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PREPARATION OF CARBON BLACK

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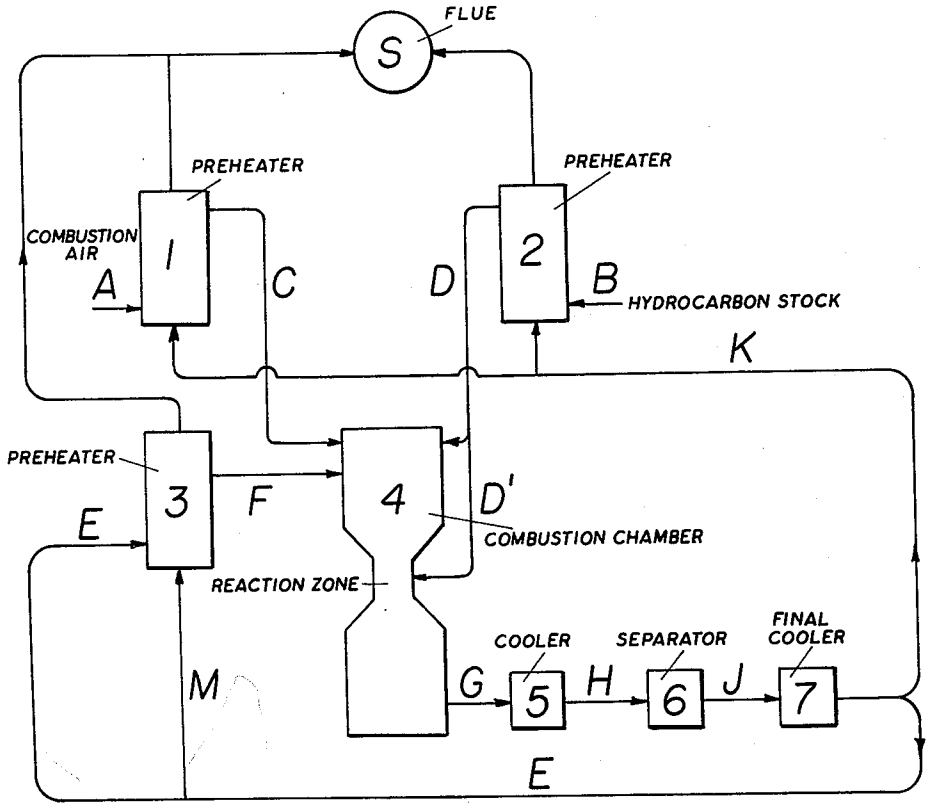

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PREPARATION OF CARBON BLACK

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This invention relates to the preparation of carbon black by incomplete combustion of hydrocarbons in gas or vapor form.

Various procedures are known for preparing carbon black by the breakdown of gaseous or vaporized hydrocarbons through incomplete combustion, but all have heretofore been beset by the difficulty that such breakdown necessarily requires the absorption of a definite amount of heat. Considering a given volume of hydrocarbon stock, if desired to break down a part thereof by incomplete combustion, it is necessary to burn a fraction of the hydrocarbons to cover the demands in heat absorbed by the breakdown reaction. The yields are accordingly poor, and in fact have ranged heretofore from about 3 to about 30% of the carbon content in the hydrocarbon stock used. Thus, from 97 to 70% of the carbon content in the hydrocarbons are lost.

It is an object of this invention to provide an improved method of carbon black preparation through incomplete combustion of gaseous and vaporized hydrocarbons, wherein the yields of carbon black are greatly increased, being as high as 90% or higher.

Another object is to provide active carbon black products of improved controllable granulometry, and specifically to provide a process wherein the operating conditions can be selectively controlled to provide desired particle sizes of from about 15 to about 300 millimicrons in the product.

In known processes of the type to which this invention relates, both the hydrocarbons, in gaseous or vapor form, and the combustion air, are delivered into the combustion space of the reactor in cool condition. For this reason the only thermal energy available to cover the heat requirements of the reaction is the heat evolved by combustion of a part of the hydrocarbon stock. It should further be noted that in all such methods the combustion proceeds with a deficiency of air, i.e. an excess of hydrocarbons. In these conditions, the combustion reaction rather than proceeding in accordance with either of the two following equations:

$$CH_4+2O_2=CO_2+H_2O-8{,}555 \text{ kcal./Nm.}^3 \text{ } CH_4 \quad (1)$$

$$C_3H_6+4.5O_2=3CO_2+3H_2O-21{,}070 \text{ kcal./Nm.}^3 \text{ } C_3H_6 \quad (2)$$

tends instead to proceed in accordance with either or both of the following equations

$$CH_4+1.5O_2=CO+2H_2O-5{,}510 \text{ kcal./Nm.}^3 \text{ } CH_4 \quad (3)$$

$$C_3H_6+3O_2=3CO+3H_2O-11{,}150 \text{ kcal./Nm.}^3 \text{ } C_3H_6 \quad (4)$$

At the same time it is found that one or both of the following reactions is simultaneously present:

$$CH_4+O_2=CO+2H_2-375 \text{ kcal./Nm.}^3 \text{ } CH_4 \quad (5)$$

$$C_3H_6+1.5O_2=3CO+3H_2-3{,}430 \text{ kcal./Nm.}^3 \text{ } C_3H_6 \quad (6)$$

Thus the amount of heat actually generated under the conditions indicated, by the combustion of a portion of the hydrocarbon stock, is only a minor fraction of the heat that would be generated by combustion of the same portion in an atmosphere containing an excess of atmospheric

oxygen. As a net result given a certain volume of hydrocarbons, in order to decompose a portion thereof by the processes heretofore available in the art, a substantially larger portion of said volume must be simultaneously burned thereby incurring great economic wastage.

In accordance with the invention the above difficulties are eliminated by the following steps:

As a first measure, the fraction of the hydrocarbon stock that is to be subjected to combustion to supply the necessary amount of heat for decomposing the remaining fraction of hydrocarbons, is burned in an excess of combustion air.

As a second measure, preferably though not necessarily applied simultaneously with the first, the combustion is made to proceed under superatmospheric pressure, e.g. in a range of about from 3 to 5 atmospheres, whereby complete combustion is more effectively ensured.

Further, the partial stream of hydrocarbon gas that is to be burned, and/or other fuel, is delivered into the reactor combustion chamber in a strongly preheated condition. Thus, where part of the hydrocarbon stock is used as the fuel, this may be preheated according to the invention to a temperature as high as or higher than the breakdown temperature thereof. Similarly, the invention contemplates preheating the combustion air (or oxygen-enriched air) to a temperature of e.g. 1600° C. As a consequence of the preheating steps, the high amount of enthalpy in the fuel and combustion air adds to the quantities of heat produced by the heat capacity of the fuels. The heat evolved in the reactor chamber is thereby greatly increased.

For controlling the combustion temperature in an optimum range, of say 1800° C., cool and/or preheated gases, e.g. part of the residual gaseous effluent from the process, are delivered into the combustion chamber.

Additionally, that portion of the hydrocarbon stock that is to undergo the breakdown reaction, preferably preheated as above indicated to about or slightly above its breakdown temperature, is discharged in heated condition into the stream of effluent gas resulting from the combustion of the remaining portion of the hydrocarbon and/or other fuel.

According to an important feature of the invention, it has been found that the yield of carbon black product can be further and considerably increased if carbon dioxide is introduced into the reagent stream. The carbon dioxide may be introduced alone or as a constituent in a suitable gaseous mixture, such as lime kiln gas, and may or not be preheated. The CO_2 thus introduced reacts with the hydrocarbons to produce an additional amount of carbon black, and it is found that the economy of the over-all process can thus be substantially increased.

For controlling the grade of the final carbon black product, the dwell time of the reagents in the reactor may be modified as from 0.08 to 0.6 second (approx.), and the reaction temperature may be controlled in the approximate range of from 1000 to 1500° C. In this connection it is noted that increasing the dwell time in the reactor at the reaction temperature increases the fineness of the product particles.

Immediately after the reaction has occurred the temperature of the reaction products should be suddenly cooled to a temperature below about 900° C.

As mentioned earlier herein, the heat required for the break-down reaction may be supplied by the complete combustion of fuels other than the hydrocarbon stock itself. For this purpose it is found to be of especial advantage to use a gas having a high CO content and having a highly uniform and constant composition, e.g. water

gas and/or hydrocarbon reforming gas. This is especially advantageous where the starting stock comprises methane for example. The air requirement for the combustion of methane is from 25 to 30% higher than that necessary for the combustion of CO, and the volume of methane combustion gases is also much higher than that of CO, for an equal heat output. Specifically, 1 cubic meter O_2 yields 6,055 kcal. when used in the complete combustion of CO, and only yields 4,270 kcal. when used for the complete combustion of methane. The combustible gases used as fuel instead of the hydrocarbon stock may be preheated to a temperature considerably higher than 1,000° C. Thus their enthalpy adds to the amount of heat generated by the combustion and increases the amount of heat available for the breakdown of the hydrocarbons.

A carbon black production process according to the invention may conveniently be performed by means of apparatus as indicated in schematic flowsheet form on the accompanying drawing, to which reference will now be made.

A preheater 1 serves to preheat a stream of combustion air delivered to it through inlet A; a preheater 2 preheats hydrocarbon stock delivered through inlet B; and a preheater 3 serves to preheat part of the residual gas effluent stream from the process recycled through conduit E. The preheated combustible and combustion gases from preheaters 1, 2 and 3 are delivered through lines C, D and F respectively into the combustion chamber at the top of a suitable reactor 4. The portion of the hydrocarbons which is to be used in the breakdown reaction proper is delivered through line D' into a midportion of the reaction chamber 4. From the base of the reactor the reaction products are delivered over a line G into a first cooler 5, where they are cooled to below about 900° C. e.g. by means of water spray. The cooled effluent then flows from cooler 5 over line H to a set of separators 6 and thence over line J to a final cooler 7. The cooled and purified effluent is recycled over lines K and M to serve as heating medium for the preheaters. A portion of the effluent may also be recycled into the main process by way of the line E as already indicated. Instead of (or in addition to) recycling the effluent gas, there may be delivered to the preheater 3 a CO_2 containing gas. In similar fashion any suitable gaseous or liquid fuel may be preheated in preheater 2. In this case a fourth preheater, not shown, may be provided for preheating the hydrocarbons to be broken down. In the drawing S designates a discharge stack or flue for the gaseous residue.

Some numerical examples will now be briefly described in order to clarify the process of the invention.

Example 1

Input:

130 kg. naphthalene preheated to 400° C.
70 Nm.³ air preheated to 1000° C.;
50 Nm.³ lime kiln gas preheated to 1000° C.

Output:

125 kg. carbon black; yield 90%.
145 Nm.³ residual gas 1,200 kcal./Nm.³.

Example 2

Input:

45 Nm.³ methane preheated to 900° C.;
105 Nm.³ air preheated to 1400° C.
138 Nm.³ residual gas preheated to 100° C.

Output:

15.1 kg. carbon black, or a yield of 78%;
270 Nm.³ residual gas at 1,200 kcal./Nm.³.

It will be immediately apparent from the above exemplary figures, to those familiar with this art, that the yields of carbon black obtainable by the method of the invention are far higher than any attainable by methods heretofore used.

What we claim is:

1. In a process for manufacturing carbon black by cracking gaseous and vaporized hydrocarbon stock, the steps of preheating said hydrocarbon stock to a temperature at least as high as the breakdown temperature thereof, separately preheating an oxygen-containing gaseous medium to a temperature of approximately 1600° C., conducting a first portion of said preheated hydrocarbon stock into a combustion zone together with an amount of said preheated gaseous medium sufficient to provide a substantial excess of oxygen in said zone beyond the theoretically required amount for complete combustion of said first portion of the hydrocarbon stock, maintaining a pressure of 3 to 5 atmospheres in said combustion zone, conducting the gaseous products of combustion from said combustion zone and the remaining portion of the preheated hydrocarbon stock into a reaction zone for endothermic reaction with each other in said reaction zone for a period between approximately 0.08 and 0.6 second, and controlling the temperature of said endothermic reaction to provide a temperature in said reaction zone between approximately 1000° C. and 1500° C. at the end of said period.

2. The process as in claim 1; further comprising the step of rapidly cooling the gaseous effluent from said reaction zone to a temperature below 900° C. so as to separate the carbon black from said gaseous effluent.

3. The process as in claim 2; further comprising the step of introducing carbon dioxide-containing gas into said reaction zone.

4. The process as in claim 2; further comprising the step of recycling a portion of said gaseous effluent into said reaction zone for controlling the temperature in the latter.

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