United States Patent [19]

Schora

[11] **3,861,885**

[45] **Jan. 21, 1975**

[54] **CARBON BLACK FUEL PRODUCTION**

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[73] Assignee: **Institute of Gas Technology,** Chicago, Ill.

[22] Filed: **Nov. 5, 1973**

[21] Appl. No.: **412,840**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 182,805, Sept. 22, 1971, abandoned, which is a continuation-in-part of Ser. No. 795,498, Jan. 31, 1969, abandoned.

[52] **U.S. Cl.** ..... **44/1 R,** 44/1 C, 44/1 F, 423/449, 423/453, 423/459, 23/259.5

[51] **Int. Cl.** **C10l 5/00,** C10l 9/10, C09c 1/48

[58] **Field of Search** ..... 423/449, 459, 453, 454; 23/259.5; 48/203, 202, 197; 44/1 R, 1 C, 1 F

[56] **References Cited**

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1,693,356	11/1928	Trent	44/1 C
1,812,230	6/1931	Aarts	423/459
1,894,126	1/1933	Schmidt	423/459
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2,716,053	8/1955	Mayland	423/459
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FOREIGN PATENTS OR APPLICATIONS

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Primary Examiner—Edward J. Meros
Attorney, Agent, or Firm—Molinare, Allegretti, Newitt & Witcoff

[57] **ABSTRACT**

The application discloses a method of production of nonpolluting ash free, sulfur free carbon black solid fuel from a polluting solid carbonaceous fossil fuel, such as coal or coal char. The coal is first pretreated to remove a hydrocarbon stream and the resultant devolatilized coal is gasified to produce carbon monoxide and hydrogen preferably with substantially no entrained produced carbon. The carbon monoxide and hydrogen product gases are then cooled under controlled conditions in a fluidized bed to precipitate out carbon black in a finely divided state. At least a portion of the hydrocarbon stream, preferably after sulfur removal by hydrodesulphurization, is then admixed with the carbon black product to produce a product useful as a nonpolluting ash free, sulfur free fuel for coal-fired turbines, as an additive to diesel fuel, and as a material for pipelining to areas where air pollution ordinances require a fuel with low sulfur content. The process disclosed for converting coal or coal char to a solid carbon black suitable for use as a nonpolluting fuel includes four basic steps: (a) devolatilization of the coal to produce a hydrocarbon stream; (b) production of a hot carbon oxide containing gas, rich in carbon monoxide, by partial combustion of the devolatilized coal with air, oxygen or an oxygen enriched air, at elevated temperature and pressure under catalytic conditions; (c) controlled removal of heat from the gas in a fluidized bed to promote the deposition of carbon; and (d) admixing at least a portion of the hydrocarbon stream, preferably after desulphurization, with the carbon produced. Preferably, the hot gas is enriched by intermediate clean-up to remove particulate matter and sulfur. All steps are preferably conducted at high pressures which favor formation of carbon and carbon dioxide from carbon monoxide. Preferably, substantially no carbon is formed in the first step, and the carbon deposition step is not appreciably auto-catalytic with respect to carbon deposition.

18 Claims, 4 Drawing Figures

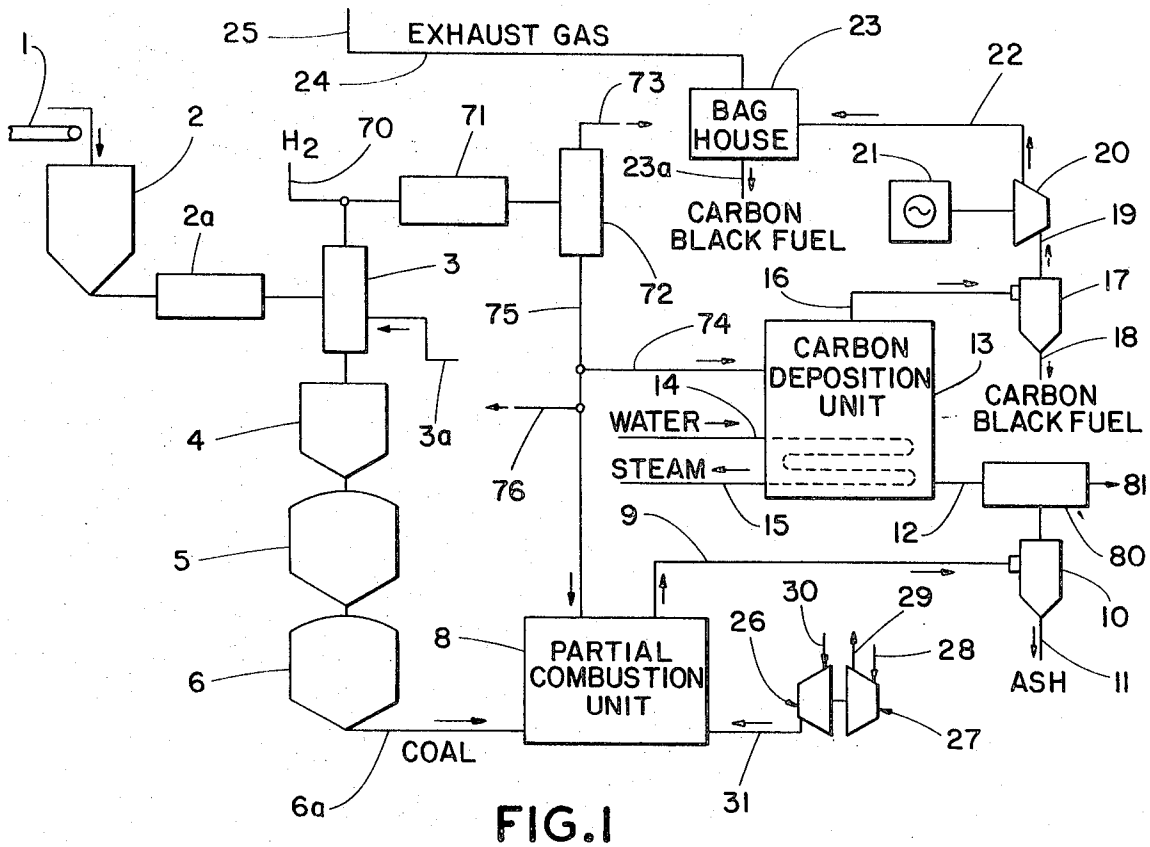

1
2
2a
3
3a
4
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6a
25
EXHAUST GAS
24
23
22
BAG HOUSE
23a
CARBON BLACK FUEL
21
20
19
17
18
CARBON BLACK FUEL
16
73
71
70
H2
72
75
74
CARBON DEPOSITION UNIT
13
14
WATER
STEAM
76
15
12
81
80
9
8
PARTIAL COMBUSTION UNIT
30
29
26
28
10
ASH
11
27
COAL
31

FIG.1

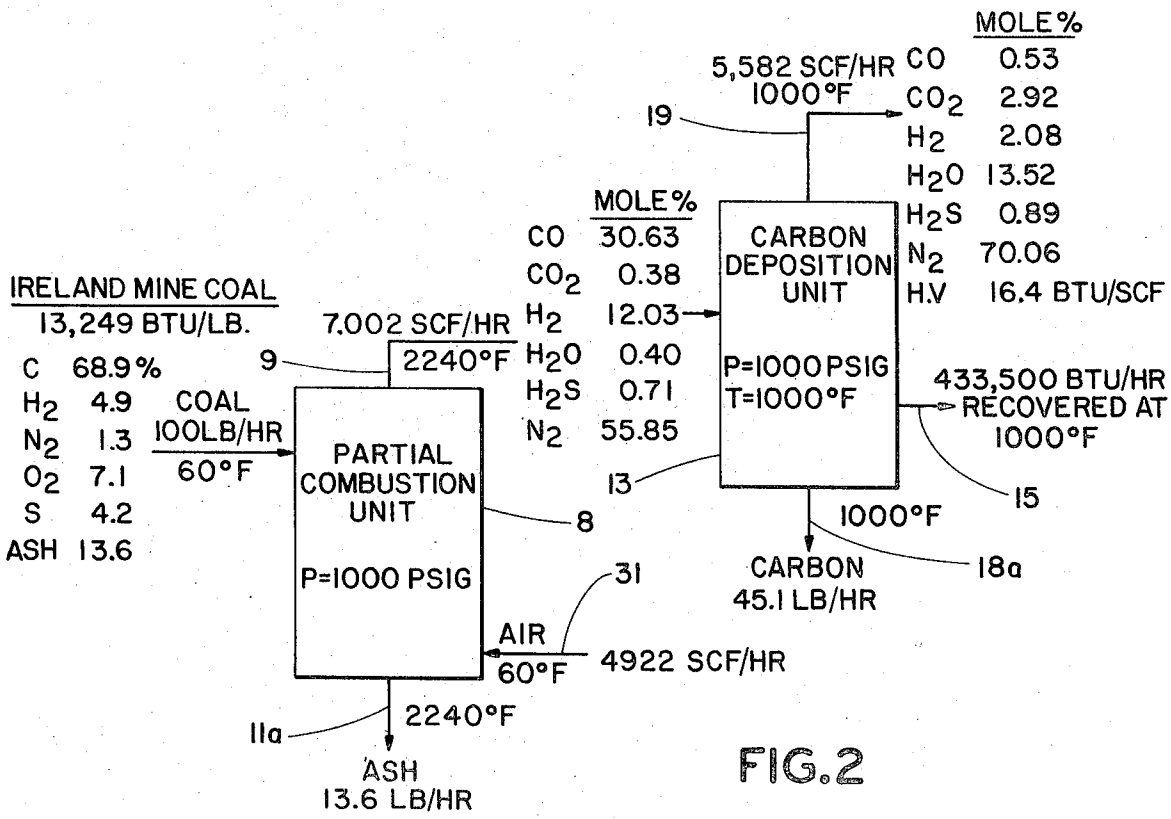

IRELAND MINE COAL
13,249 BTU/LB.
C 68.9%
H2 4.9
N2 1.3
O2 7.1
S 4.2
ASH 13.6
COAL
100LB/HR
60°F
9
7,002 SCF/HR
2240°F
PARTIAL COMBUSTION UNIT
P=1000 PSIG
8
MOLE%
CO 30.63
CO2 0.38
H2 12.03
H2O 0.40
H2S 0.71
N2 55.85
19
5,582 SCF/HR
1000°F
CARBON DEPOSITION UNIT
P=1000 PSIG
T=1000°F
13
MOLE%
CO 0.53
CO2 2.92
H2 2.08
H2O 13.52
H2S 0.89
N2 70.06
H.V 16.4 BTU/SCF
433,500 BTU/HR
RECOVERED AT
1000°F
15
1000°F
18a
CARBON
45.1 LB/HR
31
AIR
60°F
4922 SCF/HR
11a
2240°F
ASH
13.6 LB/HR

FIG.2

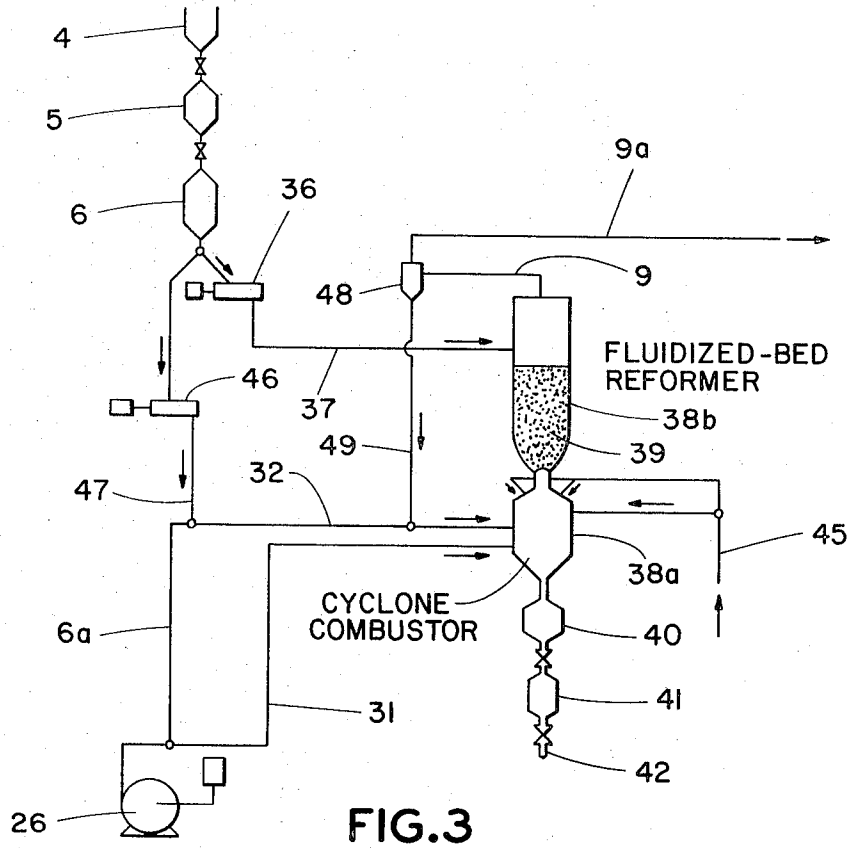

4
5
6
36
9a
9
48
FLUIDIZED-BED
REFORMER
46
37
38b
49
39
47
32
45
38a
CYCLONE
COMBUSTOR
6a
40
41
31
42
26

FIG.3

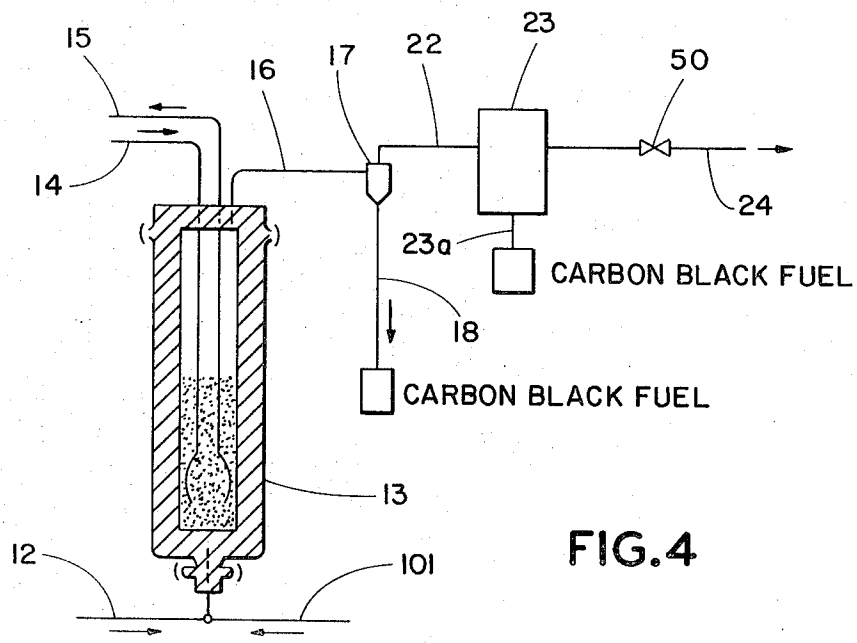

15
16
17
22
23
50
14
24
23a
CARBON BLACK FUEL
18
CARBON BLACK FUEL
13
12
101

FIG.4

CARBON BLACK FUEL PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my copending application Ser. No. 182,805 filed Sept. 22, 1971, now abandoned, which in turn is a continuation-in-part of my earlier application Ser. No. 795,498 filed Jan. 31, 1969, and now abandoned.

FIELD OF THE INVENTION

This invention relates to the production of an ash free, sulfur free carbon black for use as a nonpolluting fuel from solid carbonaceous fossil fuels, particularly coal or coal char. The coal is first devolatilized, the devolatilized coal gasified to produce gaseous carbon oxides, principally carbon monoxide, and hydrogen at elevated temperature and pressure, the gases are cooled under controlled conditions to precipitate out carbon black in a finely divided state and the volatile liquids and/or gases recovered from the devolatilization step are admixed with the carbon black to provide a relatively ash free, sulfur free fuel.

"Carbon black" is a term applied to a number of relatively pure, fine carbon materials that are produced by thermal cracking or incomplete combustion of natural gas or petroleum products such as oil. The carbon black is predominantly used for reinforcing rubber, and as a pigment in ink and paint manufacture. Carbon black has not yet found large scale utilization as a fuel source.

PRIOR ART METHODS OF CARBON BLACK PRODUCTION

Three methods of producing carbon black are now in use and include the channel process, the furnace combustion process, and the furnace thermal process. The processes, however, are designed to produce relatively low amounts of carbon black for specialty uses such as in the manufacture of tires. These processes do not contemplate nor are they suitable for large scale high volume production of carbon black as a fuel source.

THE CLASSIC CHANNEL PROCESS

In the classic channel process, carbon black is made by impinging small natural gas flames on a relatively cool metal surface or "channel." The distance between the burner pipe and the channel is varied to control the yield. A carbon black deposit is scraped from the channel, processed to remove unwanted grit, passed into a cyclone to separate it from heavy foreign particles, collected, pelletized, and then stored for shipment. The channels and burner pipe are contained in a so-called "hot house," a standard construction which contains ten parallel burner pipes and which can produce 300 to 400 pounds of rubber-grade carbon black per day. Common practice is to assemble 30 to 110 hot houses into a unit, with 2 to 12 units constituting a channel plant. A plant burning 30 to 40 MM SCF of natural gas per day will produce about 75,000 lbs. of channel black per day. Assuming that this gas is all methane, the calculated conversion efficiency is only 6.75%. Because of the development of furnace processes with better control and efficiency, the channel process has been largely abandoned. Further, there is generally no need

to convert natural gas, a good fuel, to a solid carbon fuel.

FURNACE COMBUSTION PROCESS

The furnace combustion process produces blacks of a larger particle size than the channel process and is also used mainly to produce carbon black for the rubber industry. In the furnace combustion process, a large volume of gas or preferably a mixture of oil and air undergoes combustion and cracking in firebricklined furnaces. The resultant carbon black is suspended in the spent reaction gases and is collected by a combination of electrostatic precipitators and centrifugal force. Compared to the channel process, the furnace combustion process provides more precise control of the opening variables and improves the maximum yield to about 30%. However, as in the case of the channel process, this process cannot be realistically used to produce a carbon fuel due to its low yield and the suitability of the feed material, without substantial treatment, as a fuel source.

FURNACE THERMAL PROCESS

In the furnace thermal process, carbon black is produced by thermal decomposition rather than by partial combustion of hydrocarbons. There are two variations of this process: one uses natural gas, an intermittent operation, and the other uses acetylene or petroleum products. Air and gas in proper proportion for complete combustion are fired into an insulated furnace filled with checker work. When the checkers have reached a sufficiently high temperature, the heating is discontinued and gas alone is charged. Thermal decomposition occurs in the gas phase, and the free carbon is removed in the gas stream. After a certain degree of cooling, the cycle is repeated. Reportedly up to 60% of the carbon in petroleum oil is recoverable as carbon black by this process. Again, despite higher yields, this process cannot realistically be used to produce a carbon fuel due to the ready suitability of the hydrocarbon feed as a fuel.

In all three of the above types of processes the hydrocarbon gas or oil goes directly to carbon black whether it occurs by a starved combustion, thermal cracking process such as a sooty flame produced by partial combustion of oils or gas, or by an incomplete chemical combustion process that produces carbon directly. Further, as indicated, none of these processes is designed to produce a carbon black product for use as a fuel.

An example of the prior art furnace thermal process in the Krejci U.S. Pat. No. 2,781,247 in which a cylindrical reactor furnace is heated by tangential fuel and oxidant streams that swirl throughout the axial length of the furnace, and a hydrocarbon oil is cracked at the high temperatures of the furnace. Antonsen, U.S. Pat. No. 2,733,744 illustrates a thermal process in which the cracking occurs in an atmosphere of hot hydrogen inert to the hydrocarbon. The hydrogen is heated by a conventional pebble-heater heat exchanger. The Ayers U.S. Pat. No. Re 22,886 appears to be a hybrid process best classifiable under the furnace combustion type of process. In Ayers, crude oil under extremely high pressure is sprayed in atomized form into a cylindrical furnace chamber. Simultaneously, air under pressure of about 12 lbs. per square inch is introduced to effect the desired incomplete combustion. The atomized oil is described to be vaporized and reacted almost instanta-

neously to crack and partially burn the hydrocarbons to a form of elemental carbon. The reactor burners are placed near the end opposite the high pressure oil jet, and the flame intersects the spray of oil at right angles. The resulting carbon products pass through holes in checker works into a collecting chamber. The cracking temperature of the heavy asphalt base type crude petroleum is disclosed to be above 2,300°F.

CARBON BLACK PRODUCTION FROM CARBON MONOXIDE

Specialty grade carbon black has been produced by oxidation of methane of fuel oil to carbon monoxide and then producing carbon black according to the reaction:

$$2CO \longrightarrow CO_2+C$$

Initially, the process was most commonly practiced in the presence of a metal catalyst, but the resulting metal particle-contaminated carbon black was not well suited for many uses, particularly for rubber reinforcement. Further, the catalysts were not recovered and recycled thereby adding to the expense of the process. Mayland, U.S. Pat. No. 2,716,053, describes a process for the production of carbon black from carbon monoxide in which the catalyst comprises elemental carbon derived from a tail gas stream. The Mayland process has been described as "autocatalytic" and takes two forms: in the first form, methane is oxidized with excess oxygen to prevent elemental carbon from forming in a combustor at a temperature between 2,300° and 3,000°F. to produce a gas containing carbon monoxide. The carbon monoxide stream is then quenched by a tail gas stream recycled from a later step in the process. 0.5 to 3 volumes of tail gas are used per volume of carbon monoxide-containing gas from the combustor. The relatively cold tail gas stream, containing minor amounts of unseparated carbon black, quenches the carbon monoxide-containing combustion gas to between 1,400° and 1,550°F. This is a temperature below which undesirable side reactions take place, but still in the range at which carbon monoxide reacts at a high rate to form carbon black. The quenched gas is then passed to a reaction zone wherein carbon black is formed from the carbon monoxide. The carbon black contained in the relatively cold tail gas employed as a quenching medium acts as a catalyst for the carbon black producing reaction, hence the term "autocatalytic." The stream containing carbon black formed in the reaction zone is subsequently further cooled and the carbon black is recovered. The part of the gas stream remaining after carbon black recovery and which contains a minor amount of unseparated carbon black is then used as the catalyst bearing quench gas for fresh hot gas from the carbon monoxide producing zone.

In the second alternative process of Mayland, also "autocatalytic," the carbon monoxide producing zone is operated with enough oxygen to prevent too much carbon from forming, but under such conditions that the hot carbon monoxide containing gas emerging from the reaction zone will contain a minor amount of elemental carbon which will act as the catalyst. In the recovery stage, some of the carbon dioxide recovered may further be reacted with carbon at a temperature of 1,400° to 2,300°F. to produce a carbon monoxide which is cycled back to the reaction zone. In this alternative, 0.05 to 1.0 weight per cent carbon is produced in the carbon monoxide producing zone to act as a catalyst.

Although the patent broadly indicates that other carbonaceous materials such as coal, coke, tar, and liquid hydrocarbons, as well as other normally gaseous hydrocarbons, may be processed utilizing the inventive concept of quenching the combustion zone effluent with a relatively cold tail gas containing catalytic amounts of carbon, the embodiments are restricted to a discussion of methane and preheated oxygen as the combustion reactants. Mayland discloses that the pressure in the carbon monoxide producing zone and in the reaction zone may range from 10 to 40 atmospheres pressure, which is about 150 to 600 psig. Although air is disclosed as a possible reactant, it is clear that the use of oxygen or oxygen-enriched air is important because of the process dependence on recycle gas. This is because in a recycle process using air, the build-up of nitrogen would tend to effectively suppress the reactions. Further, Mayland does not devolatilize coal prior to passage to the oxidation, nor does Mayland envisage the production of an ash free, sulfur free solid carbonaceous fuel from coal.

In still another process involving the use of carbon monoxide, Atkinson U.S. Pat. No. 2,731,328, fuel oil plus oxygen of 90% to 95% purity is reacted at high temperatures in the range of 2,000° to 3,000°F., with a preferred range of 2,000° through 2,500°F., to produce a carbon monoxide containing gas stream. The effluent gas stream is disclosed to contain, on a mole basis, about 40% carbon monoxide, 7% carbon dioxide, 36% hydrogen, and 17% steam. It is disclosed that the effluent stream containing carbon monoxide is quickly water quenched to stabilize the gas below 1,200°F., and in any event below 1,600° to 1,800°F. It is also disclosed that the water gas shift equilibrium is frozen out, and the description of the preferred embodiments indicates that the stream is quenched to between 50° and 200°F. Carbon dioxide is then removed by monoethanolamine and the resultant gas, at a temperature of 100° to 150° F. is contacted in a conversion chamber with gravitationally moving pebbles which have been cooled with steam to between 300° to 700°F. The pebbles raise the temperature of the gas sufficiently to permit formation of carbon black by an exothermic reaction. The effluent gas and pebbles from that reaction is about 900° through 1,100°F., and in any event below 1,200°F. The gases are separated from the pebbles and the pebbles are cooled for recycle to the conversion chamber. It is disclosed that the flow of reactor effluent gas and pebbles may be either cocurrent or countercurrent, but in both cases the pebbles move by gravitation in a chamber partly filled with the pebbles. In contrast to Mayland, the Atkinson process uses the pebbles in the manner of a catalyst, and the pressure disclosed for the system is from atmospheric to 15 to 25 psig., although it is stated that 100 through 400 psig may be used. As in Mayland, Atkinson discloses that low-grade carbonaceous materials, such as pulverized coal, pitch, petroleum residua, gas oils, fuel oils and the like may be used, but fails to disclose initial devolatilization of the coal or the production of an ash free, sulfur free solid carbonaceous fuel.

THE PRESENT INVENTION

OBJECTS

It is among the objects of this invention to produce

from ash and sulfur containing solid carbonaceous fossilized fuels such as coal, char, coke and the like, an ash free, sulfur free carbon black suitable for use as a solid fuel, preferably by a substantially non-autocatalytic process employing metal-type catalysts.

It is another object of this invention to provide a simple and highly efficient process for the production of carbon black for use as a fuel that operates on air alone as the oxidant, and does not require the use of enriched combustion gases such as oxygen of high purity or oxygen-enriched air, although it may be used with such enriched combustion gases.

It is a further object of this invention to provide a process for the production of carbon black for use as a fuel from coal in which a carbon monoxide rich gas and the water gas shift reaction are both utilized.

It is still a further object of this invention to employ fluidized beds in both a combustor unit and a depositor unit.

Still other objects will be evident from the description below.

SUMMARY OF THE INVENTION

This invention relates to the production of a relatively ash free, sulfur free carbon black (i.e., less than about 1 weight % ash and less than about 0.25 weight % sulfur) from carbonaceous fossile fuels, such as coal, or coal char, which carbon black is suitable for use as a fuel source in conventional burners. This process results in:

1. removal of impurities such as ash, sulphur, and iron, and 2. conversion of the carbon to a very finely divided form suitable for use as a solid fuel with good ignition and combustion properties. For example, the carbon black of the present invention is useful as a nonpolluting fuel for coal-fired turbines, an additive to diesel fuel, or as a material for pipelining to areas where air pollution ordinances require a fuel with extremely low sulfur content. This is important since the specialty grade carbon blacks such as for tire production which, despite being substantially pure carbon, are not readily combustible and are not good fuels.

Broadly, the process involves devolatilizing the coal to produce a hydrocarbon stream, containing normally gaseous and/or liquid hydrocarbons including tars or oils gasifying the devolatilized coal to produce carbon monoxide and hydrogen, cooling these gases under controlled conditions involving a fluidized bed of solid, catalytic material to precipitate out carbon in a finely divided state and admixing at least a portion of the hydrocarbon stream with the carbon. The entire process is substantially non-autocatalytic, and is preferably carried out under high pressures on the order of 50 through 100 atmospheres with a range of from about 60–75 atmospheres being particularly preferred. In the initial combustion, pulverized devolatilized coal or coal char is combusted, with or without addition of steam, under pressure such as a pressure of about 1,000 psig., at an elevated temperature such as above about 2,200°F., to produce, in a cyclone combustion zone, combustion gases, CO_2 and H_2O. The combustion gases, while in a partial combustion unit, are then contacted with a suspended or fluidized bed of coal char where the reactions

$$C+CO_2 \rightarrow 2CO$$
$$C+H_2O \rightarrow CO+H_2$$

take place thereby producing a gas rich in carbon monoxide, and which, from material balance determinations, is substantially carbon free.

The gasification step of the process is followed by the removal of ash and sulphur from the CO rich gas by conventional separation techniques. This separation is then followed by precipitation of the carbon black from the carbon monoxide in a carbon deposition unit, preferably in the pressure of the hydrocarbons to be sorbed or admixed with the carbon black, operating at elevated pressures such as between 50 and 100 atmospheres at elevated temperatures, such as below about 1,275°F., preferably between about 950° and 1,200°F., for example about 1,000°F., but at any event above the temperature at which the water gas shift reaction is frozen out. The carbon deposition unit is preferably a fluidized bed of solid, catalytic material, such as iron oxide "pebbles," which is catalytic in nature with respect to the carbon deposition. The solids are maintained at a temperature lower than the CO rich gas. All the steps in the method are conducted at high pressures in order to favor formation of carbon black and carbon dioxide from carbon monoxide and to promote the sorption of the hydrocarbons on the carbon black. Alternatively, the carbon black recovered from the carbon deposition may be admixed with at least a portion of the hydrocarbons recovered from the devolatilization step to produce a relatively ash free, sulfur free nonpolluting fuel that can be used in conventional burners. When this latter method is used, the liquid is preferably first converted to a vapor to avoid any caking or occlusion problems.

In the devolatilization step, the coal or coal char, preferably after pulverization, is treated at elevated temperatures and preferably at atmospheric pressure to remove at least a portion, if not all, of the normally gaseous and liquid hydrocarbons including volatile tars and oils contained in the coal. The amount of hydrocarbons recovered is a fraction of the coal treated and can be as low as about 10%, by weight, for certain anthracite coal and as high as about 40%, by weight for certain bituminous coals.

Preferably, however, only sufficient hydrocarbons are removed in the devolatilization step so as to impart good ignition and combustion characteristics when sorbed on the carbon black or mixed therewith. Typically, the final carbon black fuel, after hydrocarbon sorption, should contain about 1–25% volatile matter. Since the carbon produced usually has a surface area of 50–200 M^2/g, this amount of volatile hydrocarbon is generally the maximum amount of hydrocarbons that can be absorbed on the carbon, particularly when the hydrocarbons are sorbed as a vapor at elevated temperatures as encountered in the carbon deposition reaction zone. The equilibrium level of volatile hydrocarbons sorbed on the carbon black even at the elevated temperatures and pressure of the carbon deposition zone are sufficiently high to impart good ignition and combustion characterisitcs to the carbon black. However, additional volatile hydrocarbons may be added to the carbon black and the carbon black formed into solid briquettes, etc. The devolatilization step per se can be effected by means well known to those trained in the art such as by purging a fluidized bed, moving

bed or fixed bed of pulverized coal particles with gas such as nitrogen or hydrogen. For a high volatile content coal such as Illinois Bituminous coal suitable devolatilization conditions at atmospheric conditions include a temperature of about 800°–850°F. and a holding time of about 10–20 minutes. For a lower volatile content anthracite coal suitable temperatures are usually higher such as about 850°–900°F. or higher may be used. These conditions are sufficient to remove sufficient amounts of the volatile hydrocarbon (i.e., hydrocarbons which can be removed from the coal and which are gases and/or liquids at standard temperature and pressure including tars and oils and which typically have an End Boiling Point of up to about 650°–700°F.) to impart good ignition and combustion characteristics to the carbon black when added thereto.

In any event, the hydrocarbons removed from the devolatilization step usually contain about the same weight % sulfur as the initial raw coal and should be desulphurized, preferably by hydrodesulfurization, to provide a desulfurized product containing less than 0.5% by weight sulfur, preferably less than 0.1% by weight sulfur to insure that the final carbon black fuel, after addition of the volatile matter removed from the coal is relatively sulfur free.

The hydrodesulfurization of the hydrocarbon, recovered with or without prior removal of the normally gaseous hydrocarbons which may be present is effected by means well known to those trained in the art by contacting the hydrocarbon and hydrogen at hydrodesulfurization conditions with a non acidic catalyst support such as alumina containing metallic components having hydrogenation activity such as a metal selected from Group VIB and/or VIII of the Periodic Table of Elements. It is also within the scope of the present invention to crack, preferably by hydrocracking, the normally liquid hydrocarbons to lighter hydrocarbons either simultaneously with the desulfurization reaction or in a separate subsequent reaction. The use of cracking is preferred when the hydrocarbons recovered from the devolatilization step contains relatively small amounts of light hydrocarbons (C_6^-). The presence of light hydrocarbons in the final fuel is preferred since it enhances the ignition characteristics of the fuel. The hydrocracking reaction is also known to the art and usually includes higher reaction temperature than used for desulfurization alone and the use of an acidic support instead of a non acidic support. As indicated, the specific conditions used to desulfurize or crack the liquid recovered from the coal devolatilization step are all well known and need not be described in great detail. For example, reference is made to the patents classified in U.S. Pat. Office Class 208, subclasses 57, 58 and 59, such as U.S. Pat. Nos. 3,718,575, 3,544,448, 3,364,131 and 3,254,018, the teachings of which are incorporated by reference herein.

In the combustion step the devolatilized coal or coal char, with or without the addition of steam, is burned in a partial combustion unit with an amount of air just slightly deficient for converting all the carbon and hydrogen of the coal to carbon dioxide and water. The hot combustion gases are then brought into contact with a suspended or fluidized bed of pulverized coal, or preferably coal char, where the carbon dioxide and water react with the carbon of the coal or coal char to form a gas containing carbon monoxide and hydrogen, but which is substantially free of produced carbon. Although the temperature of the combustion gases is preferably between 2,300° and 3,000°F., the reactions with pulverized coal or coal char to form carbon monoxide are endothermic, and absorb heat from the combustion gases so that the temperature of the gases exiting from the partial combustion unit is about 2,240°F. After suitable purification, for ash and sulfur removal, the gases enter the carbon deposition section of the process. Because of the high temperature in the partial combustion unit, ash produced in the initial steps can be removed as molten slag. It is also advisable to remove any dust, fly ash and char carried over with the exit gases from the partial combustion unit to insure that the final carbon black product is ash free. If rapid enough reaction rates are maintained, it is possible to run the partial combustion unit in one stage, but the two stage process involving carbon dioxide and water as an intermediate before the production of the carbon monoxide is the preferred process. Preferably, the CO-rich gas from the partial combustion unit is substantially carbon free and may typically have less than from 0.1 to 0.5 mole % carbon, excluding blown-over dust.

The sulfur present in the initial devolatilized coal or char is converted to H_2S during the partial combustion or oxidation and must be removed from the gas stream before the carbon deposition step to prevent imparting of undesirable properties to the fuel. Further, hydrogen sulfide can be absorbed on the carbon black, and its presence in the gases can reduce the rate of deposition of the carbon in the fluidized bed of the carbon deposition unit. At the high temperatures used in our process, calcium oxide effectively removes the hydrogen sulfide from the gases before they pass through the carbon deposition unit. However, other methods known to the art can be used for H_2S removal. Where the carbon deposition rate is satisfactory and the presence of minor amounts of hydrogen sulfide on the carbon black is not an undesirable property, sulfur removal may take place after pressure reduction and carbon black removal, if desired.

In the carbon deposition step of the process, the gases are carefully cooled to deposit the carbon. The carbon deposition unit is basically a gas cooler, but not of conventional design since it involves the use of a fluidized bed. A fluidized bed is necessary to insured adequate heat control when large amounts of carbon black are being produced for fuel purposes. In a preferred embodiment, the carbon deposition unit contains heat exchange tubes within the bed, but may also use an external recirculating pebble-cooler. The solids in the fluidized bed are at least in partly catalytic in nature and are maintained at a relatively constant (±20°F.), lower temperature than the gases. The solids provide sites for carbon deposition. The comminuting and scouring action of the fluidized bed frees the carbon adhering to the bed material, walls, and heat exchange surfaces. The effluent from the bed is then cooled further and the carbon black removed from the gas stream either before or after pressure letdown. As an alternative to the use of heat exchange tubes in the bed, an external solid-cooling system may be employed. Residual carbon oxides in the bed effluent can be reacted with hydrogen to form additional CO and recycled to the fluidized carbon deposition bed. Preferably the desulfurized hydrocarbons recovered from the desulfurization step and which are to be sorbed on or admixed with the carbon black, are added directly to the carbon deposition

unit. This enables the liquid hydrocarbons which may be present to volatilize at the high temperature present in the deposition unit and to be effectively sorbed on the carbon in situ. This avoids the need for separate processing steps to sorb the hydrocarbons on the carbon black fuel.

The chemical reactions involved in the process are:

a. The partial combustion reactions

$$\text{coal} + \text{air} \longrightarrow CO_2+H_2O+CO+H_2+N_2$$

$$CO_2+C \longrightarrow 2CO$$

$$H_2O+C \longrightarrow CO+H_2$$

b. The carbon deposition reactions

$$2\,CO \longrightarrow C+CO_2$$

$$CO_2+H_2 \longrightarrow CO+H_2O$$

The latter reaction is the so-called water-gas shift reaction which, since not frozen out of the reactions, assists in achieving maximum carbon deposition. Known catalysts capable of promoting this watergas shift reaction are preferred as a bed material for the fluidized bed in the carbon deposition reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a diagrammatic process flow sheet of the conversion of carbon black from coal by the process of the present invention.

FIG. **2** is a diagrammatic flow sheet showing the conversion of one type of coal to carbon based on 100 lbs. of coal feed per hours.

FIG. **3** diagrammatically shows the integrated cyclone combustor and the fluidized-bed reformer of the partial combustion unit of the present invention.

FIG. **4** is a diagrammatic representation of the carbon deposition reactor of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the Figures, FIG. **1** shows by way of illustrative example a specific embodiment of the preferred process. Coal, such as Ireland mine coal containing 4.2 wt. % sulphur and 27 wt. % volatile matter, is fed by way of conveyor **1** to feed hopper **2** associated with rod mill **2A** where the coal is ground to 80% minus quarter mesh in a single rod mill. The rod mill product is fed to coal devolatilization zone **3**, wherein 60 wt. % of the volatile matter is removed from the coal by treatment with a continuous flowing hydrogen stream **3A** for 15 minutes at 850°F. The resultant hydrocarbon stream contains 1.6% by weight sulphur and is hydrodesulphurized in the presence of additional hydrogen, if required, entering via line **70** in desulphurization zone **71**, to provide a liquid stream **74**, as recovered from separation zone **72**, which is to be added to the final carbon black in carbon deposition unit **13** to provide a suitable fuel. Off gases are removed via line **73** from separation zone **72**.

The devolatilized coal in turn is passed to hopper **4**. Both hoppers **2** and **4** are atmospheric type coal hoppers. The atmospheric coal hopper **4** feeds a first pressure fed hopper **5**. The devolatilized pulverized coal is pressurized in the feed hopper **5** to an intermediate pressure and fed into high pressure feed hopper **6**. Alternatively, the pressure feed hoppers **5** and **6** may be separated by a lock hopper and valving system (not shown). The devolatilized, pulverized coal is then fed by a feeder associated with pressure feed hopper **6** to partial combustion unit **8** via line **6***a*. As discussed in more detail below with respect to FIGS. **3** and **4**, the partial combustion unit **8** comprises a cyclone-type combustor in combination with a fluidized bed char reformer. Air compressor **26** supplies ambient air at a pressure of about 1,000 psig. to the partial combustion unit in which the pulverized coal and excess desulphurized liquid removed from line **74** via line **75** is converted by oxidation to carbon monoxide via the intermediate state of carbon dioxide and water. Excess hydrogen, hydrogen sulphide and light gases are removed overhead from recovery zone **72** via line **73** for subsequent processing. If desired, excess hydrocarbon liquid can be passed to partial combustion unit **8** via line **75** for conversion to carbon black in admixture with the devolatilized coal. Preferably, however, the excess liquid is used as a liquid fuel or petrochemical feed source and is removed via line **76.** The resulting combustion gases exit by line **9** at a pressure of about 1,000 psig. at 2,249°F., and enter ash cyclone **10** where the fly ash is drawn off at **11.** The hot combustion gases exit from the ash cyclone by way of line **12** and are directed to the carbon deposition unit **13** after H_2S removal via line **21** in suitable separation zone **80.** The temperature of the gases is carefully lowered by application of water to line **14** in heat-exchange relationship with the gases and the catalytic pebbles or granules in the fluidized bed contained within the carbon deposition unit **13.** Steam exits from the heat-exchange coils through line **15** at 1,000 psig., and is directed to the drive **27,** entering at line **28** and exiting by way of pipeline **29.** The drive operates air compressor **26** which takes in air at 0 psig., 60°F. at line **30** and puts out high pressure air at 1,000 psig., 60°F., through line **31** for supply to the partial combustion unit **8** as previously described.

The carbon deposition unit contains a fluidized bed of material which is at least partially catalytic in nature and preferably catalytic with respect to the water gas shift reaction such as 100 U.S. mesh to one-fourth inch diameter, substantially spherical pebbles or granules of iron, cobalt, nickel, or mixtures or alloys thereof, or their oxides, hydroxides or carbonates. The fluidized bed has a linear velocity of 1 foot per second based on the volume of the inlet gases at operating conditions, and is maintained at a relatively constant temperature (±20°F.), which temperature is lower than the inlet CO-rich gas. The unit is a refractory-lined pressure vessel. The pressure within the vessel may be from 50 to 100 atmospheres as in the partial combustion unit, and is preferably in the range of from about 60 to 75 atmospheres, e.g., about 1,000 psig., and operates within the range of 950° through 1,200°F., preferably about 1,000°F. to take advantage of the water gas shift reaction. The carbon monoxide within the carbon deposition unit, at the controlled prevailing temperatures and pressures therein, is converted to carbon black entrained in the gases. While I do not wish to be bound by theory, at these conditions the process in accordance with this invention does not appear to be autocatalytic in nature.

The constant upward flow of the input gases through line **12** keeps the bed in the fluidized condition, and that condition promotes a constant scrubbing of the walls and heat exchange surfaces within the carbon deposition unit so that all the carbon black is entrained in the exhaust gases. The exhaust gases pass out by line **16**

at approximately 1,000 psig., and 1,000°F., to the carbon cyclone **17.** The carbon black product is taken off through line **18.** The ash and carbon cyclones are both refractory-lined pressure vessels having a maximum outside wall temperature of about 650°F. and operate at about a linear inlet velocity of 50 feet per second. The by-product gases exiting from the carbon cyclone **17** pass by line **19** through the expansion turbine **20** and electrical generator **21** for pressure letdown. The expansion turbine reduces the pressure of the exhaust gas to approximately **1** psig. and the associated electrical generator is used to recover the work done by this expansion. The excess electrical energy may be used to power the coal conveyor **1,** hopper **2,** rod mill **2A,** or the hoppers **4** through **6.** The low pressure exhaust gas has a temperature of about 500°F. and 1 psig., and passes through line **22** to the bag house **23.** Any remaining entrained carbon black is taken off through line **23***a*, and the exhaust gas at about 500°F., 0 psig. and having a heating value of 16.4 BTU/SCF passes by line **24** to flare **25.** Alternatively, the residual CO_2 content of the exhaust gas can be reacted with hydrogen to form carbon monoxide which can be recycled back to fluidized bed unit **13.**

It should be appreciated that in the present process, since the exhaust gas is merely a waste gas, there is no build-up of nitrogen by recycling the exhaust gas as a tail gas to other portions of the process. If it is so desired, the carbon dioxide content of the gas, about 13%, may be removed and recycled to the fluidized bed reformer portion of the partial combustion unit **8.** In that event, some provision for removal of the nitrogen build-up must be made, since such build-up will suppress the process both in the partial combustion unit and the carbon deposition unit. It has not proven worthwhile, from the point of view of increasing the efficiency of the process appreciably, to retain the small percentage of carbon dioxide in the exhaust gas due to the associated problems of nitrogen build-up. The nitrogen build-up is due entirely to the use of air as a source of coal oxidant. If the benefits of using the cheap oxidant source, air, is not desired, oxygen or oxygen-enriched air may be used as the oxidant source. In that event, the build-up of nitrogen may be avoided and carbon dioxide, after removal by absorption by contact with an aqueous alkanolamine, as for example, monoethanolamine, may be utilized by recycle to the fluidized bed char reformer portion of the partial combustion unit.

As indicated, a standard H_2S removal unit **80** such as a unit containing calcium oxide is interposed in line **12** to remove the sulphur originally present in the coal and substantially now converted to H_2S.

With reference to FIG. **2,** devolatilized Ireland mine coal having a heating value of about 13249 BTU/lb. is fed at the rate of 100 lbs. per hour at 60°F. to partial combustion unit **8.** This coal has been previously devolatilized to remove 16 wt. % of the coal as hydrocarbon fraction boiling up to about 700°F. and the hydrocarbons subsequently hydrodesulphurized to provide a product containing about 0.1% by weight sulphur. Air from the compressor is fed in at 60°F. through line **31** at the rate of 4922 SCF/hr. Ash, partly in the form of slag, and partly in the form of free ash from the ash cyclone, is shown schematically to be removed from line **11a** at the rate of 13.6 lbs./hr. at a temperature of about 2,240°F. The chemical analysis of the input Ireland mine coal prior to devolatilization is 68.9% carbon, 4.9% hydrogen, 1.3% nitrogen, 7.1% oxygen, 4.2% sulfur and 13.6% as ash. Air is assumed to contain about 78% nitrogen. The output combustion gases exit via line **9** to the carbon deposition unit **13,** and contain about 30.6 mole % carbon monoxide, 0.38% carbon dioxide, 12.3% hydrogen, 0.40% water, 0.71% hydrogen sulfide, and 55.85% nitrogen. There is no measurable carbon, other than dust blow-over, in the partial combustion unit product gas under these conditions.

The carbon black product, recovered from the carbon cyclone and bag house, is schematically shown as removed by way of line **18***a* at the rate of 45.1 lb./hr. The carbon black is a relatively pure carbon black in a very finely divided form which, when admixed with the hydrodesulphurized hydrocarbon yields a nonpolluting carbon black fuel containing about 15 wt. % volatile material with good ignition and combustion characteristics and is substantially ash and sulphur free. The excess hydrocarbons not deposited on the hydrocarbons can be used as a liquid fuel source or a petrochemical source. This form of carbon fuel produced by the process disclosed is useful as a nonpolluting fuel for coal-fired turbines, as an additive to diesel fuel, and as a material for coal pipelining to areas where air pollution ordinances require a fuel with low sulphur content. The carbon black product is particulate and 95% less than 5μ in size. Based on the recovery rate, the calculated conversion efficiency of the present process is about 65%. This compares favorably with the 7% maximum recovery of carbon black from the channel process and 30% maximum yield in the furnace combustion process. About 433,500 BTU/hr. is recovered at 1,000°F. in the form of steam by way of line **15,** and may be used to drive the air compressor as above disclosed. The exhaust gas exits at the rate of about 5580 SCF/hr. from the carbon deposition unit through line **19** and contains the following mole percentage of components: 0.53% carbon monoxide, 12.92% carbon dioxide, 2.08% hydrogen, 13.52% water, 0.89% hydrogen sulfide, and 70.06% nitrogen. Since that exhaust gas has a heating value of only about 16.4 BTU/SCF, it may be directed to a flare and burned off. Because of the small size and the low density of the carbon black, the resultant fuel can be admixed with pipeline gas or other gaseous carrier for transmission. For example, natural gas flow rates of as little as 0.1 ft./sec. are sufficient to entrain and transport without settling the carbon black fuel. Alternatively, this carbon black can be compressed into briquettes.

Referring now to FIG. **3,** the coal feed system is shown as in FIG. **1** by feed hopper **4** and pressure feed hoppers **5** and **6.** The output devolatilized pulverized coal is fed from pressure feed hopper **6** to both a reformer coal feeder **36** and to the combustor coal feeder **46.** Filtered air is fed by air compressor **26** through lines **6***a* and **31.** Line **31** takes direct feed air to the cyclone combustor **38***a*, and line **6***a* feeds air to entrain the devolatilized coal fed from the combustor coal feeder **46** through line **47.** Coal is entrained and passed into the cyclone combustor **38***a* by way of line **32.** As above directed, the cyclone combustor operates under a pressure of between 50 and 100 atmospheres at a temperature between about 2,300° and 3,000°F. with an amount of air just slightly deficient for converting all the carbon and hydrogen of the coal to carbon dioxide

and water, with less than 1. to 0.5% carbon. At those temperatures and pressures, some of the ash may be removed by slag removal system **40** through **42.** The ash passes first through slag quench tank **40** and then to a slag lock hopper **41** and out the line **42** as waste ash. The hot combustion gases flow upwardly from the cyclone combustor **38***a* to fluidize the coal or coke **39** in the fluidized-bed reformer **38***b*. There, the carbon dioxide and water produced in the cyclone combustor reacts with the carbon of the coal or coke **39** to form carbon monoxide-rich gases which pass out line **9.** Heavier ash and char fines may be caught in cyclone **48** and recycled through line **49** to the cyclone combustor. Using the spent char from the fluidized bed reactor or reformer **38***b*, as feed for the cyclone combustor, minimizes the amount of fly ash in the gas stream **9***a*. The fluidized bed reformer or reactor portion **38***b* of the partial combustion unit is a fluidized bed having a linear velocity of about **1** foot per second based on the volume of the inlet gases from the cyclone combustor **38***a* at operating conditions. The unit is a refractory-lined pressure vessel having an outside maximum wall temperature of about 650°F. As discussed above with reference to FIG. **1,** the carbon monoxide-rich gases pass from line **9***a* through the ash cyclone **10** and then to the carbon deposition unit with intermediate H_2S removal via line **8** from H_2S removal zone **80.** It should also be appreciated that the partial combustion unit may be built as a single unit, in which the combustor is the lower portion of a single unit, and the ash cyclone may be an internal cyclone contained in the upper end of the reformer portion of the partial combustion unit. High pressure steam may be let in at line **45** to prevent slag-char accumulation at the throat between the combustor and reformer. The film of steam or water in this critical area, by transpiration cooling, prevents the slag-char accumulation at the throat. Further, a slag quench system **40** through **42** is included to provide for the slag forming that results from some weeping of char through the gas-entry orifice at the base of the fluidized bed.

FIG. **4** shows a schematic view of the carbon deposition reactor, in which the carbon monoxide-rich hot combustion gases are fed through line **12** into the bottom of the fluidized bed of the carbon deposition unit **13.** The linear velocity of 1 foot per second based on the inlet gas at operating conditions is typical. Line **14** admits water for cooling into the fluidized bed and an excess of about 33,000 lb./hr. of steam at 1,000 psig. exit line **15** for use, inter alia, as power for the air compressor drive **27** (FIG. **1**). The fluidized bed is composed of a flowable solid, generally small granules, which denotes any solid refractory material of flowable form and size that can be utilized as a surface on which the carbon black may be deposited, and which, at least in part is catalytic with respect to the carbon deposition reaction. The granules are substantially spherical and about 100 U.S. mesh to one-fourth inch in diameter, and must withstand the temperature at least as high as the temperature in the carbon deposition unit, on the order of 950° through 1,200°F. One particularly useful bed is a mixture of "inert" refractory material, with from 25–100% of a catalytic metal, or metal oxide hydroxide, or carbonate such as iron oxide, cobalt oxide, nickel oxide, siderite, Wustite or mixtures or alloys thereof. For the inert refractory materials, sand metal alloys, ceramics, alumina, periclase, thoria, beryllia, and mullite may be used in the form of granules. Of course, the catalytic material may be used alone. Desulphurized hydrocarbons to be sorbed on the carbon formed enters via line **101** and is sorbed on the carbon black as it is being formed.

The gases exiting line **16** from the carbon deposition unit **13** carry the entrained carbon black that has been scrubbed from the surfaces of the granules by the fluidized bed's action to the cyclone where the carbon black product is separated at line **18.** The exhaust gases, after pressure drop in the expansion turbine **20,** is then fed through line **22** to a pressure bag filter **23** and additional carbon black is taken off at line **23***a*. The remaining exhaust gas passes through back pressure regulator **50** through line **24** to the burn-off flare **25.**

To investigate the nature of the reaction $2CO \longrightarrow C+CO_2$ in the fluidized bed of the process of this invention, a series of four test runs were made on a pilot plant scale reactor using a 2 inch diameter tube to retain the carbon deposition bed. In the first two runs, a sand bed having from 1.3 to 2.7% finely divided carbon intimately mixed therein was run at the conditions listed in Table **1,** to see if under the conditions of this process, the deposition was promoted by carbon itself, i.e., was "autocatalytic." In Runs 3 and 4, a catalytically active bed of iron compound, as described above was used. Specifically, a native iron carbonate $FeCO_3$ (Algoma siderite) also known under the names clay iron stone, Chalybite, or spathic iron ore, was used. At the run conditions the siderite decomposes to Wustite, a mixed iron-iron oxide composition of Fe, Fe_3O_4 and FeO.

The four runs employed a typical range of temperatures, reactor pressures, and inlet gas flow rates to insure that the results were not specifically one-condition dependent. The results are shown below in Table **1.**

TABLE I

TEST RUN:	1	2	3	4
Composition of Fluidized Bed				
Sand, wt. %	97.3	98.7	—	—
Carbon, wt. %	2.7	1.3	—	—
Iron Catalyst, wt. %	—	—	100	100
Bed Temperature, °F.	1320	1190	1330	1060
Reactor Pressure, Psig.	994	1024	1005	1000
Gas Flow Rate, SCFH	250	965	45	755
Feed Gas Composition, Mole %				
N_2	73.4	58.5	58.3	58.1
CO	26.1	34.8	30.0	30.6
CO_2	0.5	0.92	0.1	0.1
H_2	—	4.6	11.3	10.9
A	—	0.12	0.3	0.3
CH_4	—	1.1	—	—
Product Gas Composition, Mole %				
N_2	73.0	65.7	66.6	66.3
CO	26.2	34.2	17.1	16.7
CO_2	0.6	0.11	6.9	8.8
H_2	—	—	8.6	5.8
A	0.02	0.03	0.3	0.3
CH_4	—	—	0.5	2.0
C_2H_6	—	—	—	0.1
Carbon Deposited, % of CO in Feed (Calculated as carbon disappearance).	Nil	Nil	28.6	21.2

The lack of production of carbon deposited from the feed CO in Runs 1 and 2 (having finely divided carbon in the bed), as compared to substantial carbon production in Runs 3 and 4 shows both the non-carbon-autocatalytic nature of the process of this invention,

and a substantial improvement over the carbon production by prior art processes.

As will be evident to those skilled in the art, various modifications can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

What I claim is:

1. A process for the production of a non-polluting substantially ash free, sulphur free carbon black fuel comprising:

a. devolatilizing a pulverized solid carbon-aceous fossil fuel containing ash and sulphur to provide a devolatilized fossil fuel and a hydrocarbon stream;

b. oxidizing the devolatilized pulverized solid carbonaceous fossil fuel with a gas containing oxygen to form carbon monoxide-rich gas containing sulphur and ash;

c. removing the sulphur and ash from the carbon monoxide-rich gas;

d. passing said carbon monoxide-rich gas through a fluidized bed of solid material in a carbon deposition zone at least partly catalytic with respect to carbon deposition, said bed being maintained at a temperature below said carbon monoxide-rich gas temperature;

e. maintaining said solid bed material at a substantially constant temperature by contact with heat exchange surfaces to quench said carbon monoxide-rich gas to said bed temperature and to precipitate in said bed finely-divided carbon by the conversion of said carbon monoxide-rich gas while forming an exhaust gas therefrom;

f. maintaining the flow of said carbon monoxide-rich gas and said exhaust gas to entrain said carbon black therein;

g. desulphurizing the hydrocarbon stream; and

h. admixing at least a portion of the desulphurized hydrocarbon with said carbon black to produce a nonpolluting substantially ash free, sulphur free fuel having good ignition and combustion characteristics.

2. A process as in claim **1** in which said oxygen-containing gas is air.

3. A process as in claim **1** in which said carbonaceous fossil fuel is coal 80% reduced in size to minus quarter mesh.

4. A process as in claim **1** in which said oxidation step includes the steps of:

i. combusting a portion of said carbonaceous fossil fuel with said oxygen-containing gas to produce a combustion gas rich in CO_2 and H_2O, and

ii. reacting said CO_2 and H_2O with the remainder of said solid fossil fuel to produce said carbon monoxide-rich gas.

5. A process as in claim **4** in which said oxygen-containing gas is air.

6. A process as in claim **1** which includes maintaining said coal that is oxidized with said combustion gas in a substantially fluidized condition.

7. A process as in claim **1** which includes the steps of:

a. reacting residual carbon oxides in said exhaust gases with hydrogen to form carbon monoxide, and

b. recycling said carbon monoxide to said fluidized bed.

8. A process as in claim **1** wherein said heat exchange surfaces are disposed in said bed.

9. A process as in claim **1** wherein said solid bed material is a catalyst capable of promoting carbon formation and promoting a water gas shift reaction.

10. A process as in claim **1** wherein said solid bed material is in the form of granules substantially spherical in shape, and range from about 100 U.S. mesh to one-quarter inch in diameter.

11. A process as in claim **9** wherein said catalyst is selected from iron, cobalt, and nickel, alloys thereof, and oxides, hydroxides and carbonates of sodium, cobalt, nickel and alloys thereof.

12. A process as in claim **11** wherein said catalyst is a mixture of iron and iron oxides.

13. A process as in claim **12** wherein said catalyst is Wustite.

14. A process as in claim **1** wherein the desulphurized hydrocarbon is admixed with the carbon by passing the liquid to the carbon deposition zone.

15. A process as in claim **1** where the desulphurized hydrocarbon is vaporized prior to admixing with the carbon black.

16. A process as in claim **1** wherein the desulphurized hydrocarbon is admixed with the carbon in the amount of 1 to about 25 wt. % of the final product.

17. A process as in claim **1** wherein a portion of the hydrocarbon stream is passed to the oxidation step for conversion to CO.

18. A process as in claim **1** wherein the hydrocarbon stream is also subjected to cracking.

* * * * *