

Feb. 19, 1957

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2,782,101

MANUFACTURE OF CARBON BLACK

Filed Aug. 22, 1951

Fig. 1.

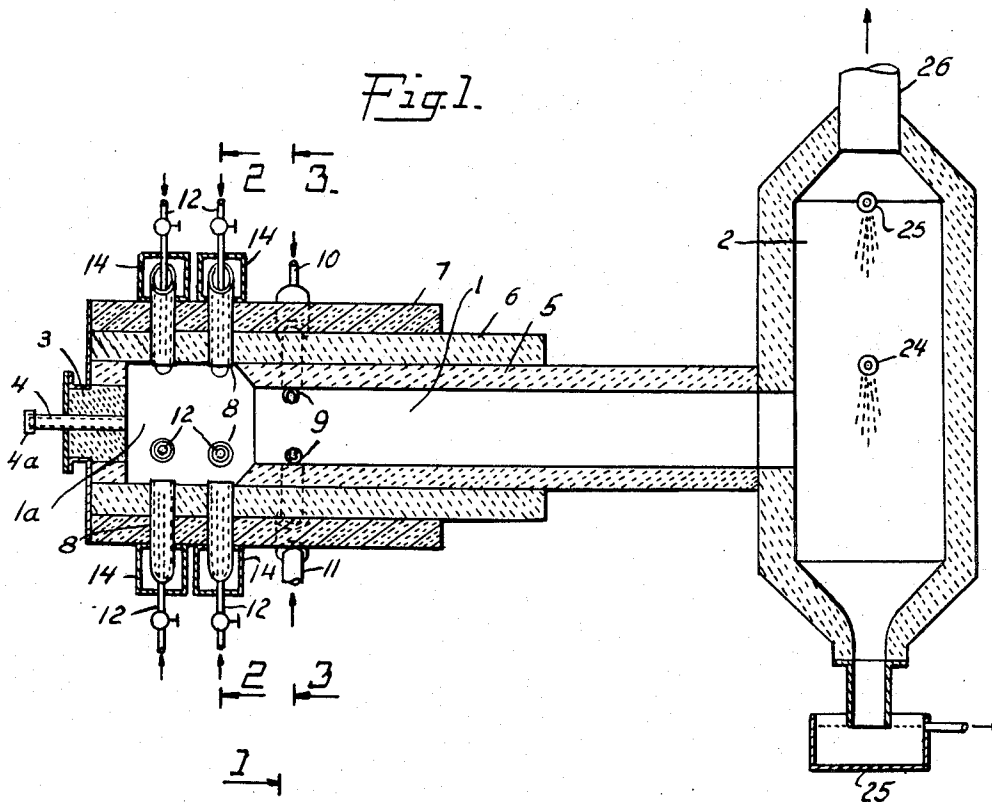


Fig. 2.

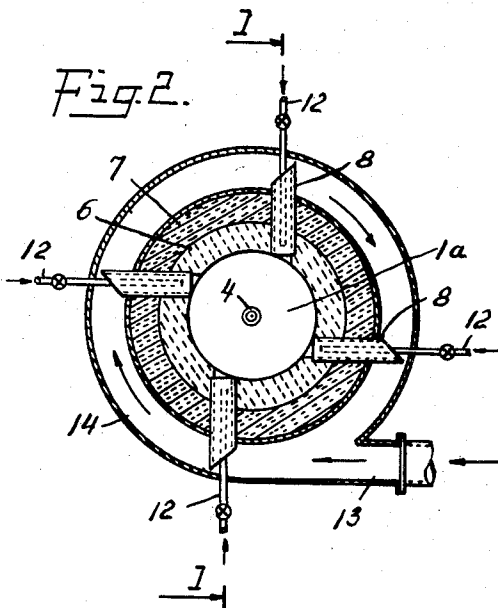
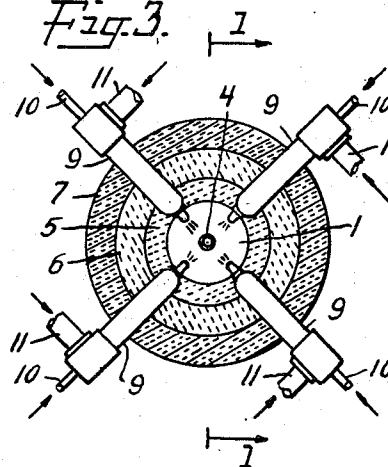


Fig. 3.



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2,782,101

MANUFACTURE OF CARBON BLACK

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Application August 22, 1951, Serial No. 243,020

5 Claims. (Cl. 23—209.4)

The present invention relates to the manufacture of furnace black and, more particularly, to a process of the type involving the thermal decomposition of a hydrocarbon by rapidly, uniformly mixing it with a hot gaseous medium at a temperature in excess of that at which the hydrocarbon is decomposed to carbon black.

In my copending application, Serial No. 195,530 filed November 14, 1950, now Patent No. 2,659,663, I have described and claimed a process of the type noted in which a mixture of a fluid hydrocarbon fuel and an oxygen containing gas, air, for instance, is injected through one or more blast burner ports into one end of an elongated cylindrical reaction chamber in a direction substantially tangential to the inner chamber wall and is burned therein to form a swirling cyclone of hot blast flame gases passing longitudinally through the chamber, and the hydrocarbon to be decomposed, herein designated "make," is separately injected into the swirling body of hot gases in a substantially radial direction at a point, or points, downstream from the burner ports and near the periphery of the swirling gas stream.

The present invention is directed primarily to improvements in processes of the type described in said application whereby the yield of carbon black may be substantially increased.

A particularly desirable aspect of the process of said application is the operation thereof in which the hydrocarbon make is a heavy, high molecular weight material containing large proportions of aromatic constituents, for instance, heavy hydrocarbon fractions or residuum resulting from the cracking of petroleum to produce motor fuel. The present invention is particularly applicable to operations in which a hydrocarbon make of that type is used.

For smooth operation of the tangential blasts in processes of this type, it has been found that the combustible mixture should contain a proportion of oxygen such as results in an oxidizing blast flame. Where smaller proportions of oxygen, or air, are used, one is apt to experience "flare backs," into the burner ports, unless the hydrocarbon injection nozzles of the blast burners are advanced to a position where they are subject to rapid destruction by radiant heat from the furnace chamber.

I have found, however, that by producing a substantially non-oxidizing blast flame, the yields of furnace black produced in operations such as just described may be substantially increased. It appears that, in operations of this type where an oxidizing blast is used, a considerable portion of the hydrocarbon make, or else the carbon black resulting therefrom, is normally burned and the yield of the operation proportionately reduced.

I have further found that the yields of furnace black per unit quantity of hydrocarbon make in operations of the present type, wherein oxidizing blasts are used, may be materially increased by introducing into the hot, oxidizing blast flame gases, prior to mixing the hydrocarbon make therewith, an oxygen-scavenger in a proportion sufficient to combine with the active oxygen or oxidiz-

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ing components of the blast flame gases to reduce the oxidizing capacity of those gases to below the dynamic equilibrium point, i. e., to neutralize the oxidizing capacity of those gases under the prevailing temperature and time conditions of the particular operation.

As the oxygen-scavenger, I may use a flue gas preferably hot, containing substantial proportions of hydrogen for combining with the oxidizing components of the blast flame gases or I may use other material in the form of gas, or vapor, which will combine with those oxidizing components to form gaseous reaction products which may be readily separated from the carbon black. For instance, I may use for this purpose an inexpensive grade of natural gas, or other low molecular weight hydrocarbons, or I may use substantially pure hydrogen, where such is economically available. This oxygen-scavenger, i. e., reducing agent, is introduced into the combustion zone of the reaction chamber, separately from the combustible mixture supplied through the blast ports in such a way that it will become intimately admixed with the oxidizing blast flame gases before the oxidizing constituents of those gases can consume or otherwise react with the radially injected hydrocarbon make.

The process will be further described and illustrated by reference to the following drawings of which—

Figure 1 is the longitudinal, sectional view in elevation of the reaction chamber, together with accessories, including adjacent cooling equipment;

Figure 2 is a transverse section of the reaction chamber along the line 2—2 of Figure 1; and

Figure 3 is a transverse section of the reaction chamber along the line 3—3 of Figure 1 showing more clearly the arrangement of hydrocarbon make injection nozzles.

In the apparatus shown, the numeral 1 indicates a cylindrical reaction chamber, one end of which opens into the vertical cooler 2. At its left-hand end, the reaction chamber opens into a somewhat enlarged combustion chamber 1a which is closed at its upstream end by a block of refractory material 3 through which pipe 4 extends axially, through which the blast burners may be ignited and which, when not in use, is normally closed by the cap 4a.

The chamber 1 is delineated by the cylindrical wall 5 of highly refractory material which, in turn, is covered by a second layer of furnace refractory 6 which also delineates the combustion chamber 1a. This outer layer of refractory material is covered by layer 7 of heat-insulating material. Extending through the layers of refractory and heat-insulating material forming the furnace side wall, substantially perpendicular to the longitudinal axis of the chamber are four blast burners 8, each entering the combustion chamber in a circumferential or tangential direction, as more clearly shown in Figure 2 of the drawings. The apparatus shown is provided with two identical sets of these blast burners positioned at different distances from the block 3. In operation, only one or both sets of the burners may be used as desired, or one or more burners of the separate sets may be used.

Further downstream, the furnace chamber is provided with a set of four radially directed hydrocarbon make injection nozzles 9, spaced 90° apart and extending through the furnace side wall, as more clearly shown in Figure 3 of the drawings. These nozzles are provided for the injection into the furnace chamber of liquid hydrocarbon to be decomposed and are normally positioned with their inner ends substantially flush with the inner wall of the furnace chamber. The present invention is independent of the particular type of nozzle used, the type shown in the drawing being one into which the liquid hydrocarbon make is passed through the tube 10

and to which an atomizing gas is supplied under pressure through the tube 11.

Hydrocarbon fuel is supplied to the blast burners through valved tubes 12 projecting axially through the respective burner ports and terminating short of the inner wall of the combustion chamber. Air for combustion is forced by any suitable means through the conduit 13 and introduced tangentially into the annular duct 14, as more clearly shown in Figure 2 of the drawing, each set of blast burners being equipped with a separate air duct. The outer ends of the burner ports 8 open into the air ducts 14 and, advantageously, are shaped, as shown in the drawing, to utilize the whirling of the air in the duct to facilitate the directing of the air through the respective ports.

In the usual operation of the carbon black furnace illustrated, a combustible mixture of the air supplied through conduit 13 and the hydrocarbon fuel supplied through tubes 12 is tangentially injected at high velocity into the combustion chamber and is burned therein to form a swirling cyclone of blast flame gases passing longitudinally through the reaction chamber. Liquid hydrocarbon make is radially injected into this swirling body of hot gases through the spray nozzles 9 and is substantially instantaneously mixed therewith and is decomposed by heat absorbed therefrom to form carbon black in suspension in the furnace gases.

The resultant suspension of carbon black in furnace gases flows from the reaction chamber and upwardly through the vertical cooler 2 wherein the suspension is cooled by contact with water sprays 24. Any unvaporized water from these sprays, together with any carbon knocked out of suspension, passes downwardly from the vertical cooler into the sump 25 and the cooled suspension passes from the upper end of the vertical cooler through conduit 26 to conventional separating and collecting apparatus as is well understood by the art.

As previously noted, it is generally desirable to so proportion the hydrocarbon fuel and air in the combustible mixture to produce a steady flame which will not vibrate excessively, or flare back into the burner ports and as a result thereof, the blast flame gases will be of an oxidizing character.

The oxygen-scavenger is mixed with these hot blast flame gases prior to the mixing of the hydrocarbon make therewith. This may be accomplished by introducing the oxygen-scavenger into the upstream end of the combustion chamber by any suitable means, for instance, through the tube 4, or where only one set of blast burners is being used, the oxygen-scavenger may be introduced through one or more burners of the other set, no oxygen being supplied to the burner ports through which the oxygen-scavenger is introduced.

The optimum proportion of the oxygen-scavenger to be used is dependent upon other operating conditions and should, of course, be increased with an increase in the oxidizing characteristics of the blast flame gases. The proportion of oxygen-scavenger will also depend upon the capacity of the scavenger to react with, or neutralize, the oxidizing constituents of the blast flame gases.

Where a hydrocarbon gas, for instance, natural gas of the type charged to the blast burners, is used as the oxygen scavenger, I have found that ratios of air to total gas, i. e., fuel gas plus auxiliary gas or oxygen scavenger, may be reduced as low as 6.85:1 in operations of the type shown without producing any carbon black from either the fuel gas, or the auxiliary gas. This is apparent from the absence of carbon black in the resultant combustion gases. However, it is generally advantageous that the ratio of air to total gas be not lower than about 9:1.

The ratio of air to total gas required for complete combustion of the fuel gas will, of course, vary with the character of the fuel gas and burning conditions. This

is readily determined by simple flue gas analysis under the particular operating conditions prevailing. In accordance with my present invention, it is generally advantageous to introduce sufficient auxiliary gas to bring the total amount of gas introduced, i. e. fuel gas plus auxiliary gas, to a proportion such that about 85% to 90% theoretically complete combustion is effected. This will usually require a ratio of air to total gas within the range of about 9.3:1 to 9.8:1.

The purpose of the auxiliary gas is to scavenge not only excess free oxygen but also further to reduce any oxidizing components of the blast flame gases, for instance, CO₂ and water vapor, in order to retard or minimize robber side reactions which tend to reduce the yield of carbon black per unit of hydrocarbon make. For optimum results, under conditions usually encountered in operations of the type described, sufficient auxiliary gas should be used to effect a reduction of the oxidizing components of the blast flame gases to an extent such that the CO₂ content of the resultant gases is within the range of about 4.5% to 10%, the CO content is within the range of about 9.5% to 3%, the O₂ content does not exceed about ½% and no appreciable amount of illuminant is present.

The invention, and the advantages obtained thereby will be further illustrated by the following specific examples of operations carried on in commercial sized apparatus of the type shown. In each of these examples, air for combustion was supplied at the rate of 180,000 cubic feet per hour and the ratio of combustion air to fuel gas supplied through the blast burners was in each case 11.4:1. Other operating conditions and the yield obtained thereby are set forth in the following table. In each of the examples, except 1 and 5, an oxygen scavenger was used in accordance with the present invention, the scavenger being natural gas of the same type as was used as the fuel gas. In Examples 1 and 5, no oxygen scavenger was used, these examples being included for comparative purposes.

TABLE

Example.....	1	2	3	4	5	6	7	8
Hydrocarbon make, gals./hr.....	168	168	156	144	198	168	150	138
Scavenger gas, cu. ft./hr.....	0	3,120	4,520	6,000	0	3,120	4,500	4,500
Ratio, air/total gas..	11.4	9.52	8.87	8.28	11.4	9.52	8.90	8.90
Yield of carbon, lbs./gal. of make....	3.52	3.98	4.55	5.0	3.26	3.85	4.23	4.61

In Examples 1 to 4, inclusive, above, the hydrocarbon make was a so-called pressure tar obtained by the thermal cracking of cycle stock from a catalytic cracking operation. In Examples 5 to 8, inclusive, the hydrocarbon make was a residuum obtained from the straight thermal cracking of an aromatic crude. Both of these materials are highly aromatic.

Example IX

In an operation carried on in apparatus similar to that just described, to which air was supplied through the blast burners at the rate of 180,000 cubic feet per hour and a fuel gas of 1020 B. t. u. value and which theoretically required an air-gas ratio of 10.6:1 for combustion was used, I have, with advantage, used an air-blast gas ratio of 11.6:1 and supplied natural gas of the same type, as the scavenger gas, at the rate of 3500 to 3750 cubic feet per hour. By such operations, the yield of carbon black per gallon of hydrocarbon make was very substantially increased over that obtained by operations under comparable conditions, except that the scavenger gas was not employed.

Example X

In operations carried on in similar apparatus, using fuel gas of the type used in Example IX and to which

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air was supplied at the rate of 180,000 cubic feet per hour, the ratio of air to fuel gas being 11.8 and hydrocarbon make being introduced at the rate of 162 gallons per hour, I have, with advantage, introduced axially into the combustion chamber auxiliary gas of the same type as the fuel gas at the rate of 4500 cubic feet per hour, and obtained yields of carbon black equivalent to 4.85 pounds per gallon of the hydrocarbon make.

I have found that low molecular weight paraffinic hydrocarbons, such as normally present in natural gas, are much more reactive with respect to oxygen than are the heavier aromatic hydrocarbons. Because of this difference in oxidation rate, I may, with advantage, use such low molecular weight hydrocarbons, advantageously, natural gas, as the oxygen-scavenger in operations where heavy aromatic hydrocarbons are used as the hydrocarbon make.

As previously indicated, the invention is especially applicable to operations in which heavy, high molecular weight hydrocarbons, such as result from the cracking of petroleum, are used as the make and particularly where the make is one comprising around 20-95%, usually in the range of 60-95%, by weight of aromatic constituents, as determined by the test method D-875-46T of the American Society for Testing Materials. As examples of such heavy hydrocarbons, there may be mentioned heavy residuum oils, or tars, such as fuel oil #5, #6, or Bunker C and products known to the trade as "pressure tar," or "flash drum tar" characterized by high aromaticity, low pour point, and high specific gravity. Preferred tars of this type are those having A. P. I. values from +10 to -6, SSU furul viscosities at 122° F. of from 125 to 250, and which are soluble in pentachlorophenol and have specific gravities of from 0.95 to 1.1. These products are readily available from most refineries using thermal cracking methods. In use, these heavy tars are preheated to about 250° F. or as required to reduce the viscosity for atomization, but not to exceed 500° F. Another efficacious procedure is to dilute the heavy residuum products with an aromatic cycle stock to secure the desired pour point.

I claim:

1. In the process for producing furnace blacks by decomposing hydrocarbons by which a combustible mixture of a fluid hydrocarbon fuel and an oxygen-containing gas is blasted into one end of an elongated, cylindrical

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reaction chamber in a direction substantially tangential to the chamber walls and burned therein to form a turbulent swirling body of oxidizing blast flame gases passing longitudinally through the chamber at a temperature in excess of that at which hydrocarbons are decomposed to form carbon black, and the hydrocarbon make to be decomposed is separately injected into the swirling gases at a point downstream from the entry of said gases to the chamber, the steps of injecting into the hot gas stream a normally liquid hydrocarbon make containing a substantial proportion of aromatic constituents and neutralizing the oxidizing capacity of the blast flame gases passing through the chamber by separately injecting into, and rapidly uniformly mixing with, said gas stream, prior to the mixing of the hydrocarbon make therewith, a normally gaseous reducing agent substantially free of aromatics.

2. The process of claim 1 in which the reducing agent is natural gas.

3. The process of claim 2 in which the relative proportion of air to total gas, i. e. hydrocarbon fuel plus reducing agent, is such as to effect 85% to 90% theoretically complete combustion of the total gas.

4. The process of claim 1 in which the hydrocarbon make is a tar-like hydrocarbon obtained by the thermal cracking of cycle stock from a catalytic cracking operation.

5. The process of claim 1 in which the hydrocarbon make is a heavy high molecular weight hydrocarbon residue resulting from the cracking of petroleum and comprising 20%-95% by weight of aromatic constituents.

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