# CARBON BLACK FROM COAL BY THE HYDROCARB PROCESS

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## INTRODUCTION

Carbon black is an ancient material and has been produced for over a century by several traditional processes.[1] The raw materials have been mainly residual oils from refineries and from natural gas. Furnace black is made by partial combustion of oil. Channel black is made by partial combustion of natural gas and the carbon is collected on iron channels. Thermal black is made from the thermal decomposition of natural gas (methane). About 2 million tons of carbon black is sold in the U.S. About 85% of the carbon black goes into the manufacture of tires for automotive purposes. It is a vulcanization and strengthening agent. The remainder goes into pigments, printing inks, and fillers. The largest part of carbon black, that which is used in tires is made from residual oil by the furnace black process. The smaller fraction is made by the thermal black process from natural gas.

There have been a number of attempts in the part to produce carbon black from coal. The recent ones deal with partial combustion in a sooty flame and collecting the fine carbon soot. However, the yields are poor and have never reached even advanced development stage. The value of searching for an alternative feedstock to oil and gas for carbon black production is important when considering the competitive use of the basic natural raw materials as energy sources, oil and gas being premium fuels. The resource of coal is an order of magnitude greater than oil and gas and as a source of carbon, coal as a feedstock is the cheapest.

Over the last six years we have conceived and are developing a process for producing carbon from coal primarily to satisfy the energy market. However, the process has implications for the carbon black commodity market.

## THE HYDROCARB PROCESS

The HYDROCARB process was conceived and developed for the purpose of producing a clean carbon fuel and coproduct gaseous and liquid fuel coproducts[2,3,4] from any carbonaceous feedstock and particularly from coal.

The process basically consists of two major steps. In the first step, coal is hydrogenated to produce methane. In this step, the carbonaceous raw material is gasified with a recycled hydrogen-rich gas stream to form a light hydrocarbon, methane-rich gas, while the non-volatile ash remains behind. With the optional addition of limestone to the feed material, sulfur in the feedstock is removed as non-volatile calcium sulfide which is later oxidized to calcium sulfate for disposal. The methane-rich gas which also contains carbon monoxide and smaller amounts of water and carbon dioxide is sent to a recuperative condenser. For the production of methanol, the carbon monoxide and hydrogen in the process gas is catalytically combined to produce methanol. The deoxygenated methane-rich gas stream is then sent to a methane decomposer where the methane is cracked to pure particulate carbon and hydrogen gas. The pure carbon is removed as a clean product and most of the hydrogen-rich gas is returned to the coal hydrogenator. The two basic steps are then coal hydrogasification in a hydropyrolysis reactor (HPR) and methane decomposition in a methane pyrolysis reactor (MPR). Table 1 outlines the process chemistry and Table 2, gives a schematic broadening of the process to any carbonaceous raw material feedstock and indicates the co-product options, which include either a hydrogen-rich gas, a methane-rich gas, and methanol. Figure 1 shows one version of a process flow sheet. The methanol co-product option appears most attractive because of its usefulness as a high value chemical commodity and an environmentally preferable liquid transportation fuel.[5]

Among the important features of the process which assures high efficiency, is the fact that the hydrogasification or hydropyrolysis step is exothermic, giving off heat and the methane pyrolysis step is endothermic absorbing heat. By transferring heat from step 1 to step 2, the process efficiency is greatly enhanced. This is accomplished by circulating solid alumina pellets as a heat transfer and transport media through the hydropyrolyzer and to the methane pyrolyzer as shown in Figure 1. The reactors can be either moving bed or fluidized bed types.

The process is based on sound thermodynamic, and process chemistry principles. Experimental data for the hydropyrolysis and methane decomposition through pilot plant scale are available. Engineering demonstration is yet to be performed.

PROPERTIES OF CARBON BLACK

Because the carbon black is ash- sulfur- and nitrogen-free it is a potentially ideal coal derived fuel which can be utilized in heat engines, i.e., diesels and turbines, as well as in power plant and industrial boilers with little modification. Its major drawback is that it has no volatility resulting in a higher ignition temperature. Radiant combustors or additives of oil or methanol can solve that problem for use in conventional systems. Because the density of carbon black is high (1.8 to 2.0 gm/cc) it can be added to hydrocarbon fuels to volumetrically energy densify those fuels. Fig. 2 shows that adding carbon to methanol will increase the heating value of hydrocarbon fuels. A 55% carbon black-45% methanol slurry has a HHV equivalent to that of gasoline.

We have produced carbon black from methane in our laboratory in a countercurrent moving alumina bed reactor at 1000°C and 800 psi which is about the design conditions for the HYDROCARB process. Photomicrographics of the carbon black are shown in Fig. 3. The figure compares the collected carbon with a commercial grade carbon designated as N-990 produced by the thermal black process from natural gas. The HYDROCARB carbon black shows similar spherical particles ranging in size from 0.3 to 1.0 micron agglomerated up to about 4.0 microns. The commerical grade ranges from 0.2 to 0.5 microns with aggregates of over 100 microns. Geometrically, the laboratory carbon black appears in the range of thermal black. We have yet to examine the surface properties or whether other particle sizes can be produced at different reactor conditions. Further characterization must be performed to determine whether commodity grade carbon black can be produced and especially its suitability for the tire market.

ECONOMIC ESTIMATES

Preliminary economic estimates of the production of carbon black in large scale coal plants using the HYDROCARB process have been made. For a 25,000 T/D high volatile bituminous coal feedstock it is estimated that the production capacity would be about 16,000 T/D maximum and taking credit for by-product hydrogen would be priced at between 3.5¢ and 5.0¢ per pound competing with $2.50 to $3.50/MMBTU or $15 to $21/Bbl of oil.[2,3] This price includes 15% return on plant equity. It is instructive to compare the economics of the manufacture of commercial carbon black from various fossil fuel resources with that projected for the HYDROCARB prices. Based on 1986 prices, Table 2 indicates that carbon black from natural gas (thermal black) and crude oil (furnace black) ranged in price from 16¢ to 35¢ per pound depending on the more than a dozen different grades produced by the industry. Recent (1990) prices run up to as high as 50¢/lb.

From the raw feedstock point of view, the cost of contained carbon from natural gas and oil ranges from about 6 to 10¢ per pound and remembering that residual oil from crude may be somewhat lower. However from coal, the contained carbon ranges from 1.1 to 1.8¢ per pound which is from 5 to 10 times lower than for oil or gas. If the HYDROCARB carbon can be found to be suitable for the tire as well as for other commodity markets, then the estimated selling price would be 3 to 10 times less than the commodity selling price of carbon black. If off-grade carbon black which is only available at times in limited quantity for as low as 10¢ per pound HYDROCARB carbon would be 2 to 3 times lower. However, one 25,000 T/D HYDROCARB plant would produce almost 3 times the entire annual capacity of commodity carbon black in the U.S. Therefore, HYDROCARB carbon black designed for supplying the fuel market could easily supply all the commodity market as a by-product.

## CONCLUSION

HYDROCARB process carbon black designed primarily for the energy market can supply the commercial commodity market at much reduced prices. Much additional work is necessary to determine the characteristics of HYDROCARB carbon black for suitability for tire manufacture as well as for any other possible large scale commodity market. Process demonstration of an integrated system is necessary to prove the ability to scaleup the process to commercial size.

## REFERENCES


1) J.B. Donnet and A. Voct, Carbon Black, Marcel Dekker, Inc., New York (1976).

2) E.W. Grohse and M. Steinberg, "Economical Clean Carbon and Gaseous Fuels from Coal and other Carbonaceous Raw Material," BNL 40485, Brookhaven National Laboratory, Upton, NY 11973 (November 1987).

3) M. Steinberg and E.W. Grohse, "Economical Clean Carbon Fuel and Co-product Gaseous and Liquid Fuel from Coal," BNL 42489, Brookhaven National Laboratory, Upton, NY 11973 (September 1989).

4) M. Steinberg, "Coal to Methanol to Gasoline by the HYDROCARB Process," BNL 43555, Brookhaven National Laboratory, Upton, NY 11973 (August 1989).

5) R.H. Borgwardt, M. Steinberg, E.W. Grohse, and Y. Tung, "Biomass and Fossil Fuel to Methanol and Carbon via the HYDROCARB Process," Presented at the Institute of Gas Technology Conference in Energy from Biomass XV, Washington, D.C., March 27, 1991 (to be published in Proceedings of Conference).

6) G. Wei and M. Steinberg, "Carbon Black Slurries, Preparation and Characteristics," BNL 43732, Brookhaven National Laboratory, Upton, N.Y. 11973 (November 1989).

TABLE 1

HYDROCARB PROCESS FOR
PRODUCTION OF ASH-FREE AND SULFUR-FREE
CLEAN CARBON FUEL (CARBOLINE) AND FUEL GAS FROM COAL

TWO BASIC STEPS:

I. HYDROGASIFICATION OF COAL WITH HYDROGEN TO METHANE.

BITUMINOUS COAL + HYDROGEN ⟶ METHANE + WATER + HYDROGEN + ASH

$$CH_{0.8}\,O_{0.08}\,S_{0.016}\,N_{0.015} + 2H_2 + \text{ASH} + \text{LIMESTONE } (CaCO_3) \longrightarrow CH_4 + 0.08\,H_2O + 0.32\,H_2 + 0.008\,N_2 + \text{ASH} + CaS$$

REACTION IS −18 KCAL/MOL EXOTHERMIC.

II. THERMAL DECOMPOSITION OF METHANE.

METHANE ⟶ CARBON BLACK + HYDROGEN.

$$CH_4 \longrightarrow C + 2\,H_2$$

REACTION IS +18 KCAL/MOL ENDOTHERMIC.

HYDROGEN IS RECYCLED. EXCESS HYDROGEN IS A CO-PRODUCT. CARBON BLACK IS A FUEL AND CAN BE SLURRIED WITH WATER TO PRODUCE CARBOLINE CWM PRODUCT.

OVERALL COAL CRACKING REACTION

$$CH_{0.8}\,O_{0.08}\,S_{0.016}\,N_{0.015} + \text{ASH} + CaCO_3 \longrightarrow C + 0.32\,H_2 + 0.08\,H_2O + 0.008\,N_2 + \text{ASH} + 0.016\,CaSO_4 \text{ INERT}$$

B.7

Table 2

Comparative Economics of Carbon Black Production in the U.S.
From Various Fossil Energy Resources (1986)

| Resource | Natural Gas | Crude Oil Residuals | Coal (Proposed) |
|---|---|---|---|
| <u>Raw Material Cost</u> | | | |
| \$/MMBtu | 2.00 to 3.00 | 2.50 to 3.50 | 1.00 to 0.70 |
| \$/MSCF | 2.00 to 3.00 | - | - |
| \$/Bbl | - | 15.00 to 21.00 | - |
| \$/ton | - | - | 25.00 to 10.00 |
| ¢/lb of contained C | 6.3 to 9.5 | 6.2 to 8.7 | 1.8 to 1.1 |
| <u>Present Prices of Carbon Black</u> | | | |
| Commodity Grade: | | | |
| ¢/lb | 16 to 35 | 16 to 35 | Suitability for tire manufacture still to be established |
| \$/ton | 320 to 700 | 320 to 700 | |
| \$/MMBtu | 11.35 to 24.80 | 11.35 to 24.80 | |
| Offgrade (for fuel): | | | |
| ¢/lb | 10 (est'd) | 10 (est'd) | 3.5 - 5.0 |
| \$/ton | 200 | 200 | 70 to 100 |
| \$/MMBtu | 7.10 | 7.10 | 2.50 to 3.50 |
| <u>Total Present U.S. Capacity for The Production of Carbon Black</u> | | | |
| Tons/year | $0.2 \times 10^6$ | $2.0 \times 10^6$ | $5.3 \times 10^6$* |
| Tons/day | 600 | 6,000 | 16,000 |
| <u>Estimated Present Availability of Fuel Grade Carbon Black</u> | | | |
| Tons/day | 200 (est'd) | 2,000 (est'd) | 16,000* |
| No. of plants | 1 | 10 | 1 |

*Proposed HYDROCARB plant. This is the production capacity for one 25,000 T/D coal plant producing carbon black and fuel gas (corresponding to a total fuel equivalent 83,500 BPD FOE oil refinery).

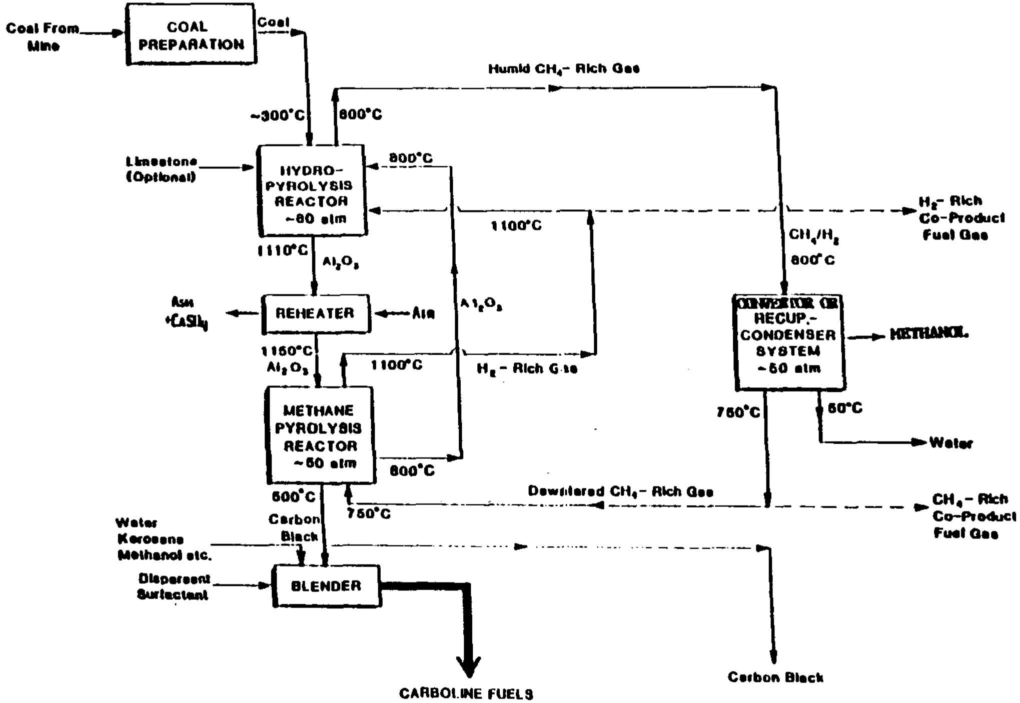



Figure 1. Clean Coal-Derived Fuels via the Hydrocarb Process

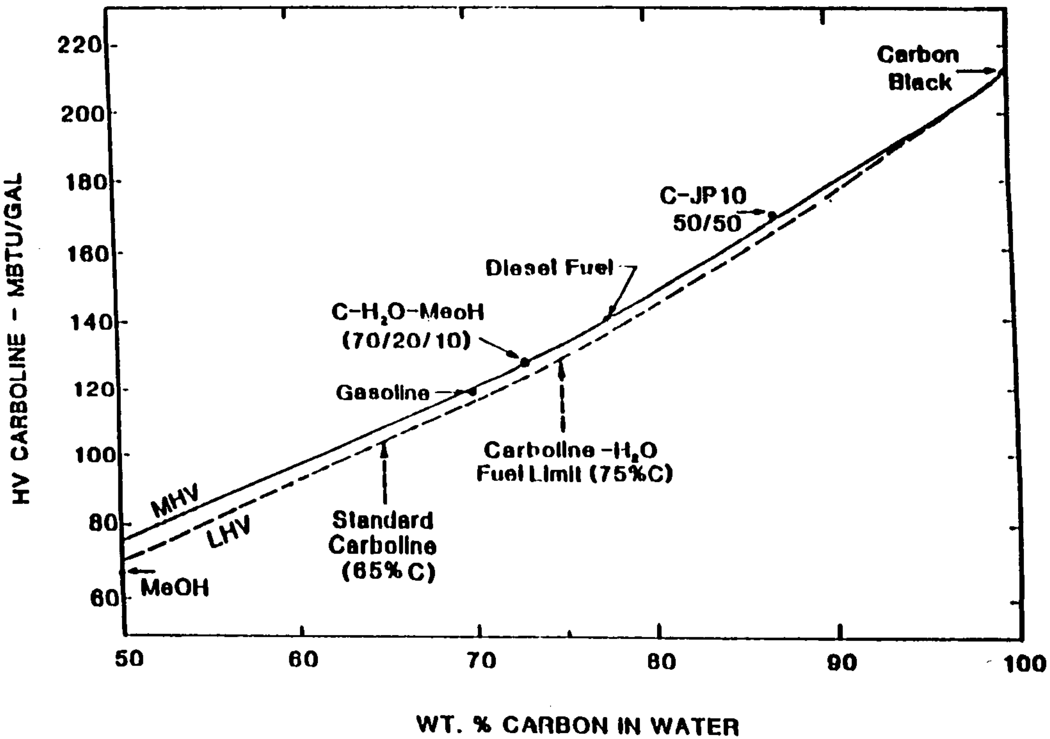
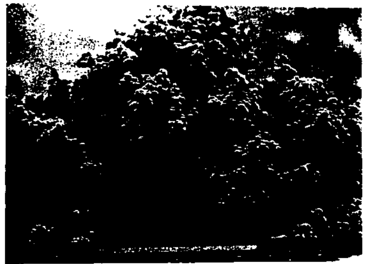
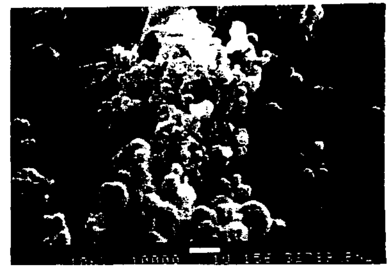



Figure 2. Heating Values of Carboline and Competitive Fuels



No.1 500 X

No.1 10,000 X



No.1 10,000 X

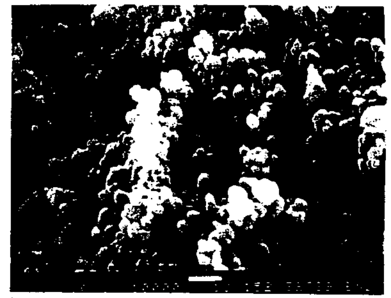
No.2 500 X

NO. 1 - C-BLACK FROM BNL MOVING BED REACTOR RUN NO. 1099 - PLUG IN REACTOR FORMED AT 800 PSI AND 1000°C - 0.5 TO 1μ AGGLOMERATED TO ~4μ

NO. 2 - C-BLACK FROM HUBER CO. - COMMERCIAL GRADE N-990 PARTICLE SIZE 0.2 TO 0.5μ

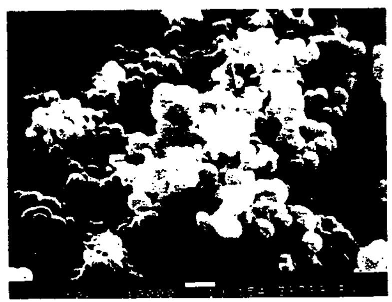
NO. 3 - C-BLACK FROM BNL MOVING BED REACTOR RUN NO. 1099 FILTER LOCATION FORMED AT 800 PSI AND 1000°C - 0.3 TO 2.0μ

Figure 3. Photomicrographs of Carbon Black



No.2 10,000 X

No.3 500 X



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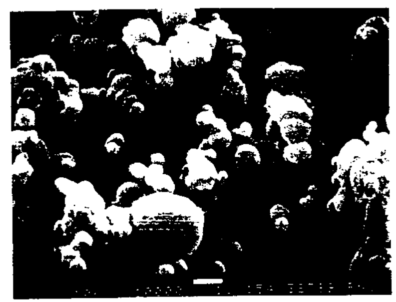

No.3 10,000 X