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CARBON BLACK PRODUCED BY THE PYROLYSIS OF COAL

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INTRODUCTION

In 1968 the total production of carbon black in the United States was 2838 million pounds, a 12.5% increase over that of 1967.1/ Production has increased steadily since 1942, averaging more than 5% annually. Figure 1 lists the annual production of carbon black since 1942 and illustrates its growth. 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 with the remainder 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--accounts for some of the increased carbon black demand. Rising sales of motor vehicles have also contributed to the increased demand for black.

Until 1945 almost all carbon black was made by the channel, gas-furnace and thermal processes from natural gas.2/ Since the introduction of the oil-furnace process in 1945, three-fourths of the carbon black is made from liquid hydrocarbons.

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 still remains the principal source of the premium grades of blacks used in the paint and lacquer and printing ink industries.

The thermal process produces coarser blacks giving softer rubber stocks more desirable for tire carcasses in contrast to the narrow range of fine particle blacks produced by the channel process. In the thermal process natural gas is heated to 1350°-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 increasing an average of 8.1% per year from 1956 to 1966.

The U.S. Bureau of Mines in their 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°-1350° C.

DESCRIPTION OF EQUIPMENT

A flow sheet of the experimental unit is shown in Figure 2. Coal sized to 70% minus 200 mesh is dropped in free-fall through a preheat zone (850° C.) and then the reaction zone in the presence of a carrier gas, generally bottled nitrogen. Ammonia, argon, and air have also been used.3/

Partial decomposition of the coal occurs at the elevated reactor temperature (1250°-1350° C.). The char and heavier solids are collected at the bottom of the vertical reactor while the carbon black is carried by the gas stream (consisting

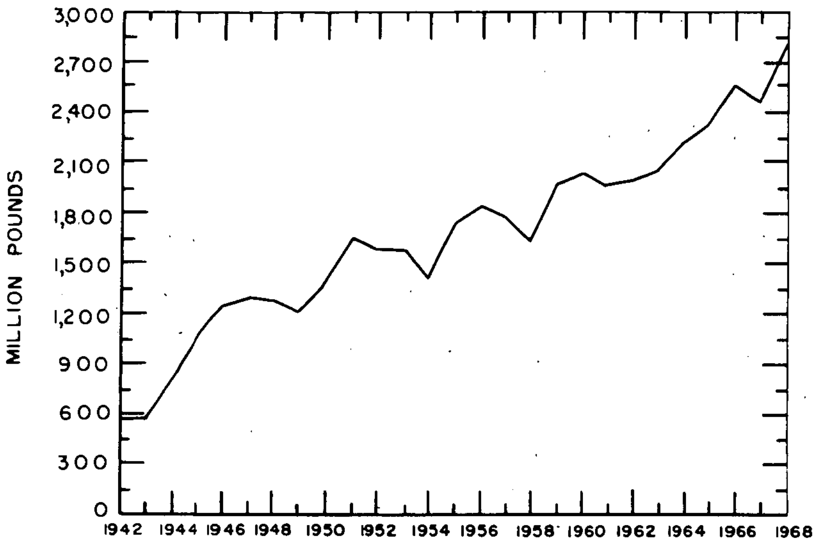

Figure 1 - United States production of carbon black 1942-1968.[2/]

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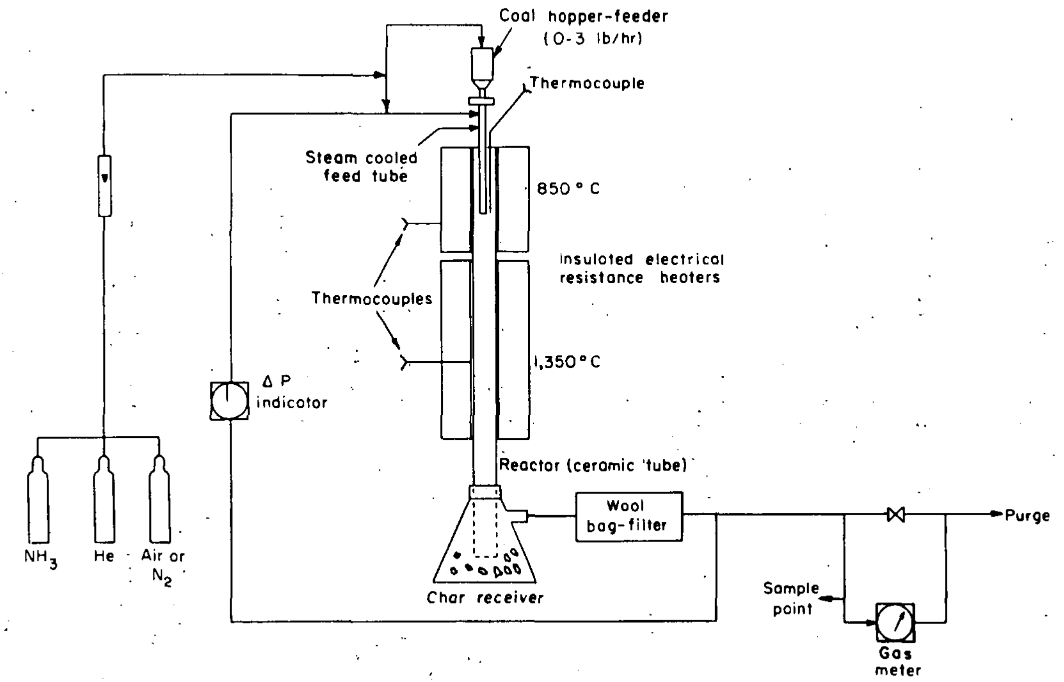


Figure 2. — Flow sheet of experimental unit for producing carbon black from coal.

of product gas and carrier gas) to a bag filter where it is collected. The coal discussed in this report (unless otherwise noted) was high-volatile A bituminous (hvab) Pittsburgh seam from Bruceton, Pennsylvania, containing about 37% volatile matter.

Part of the carrier gas enters the reactor with the coal adding greater velocity to the falling coal. The remainder of the carrier gas 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 (3-1/4-inch i.d. and 3-1/2-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 center 20 inches of the tube or the reaction zone.

The bottom section of the reactor tube, which is 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 dilute phase. The carrier 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[4,5] 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 of the carbon black were determined; particle size was measured by electron microscope, and BET surface area was determined.

EXPERIMENTAL RESULTS AND DISCUSSION

Typical Test Data

Typical data from tests for carbon black from coal are shown in Table I which is the averaged data for ten 2-hour tests. The coal feed rate was 676 g./hr. (1.5 pounds per hour), and 10 cubic feet per hour of nitrogen was used as carrier gas. Although the reactor temperature was leveled off at 1252° C. before the introduction of coal, when coal feed was initiated, the reactor temperature increased to 1332° C. after one hour of operation, increasing to a maximum of 1366° C. after two

*The trade name of this product is given for identification only and does not imply endorsement by the Bureau of Mines.

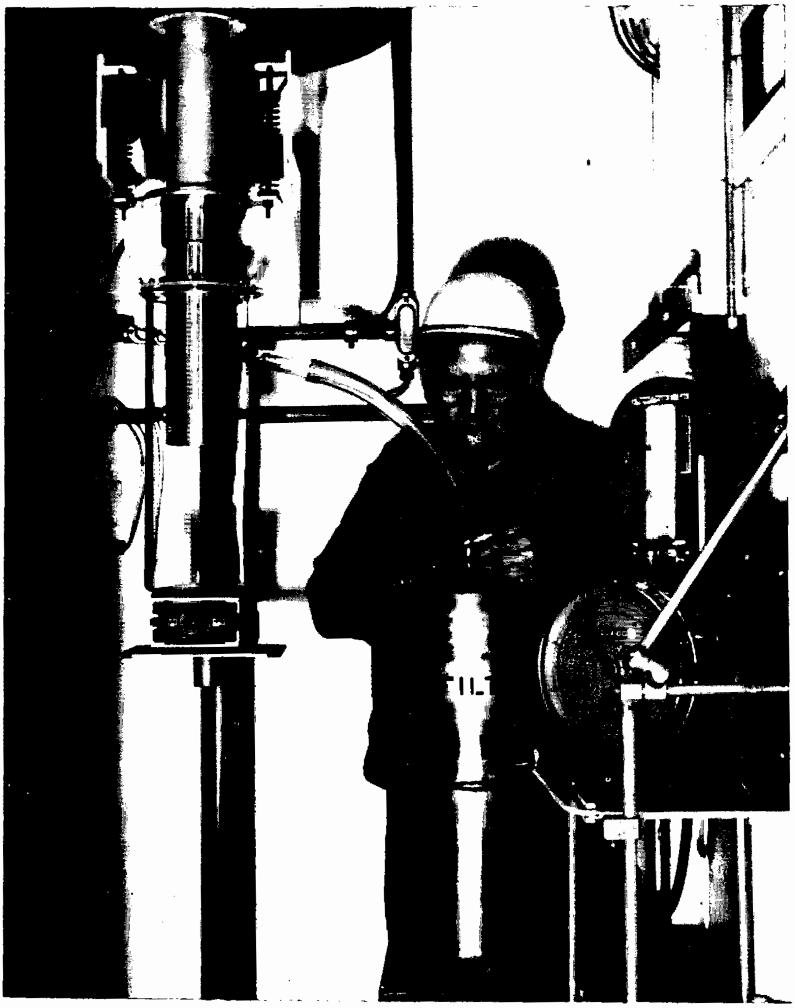


Figure 3 - Carbon black reactor and recovery unit.

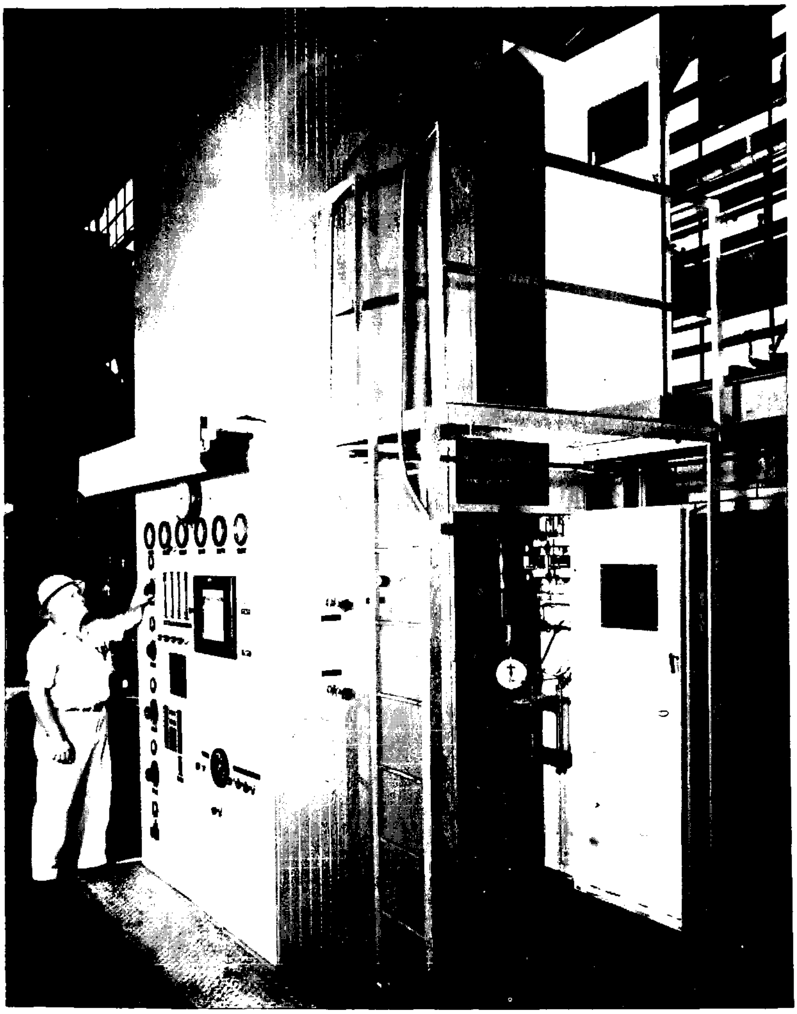


Figure 4-Panel board and external structure of carbon black unit.

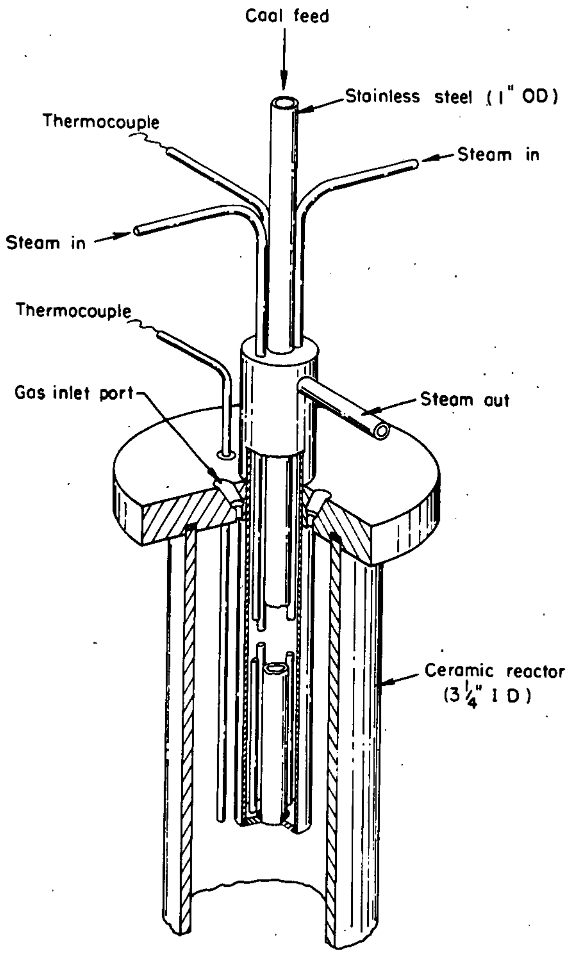
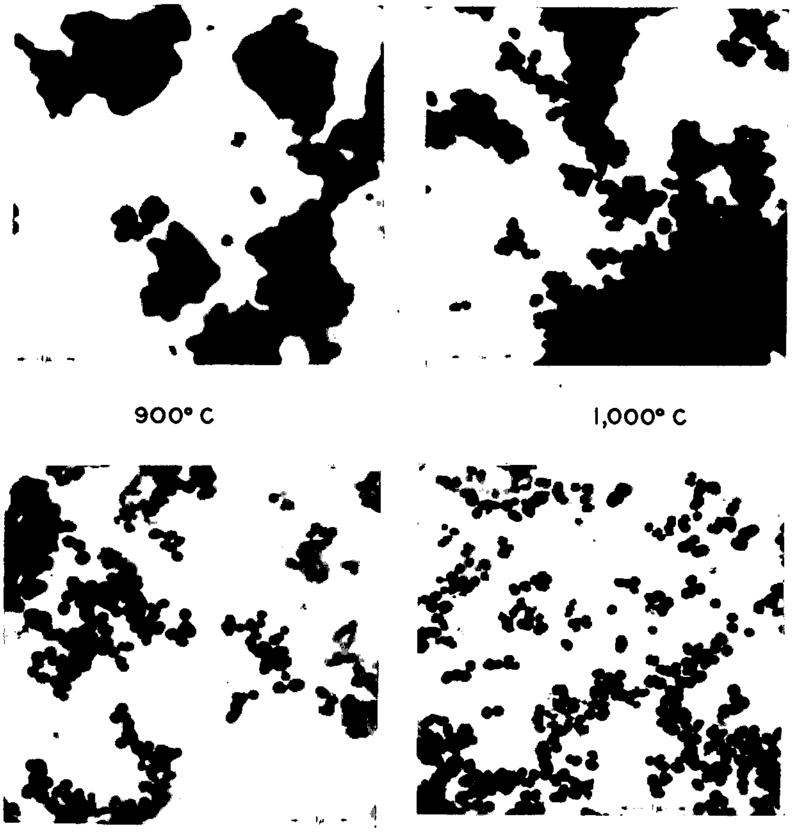


Figure 5.–Steam cooled coal feed system.



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	Yield: Percent 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

	Solids Analyses, %: Proximate				Ultimate						Surface Area, $m.^2/g.$
	M.	V.M.	F.C.	Ash	H_2	C	N_2	O_2	S	Ash	
Coal........	1.4	36.8	54.8	7.0	5.3	77.4	1.6	6.9	1.8	7.0	----
Char........	.4	8.1	79.5	12.0	1.5	81.7	1.4	1.8	1.6	12.0	1.5
Carbon Black	.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	CO_2	0.5
CO	14.1	HCN	0.5
CH_4	3.5	H_2S	0.4
C_2H_4	0.8	O_2	0.1

a/ Particle size, 70% through 200 mesh.

hours of operating time. The yields of carbon black were different for the two-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 two 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%, which is well below the 1% maximum preferred by the rubber industry. The sulfur content of the carbon black, 1.0%, would not be harmful for use in rubber as sulfur is added when the black is compounded with rubber.

The product gas generated amounted to about 10 cubic 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 g./hr. (-325 mesh) and the nitrogen flow 4 cubic feet per hour, while in the test at 1350° C, the coal feed rate was 676 g./hr. (70% -200 mesh) and the nitrogen flow 10 cubic 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 as compared to less than 1% volatiles in the black made at 1350° C. 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 8.7% to 19% of the raw coal fed. Additional amounts of carbon black are visible in the char but are not 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. Results of these tests are shown in Table III. Coal feed rates were about 1.5, 2, 2.5, and 3 lb./hr. and 12 cu. ft./hr. of nitrogen carrier gas was used. Consistent carbon black yields of about 15-16% were obtained at all coal feed rates. The properties of the carbon black were similar, the ash content ranging from 0.8 to 1.1% and the surface area about 15 $m.^2/g$. 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.

TABLE II. EFFECT OF TEMPERATURE ON CARBON BLACK YIELD AND QUALITY

	Carbon Black				Product Gas, % N_2-Free			
Temp., ° C.	Yield, % of Coal Feed	Carbon %	Ash, %	Volatiles, %	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	.7	15.6	58.3	13.8	23.3	1.5
1100	11.3	92.6	.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./HR. NITROGEN, INITIAL TEMPERATURE 1250° C

Test No.	Coal Feed Rate, g./Hr.	Max. Temp. Reached, ° C.	Product Gas, Cu.Ft./Hr.	Yield: Carbon Black, g./Hr.	Yield: % of Coal Feed	Char, gm./Hr.	% of Coal Feed	Carbon Black Properties: Ash, %	Carbon Black Properties: Benzene Extract-ables, %	Carbon Black Properties: Surface Area, m.²/g.
CBL-43	685	1360	11.25	102	14.9	418	61	1.0	1.6	14.0
CBL-34	925	1350	15.11	150	16.2	535	58	0.8	1.8	----
CBL-37	1210	1300	20.14	196	16.2	717	59	0.8	2.6	15.1
CBL-40	1352	1320	20.41	215	15.9	830	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, .1-0.5; H_2S, 0-0.8; O_2, 0-0.5

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-cubic foot increments between 8 and 20 cu. ft./hr. giving calculated gas residence times of 1.75 to 3.15 sec. The results of the tests are given in Table IV. At a constant coal feed of about 1.5 lb./hr. 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 rubber and cure properties of natural rubber formulated with these blacks. Carbon blacks listed are: two commercial thermal blacks P-33 (Fine, F.T.) and Thermax (Medium, M.T.); three blacks from hvab coal, one made at 1250° C., one at 1400° C., and the third at 1250° C., but made in an oxidizing atmosphere (20.6% O_2); a carbon black made from cannel coal at 1250° C. and one made from Spencer Chemical Company de-ashed coal.

In general, the properties of the 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 and could contribute to the higher vulcanizate modulus.

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 $m.^2/g.$ which is in the range of the next higher classification of black, the SRF or semi-reinforcing furnace grade. The oxygen atmosphere also changed other carbon black properties, increasing the 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 V). 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. In some cases the coal-black product cure rates were faster and some were slower, but they were generally in the same range.

TABLE IV. - TESTS WITH VARYING NITROGEN FLOWS; COAL (HVAB, 70%-200 MESH)
FEED RATE 685 g./HR., INITIAL TEMPERATURE, 1250° C.

					Yield			Carbon Black Properties		
Test No.	N_2 Flow Cu.Ft./Hr.	Calculated 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, $m.^2/g.$
CBL-41	8	3.15	10.35	1360	71	10.4	62	0.6	2.3	14.0
CBL-42	10	2.77	11.00	1360	87	12.7	66	.8	2.0	15.1
CBL-43	12	2.47	11.25	1360	102	14.9	61	1.0	1.6	14.0
CBL-44	14	2.29	11.02	1340	107	15.6	61	.9	1.6	14.3
CBL-45	16	2.04	12.05	1340	104	16.8	61	1.0	1.4	14.7
CBL-46	18	1.87	12.72	1330	133	19.4	58	1.0	1.2	14.2
CBL-47	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 AND THEIR NATURAL RUBBER COMPOUNDS

	Commercial Thermal		Carbon Black From Coal, Non-Oxidizing Atmosphere				Hvab Coal Oxidizing Atm., 1250° C.
	Fine (P-33)	Medium (Thermax)	Hvab Coal 1250° C.	Hvab Coal 1400° C.	Cannel Coal	Spencer De-ashed Coal	
Carbon Black Properties							
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
Rubber Properties (Cured at 293° F.)							
25' L300	820	1080	1030	1010	900	1240	1390
25' Tensile	2080	2230	1830	1710	2120	2170	1700
25' Elongation	555	525	485	470	540	530	390
25' 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# 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

Economic Outlook

An earlier cost study[3] indicated that carbon black could be produced for about 3.1¢/lb. This estimate was based on a carbon black yield of 10% which was obtained in our earlier work. Since the yields have now been increased to 20%, a new cost study is under way but is not complete at this time. However, on a raw material basis only, one pound of coal costing 0.25¢ produces 0.2 pounds of carbon black worth about 1.25¢ (using a carbon black selling price of 6.25¢/lb.). On this basis, carbon black from coal looks quite attractive economically.

Although much interest has been shown in the process for which a U.S. Patent was granted,[6] to our knowledge there is no carbon black being made commercially from coal today.

CONCLUSIONS

Carbon black has been produced in bench scale by the pyrolysis of coal at 1250°-1350° C. Yields of carbon black from Pittsburgh seam coal (hvab) have been about 20% by weight based on the coal feed.

Carbon black properties can be controlled by selective control of operating variables. Residence time appears to be an important variable in the production and quality of carbon black from coal.

Carbon blacks from coal have been tested and compounded with rubber by several industrial companies. The black produced from coal has been evaluated as a substitute for commercial thermal black.

Preliminary cost studies indicate that commercially acceptable carbon black could economically be produced from coal.

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