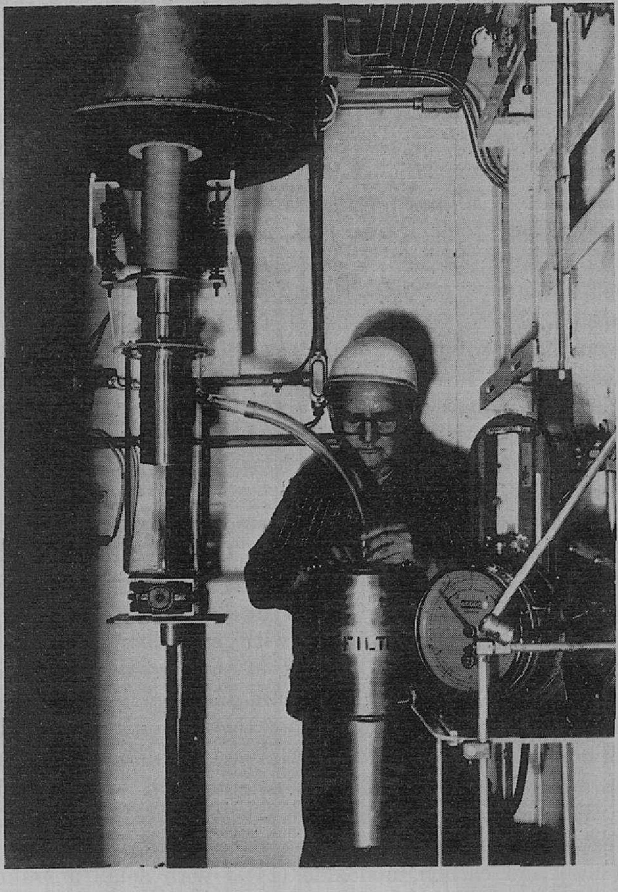


Figure 3. Carbon black reactor and recovery unit

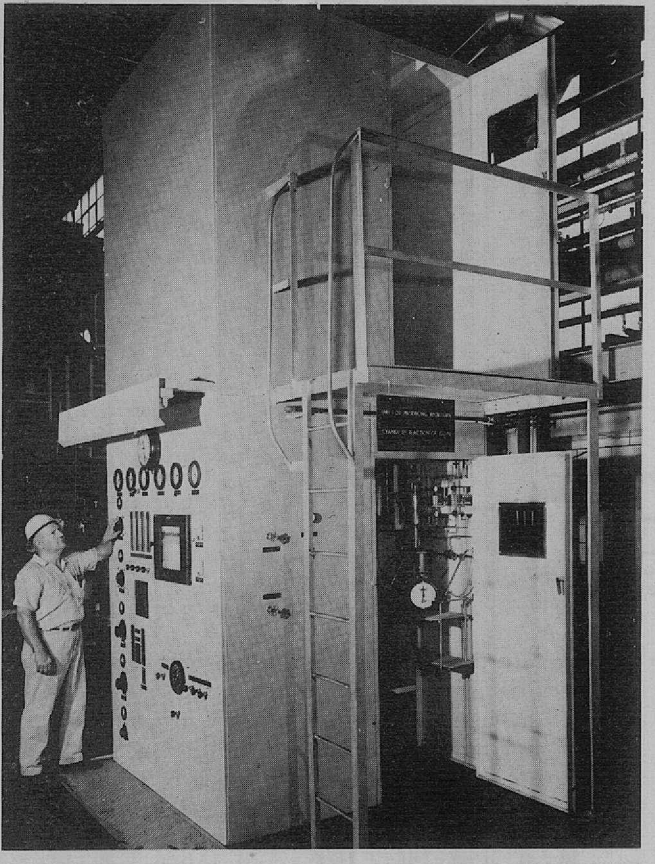


Figure 4. Panel board and external structure of carbon black unit

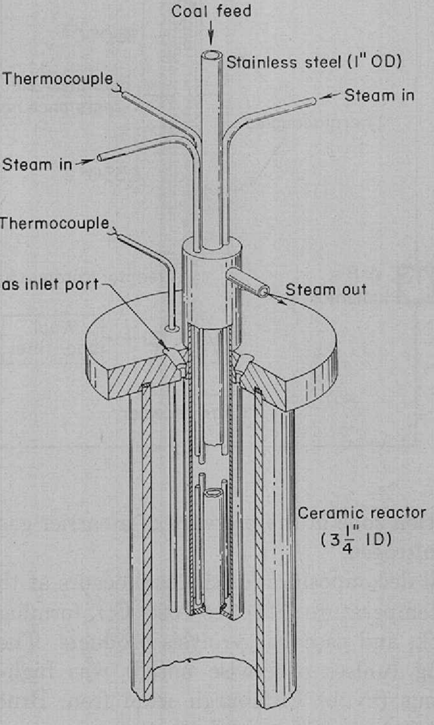


Figure 5. Steam-cooled coal feed system

of the carbon black were determined; particle size was measured by electron microscope.

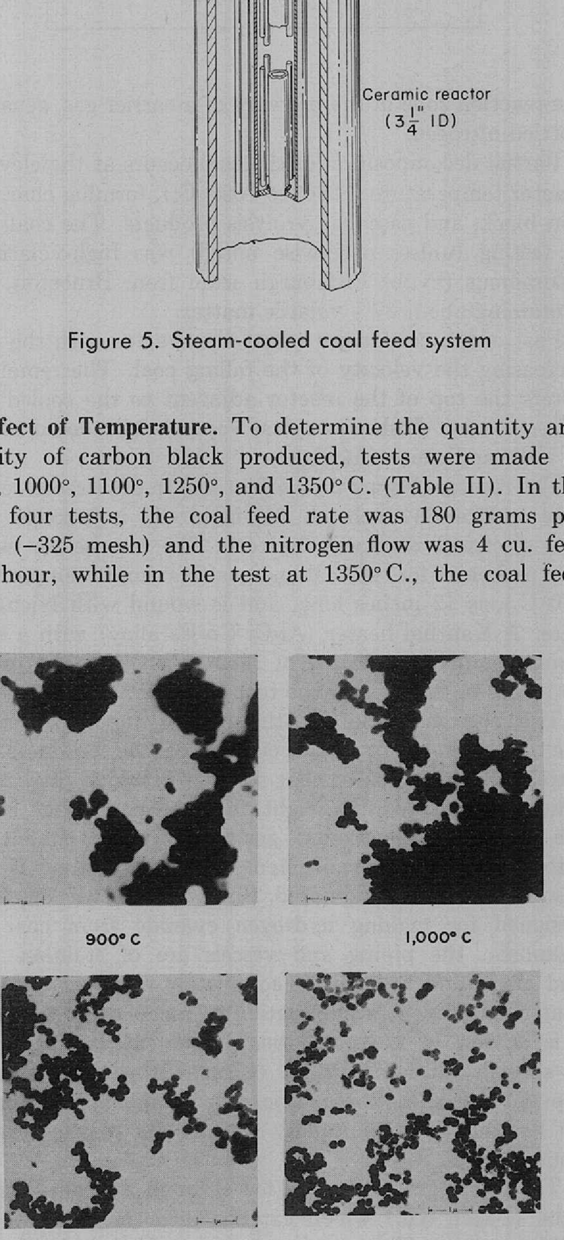
Results and Discussion

Typical Test Data. The averaged data for ten 2-hour tests are shown in Table I. The coal-feed rate was 676 grams per hour (1.5 pounds per hour), and 10 cu. feet per hour of nitrogen was used as carrier gas. Although the reactor temperature was leveled off at 1252° C. at the start of the test, it increased to 1332° C. after one hour of operation with coal and to a maximum of 1366° C. after 2 hours of operating. The yields of carbon black were different for the 2-hour test periods, averaging 17.9% for the first hour and 20.2% for the second hour. The yield percentages are based on the weight of carbon black collected per weight of raw coal fed. The char produced was not measured for the first hour, but the total collected for 2 hours was 700 grams.

Proximate and ultimate analyses of the raw coal, char, and carbon black are shown in Table I. The volatile matter remaining in the char was 8.1%, which should be sufficiently high to permit its use as fuel (although it may have to be mixed with coal for satisfactory combustion). The ash content of the carbon black was 0.4%, well below the 1% maximum preferred by the rubber industry. The sulfur content of the carbon black, 1.0%, is not believed to be harmful for use in rubber, as sulfur is added when the black is compounded with rubber.

The product gas generated amounted to about 9 cu. feet per pound of coal and consisted mainly of hydrogen (80%) and carbon monoxide (14%) with small amounts of hydrocarbons and other gases.

Effect of Temperature. To determine the quantity and quality of carbon black produced, tests were made at 900°, 1000°, 1100°, 1250°, and 1350° C. (Table II). In the first four tests, the coal feed rate was 180 grams per hour (−325 mesh) and the nitrogen flow was 4 cu. feet per hour, while in the test at 1350° C., the coal feed



900° C 1,000° C

1,100° C 1,250° C

Figure 6. Electron micrographs of carbon black from hvab coal

Table I. Data from Typical 2-Hour Test for Producing Carbon Black From Coal

Coal Feed Rate, g./hr.[a]	N_2 Flow, Cu. Ft./Hr.	Starting Temp., °C.	Max. Temp., °C.	Off-Gas (Less N_2), Cu. Ft./Hr.	Yield: Carbon black, g./hr.	Yield: % of feed	Char, G.
Conditions First Hour							
676	10.21	1252	1332	13.42	121	17.9	Not measured
Conditions Second Hour							
676	10.21	1317	1366	13.81	136	20.2	700[b]

Solids Analyses, %

	Proximate: M	V.M.	F.C.	Ash	Ultimate: H	C	N	O	S	Ash	Surface Area, M.²/G.
Coal	1.4	36.8	54.8	7.0	5.3	77.4	1.6	6.9	1.8	7.0	...
Char	0.4	8.1	79.5	12.0	1.5	81.7	1.4	1.8	1.6	12.0	1.5
Carbon black	0.5	0.7	98.4	0.4	0.6	96.6	0.8	0.6	1.0	0.4	8.4

Product Gas Analyses, % (Nitrogen-Free Basis)

H_2 80.1	CH_4 3.5	CO_2 0.5	H_2S 0.4
CO 14.1	C_2H_4 0.8	HCN 0.5	O_2 0.1

[a] Particle size, 70% through 200-mesh. [b] Total for 2 hours.

Table II. Effect of Temperature on Carbon Black Yield and Quality

Temp., °C.	Carbon Black: Yield, % of coal feed	Carbon, %	Ash, %	Volatiles, %	Product Gas, % N_2-Free: H_2	CO	CH_4	C_2+
Coal Feed Rate 160–200 G./Hr., N_2 Flow 4 Cu. Ft./Hr.								
900	8.7	89.6	0.2	20.6	48.1	17.2	24.5	6.7
1000	9.7	90.0	0.7	15.6	58.3	13.8	23.3	1.5
1100	11.3	92.6	0.1	6.5	67.5	14.5	15.2	0.6
1250	9.9	94.2	1.0	7.0	75.2	13.9	5.9	2.0
Coal Feed Rate 676 G./Hr., N_2 Flow 10 Cu. Ft./Hr.								
1350	19.0	96.6	0.4	0.7	80.1	14.1	3.5	0.8

Table III. Tests Using Different Feed Rates of Coal (Hvab, 70% – 200 Mesh), 12 Cu. Ft. per Hr. Nitrogen, Initial Temperature 1250° C.

Coal Feed Rate, G./Hr.	Max. Temp. Reached, °C.	Product Gas, Cu. Ft./Hr.	Carbon Black: G./hr.	Carbon Black: % of coal feed	Char, % of Coal Feed	Carbon Black Properties: Ash, %	Benzene-extractables, %	Surface area, m.²/g.
685	1360	11.25	102	14.9	61	1.0	1.6	14.0
925	1350	15.11	150	16.2	58	0.8	1.8	...
1210	1300	20.14	196	16.2	59	0.8	2.6	15.1
1352	1320	20.41	215	15.9	61	1.1	3.7	15.4

Range of product gas analyses, % H_2, 72–84; CO, 12–21; CH_4, 4.7–8.6; CO_2, 0.5–1.3; HCN, 0.6–1.0; C_2H_4, 0.1–0.5; H_2S, 0–0.8; O_2, 0–0.5

rate was 676 grams per hour (70% – 200 mesh) and the nitrogen flow was 10 cu. feet per hour.

Although carbon black is formed by the pyrolysis of coal at temperatures between 900° and 1350° C., all the tars are not removed at the lower temperatures. Chemical analyses indicate that carbon black made at 900° C. still contains 20% volatile matter, compared to less than 1% volatiles in the black made at 1350° C. The agglomeration of particles and heavy dark areas in the electron micrographs of Figure 6 illustrate the presence of tar at the lower temperatures. At the lower temperature (Table II) the carbon content of the black produced is about 90%, while at 1350° C. it exceeds 96%.

Product gas analyses also show the effect of temperature. When the temperature was increased from 900° to 1350° C., the hydrogen content of the product gas increased from 48 to 80%, while the methane decreased from 25 to 4%. At the higher temperatures, more methane was decomposed to hydrogen and carbon. Carbon black yields based on recovered product varied from 8.5 to 19% of the raw coal fed. Additional amounts of carbon black were visible in the char but were not separated and recovered.

Effect of Varying Coal Feed Rates. Tests were made with varying feed rates of coal to determine the effect on the carbon black produced (Table III). Coal feed rates were about 1.5, 2, 2.5, and 3 pounds per hour (685 to 1352 grams per hour), and 12 cu. feet per hour of nitrogen carrier gas was used. Consistent carbon black yields of about 15 to 16% were obtained at all coal feed rates. The properties of the carbon black were similar; the ash content ranged from 0.8 to 1.1%, and the surface area was about 15 sq. meters per gram. The benzene-extractable content of the black, however, increased with increased coal feed.

The yield of char varied from 58 to 61% of the coal feed. The volumes of product gas obtained are listed for each test, along with a range of product gas analyses for all tests.

Effect of Varying Carrier Gas Flows. The residence time of the gas and coal in the reaction zone can be controlled by the flow of carrier gas. A series of tests was made in which the carrier gas flow was varied in 2-cu.-foot increments between 8 and 20 cu. feet per hour, giving calculated gas residence times of 1.75 to 3.15 seconds (Table IV). At a constant coal feed of about 1.5 pounds per hour with increasing carrier gas flow, the yield of carbon black increased from 10 to 20%; the product gas increased slightly and the char yield decreased slightly. The ash content of the carbon black increased from 0.6 to 1.1%. Thus, with shorter residence time, the yield of carbon black is increased, as is its ash content. With high carrier gas flows, additional ash particles are physically carried by the gas stream from the char collector to the bag filter along with carbon black. The carrier gas flow should be controlled so as to give the maximum yield of carbon black without exceeding the maximum desirable ash limit of 1%.

Evaluation of Carbon Blacks from Coal. Samples of coal-derived carbon blacks were evaluated with commercial blacks in rubber compounding tests by several industrial companies. Table V lists some of the physical-chemical properties of the blacks, and Table VI lists rubber and cure properties of natural rubber formulated with these blacks in identical formulations. Carbon blacks listed are two commercial thermal blacks P-33 (fine, FT) and Thermax (medium, MT); three blacks from hvab coal, one made at 1250° C., one at 1400° C., and the third at 1250° C. but in an oxidizing atmosphere (20.6% O_2); a carbon black made from cannel coal at 1250° C.; and one made from Spencer Chemical Co. de-ashed coal.

In general, the properties of carbon blacks from coal are similar to those of the commercial thermal carbons. The coal blacks are higher in oil absorption, ash, and total sulfur, which in a rubber compound results in higher modulus, higher hardness, shorter elongation, and faster cure rate.

The free sulfur contained by all the coal-carbon blacks is a significant amount and is in all probability available for vulcanization.

The variance of values of the coal-black properties indicates that control of these properties can be maintained by proper selection of feed materials and operating variables. For example, when oxygen was used with hvab coal, the surface area of the carbon black increased from about 16 to 40 sq. meters per gram, which is in the range of the next classification of black, the SRF or semi-reinforcing furnace grade. The oxygen atmosphere also changed other carbon black properties, increasing the

Table IV. Tests with Varying Nitrogen Flows

[Coal (hvab, 70% – 200 mesh) feed rate 685 grams/hr., initial temperature 1250 C.]

				Yield			Carbon Black Properties		
N_2 Flow, Cu. Ft./Hr.	Calcd. Gas Residence Time, Sec.	Product Gas, Cu. Ft./Hr.	Max. Temp. Reached, ° C.	Carbon black, g./hr.	% of coal feed	Char, % of Coal Feed	Ash, %	Benzene extractables, %	Surface area, m.²/g.
8	3.15	10.35	1360	71	10.4	62	0.6	2.3	14.0
10	2.77	11.00	1360	87	12.7	66	0.8	2.0	15.1
12	2.47	11.25	1360	102	14.9	61	1.0	1.6	14.0
14	2.29	11.02	1340	107	15.6	61	0.9	1.6	14.3
16	2.04	12.05	1340	104	16.8	61	1.0	1.4	14.7
18	1.87	12.72	1330	133	19.4	58	1.0	1.2	14.2
20	1.75	12.80	1325	138	20.1	58	1.1	1.4	15.3

Range of product gas analyses, % H_2, 75–84; CO, 13–19; CH_4, 3–5; CO_2, 0–3.8; H_2S, 0.2–0.8; O_2, 0–0.3; C_2H_4, 0–0.5

Table V. Properties of Commercial and Coal-Derived Carbon Blacks

	Commercial Thermal		Carbon Black from Coal, Nonoxidizing Atmosphere				
			Hvab Coal				
	Fine (P-33)	Medium (Thermax)	1250° C.	1400° C.	Cannel coal	Spencer de-ashed coal	Hvab Coal, Oxidizing Atm., 1250° C.
Benzene extracts, %	1.0	0.3	3.4	1.6	2.4	6.1	5.8
Transmission, %	1.0	2.0	1.0	...	2.0	2.0	1.0
Oil absorption, gal/100 lb.	5.0	4.0	6.5	...	6.8	7.7	10.2
Ash, %	0.9	0.16	0.40	0.5	0.66	0.17	1.44
Total sulfur, %	...	...	0.61	0.36	0.78	0.59	0.95
Nitrogen surface area, m.²/g.	12.0	7	10	15	11	14	12
Electron microscope surface area, m.²/g.	15.0	9	16	...	18	...	40

Table VI. Properties of Natural Rubber from Commercial and Coal-Derived Carbon Blacks

	Commercial Thermal		Carbon Black from Coal, Nonoxidizing Atmosphere				Hvab Coal Oxidizing Atmosphere, 1250° C.
	Fine (P-33)	Medium (Thermax)	Hvab Coal 1250° C.	Hvab Coal 1400° C.	Cannel coal	Spencer de-ashed coal	
			Rubber Properties (Cured at 293° F.)				
25 min. L300	820	1080	1030	1010	900	1240	1390
25 min. tensile	2080	2230	1830	1710	2120	2170	1700
25 min. elongation	555	525	485	470	540	530	390
25 min. S. hardness	59	55	63	63	64	67	77
			Rheometer Cure Properties at 320° F.				
Minimum torque	1.7	1.0	2.2	0.7	1.5	2.8	5.3
Time to 7 lb. rise, min.	3.5	3.9	3.5	4.8	3.0	3.0	3.0
Time to 90% torque, min.	10.7	11.9	9.8	11.5	8.4	9.0	8.6
Rate (in.-lb./min.)	10.4	9.9	13.6	10.0	15.5	13.2	18.4

benzene-extractables and oil absorption values and, in turn, imparting different qualities to the rubber formulated with it.

The properties of the rubber compounds made from coal black were similar to those made from commercial blacks using identical formulations (Table VI). Generally, the coal carbon gave higher 300% modulus, higher hardness, and slightly lower tensile strength. Elongation with the coal product was both higher and lower—the hvab coal blacks gave lower elongations than the commercial product.

The cure properties of the rubbers compounded with coal-derived carbon black were equivalent to those compounded with commercial thermal blacks. Some coal-black product cure rates were faster and some were slower, but they were generally in the same range.

Economic Outlook

A cost study was made by the Process Evaluation Group (Morgantown, W. Va.) for producing carbon black from coal based on experimental data including a yield of 20%. Electrical heating was assumed as in the bench-scale tests; a plant capacity of 100,000,000 pounds per year was chosen. The total estimated capital investment was $10,824,000.

Based on a coal cost of $4.00 per ton, the operating costs before profit and taxes would be 2.22 cents per pound of carbon black product, allowing by-product credit. Addition of 12% gross return on investment and 20-year depreciation costs would give production costs of 4.09 cents per pound of product. With the current market price of thermal black of 6.25 cents per pound, a rate of return of 23% is estimated based on a 20-year plant life.

Credit has been allowed in the cost figures for excess char produced ($4.00 per ton). Some of the char and the scrubbed product gas (containing about 80% hydrogen) are consumed in the steam plant for power generation. Electrical heating, which was used in the test unit and in the cost figures, is highly expensive, accounting for greater than 40% of the capital costs in the estimate. If a cheaper method of heating can be used, production costs would be decreased considerably.

Although much interest has been shown in the process, for which a U. S. patent has been granted (Johnson, 1969), to our knowledge there is no carbon black being made commercially from coal today.

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