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PROCESS FOR MAKING FIBROUS CARBON

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The present invention relates to a novel form of carbon and process for making the same. More specifically, the principal object of the invention is to produce carbon in fibrous form by a process involving slow pyrolysis of hydrocarbon vapors. Other objects will also be apparent from the following detailed description of the invention.

Broadly stated, the process of the invention comprises passing a hydrocarbon gas, preferably diluted, through a cracking zone maintained at a temperature between 1150° and 1450° C. using a residence time of at least about 0.4 second and depositing fibrous carbon on one or more inert surfaces positioned within the cracking zone.

The success of the invention is due, at least to a substantial extent, to the discovery that fibrous carbon can be produced by very slow pyrolysis of hydrocarbon gas using definite and critical ranges of temperature, contact time, degree of concentration of hydrocarbon in the gas subjected to treatment, and degree of concentration of S as H₂S in the gas.

It will be appreciated from the foregoing that the present process is significantly different from the well-known pyrolysis of, for example, natural gas to produce carbon black. Such blacks are characterized primarily by their very low particle size. In contrast, the carbon of the instant invention is in the form of fibers usually of macroscopic size as a result of the critical reaction conditions of temperature, time, and concentration referred to above.

The invention is illustrated, but not limited, by the following examples:

Example I

Coke oven gas containing approximately 30% CH₄ and 55% H₂ was passed through a silica tube heated by a globar electric furnace. Temperatures were measured by a platinum-platinum rhodium thermocouple installed in a silica well. The flow rate was 0.322 liter/min., the temperature controlled at 1350° C. and the residence time in the tube was 2 seconds. A total of 8.37 grams of CH₄ were fed in this manner. A total of 4.2 grams of carbon was recovered, part of which was in the tube and part in the water quenching system used for cooling the exit gases. The carbon in the tube was made up in part of long gray carbon fibers spread out in the direction of gas flow from the entrance port and the thermocouple well, somewhat like a fan. The long whiskers of carbon fibers represented 7% of the carbon fed as methane and the total carbon was 62% of carbon fed as methane. Microscopic

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investigation showed very uniform mono filament fibers of around 4 micron diameter. The surface area was approximately equivalent to solid rods with a surface roughness factor of 2 to 4.

The electron microscope showed smooth rod-like filaments having average diameters between 4.3 and 4.7 microns. The air-blown, vacuum-dried material was substantially pure carbon and gave the following analysis: Carbon, 99.75%; hydrogen, 0.00%.

The flexible fibrous carbon was attached to a substrate of carbon which became progressively harder the closer it was to the walls of the ceramic tube and thermocouple well. Samples carefully shaped from all but the hardest parts of this substrate were shown under the microscope to consist principally of short fibers. The hard substrate was thus shown to have a fibrous structure.

Example II

A series of runs were made at approximately 1300° C. at contact times from about 0.15 to 9 seconds in apparatus similar to that described in Example I. The fiber yield was based on the amounts of carbon mats or whiskers obtained.

| Runs | 1 | 2 | 3 | 4 | 5 |
|--|------|------|------|------|------|
| Flow Rate (liters/min.) ¹ | 3.3 | .76 | .77 | 0.32 | .057 |
| Contact time (seconds) | 0.15 | 0.66 | 0.64 | 1.5 | 8.8 |
| OH ₄ charged (grams) | 22 | 14 | 20 | 12 | 5.7 |
| Carbon, Total Deposited (grams) | 1.3 | 3.9 | 6.7 | 4.2 | 2.9 |
| Yield on C in OH ₄ charged (percent): | | | | | |
| (a) Carbon Total | 8 | 36 | 44 | 53 | 67 |
| (b) Fiber | 0 | 3 | 4.0 | 5 | 9 |

¹ Room temperature.

A run carried out at 1250° C. gave approximately the same results as obtained at 1300° C. Fibrous carbon was also obtained using 1150° C. or 1450° C. However, with temperatures below 1150° C. or above 1450° C. little to no fibers were formed.

The above runs show that there is an increase in yield of both carbon black and fibrous carbon with increased contact time. Thus, as indicated, no carbon fibers were obtained in Run #1, i. e., when using a contact time of about .15 second. Production of significant amounts of fibers started at about 0.4 second. Hence, the residence or contact time for exposing the hydrocarbon should be at least 0.4 second and may desirably go as high as 15 seconds and even higher.

Example III

A series of runs were made using various concentrations of hydrogen sulfide (H₂S) in the gas stream as a catalytic agent for fibrous carbon growth. These runs were made at approximately 1350° C. using contact times of from 1.0 to 1.5 seconds. The apparatus of Example I was changed by attaching a baffle to the gas inlet tube. This baffle was a cone ¾ inch long made of 30 x 30 Nichrome wire gauze. This dispersed the gas stream. A quartz baffle worked equally well. The results are summarized in the following table:

| Run No. | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|------|------|------|------|------|------|------|------|
| Flow Rate (liter/min.) Coke Oven Gas | 0.33 | 0.46 | 0.45 | 0.45 | 0.39 | 0.42 | 0.38 | 0.46 |
| Hydrogen Sulfide Charged (H ₂ S Mol percent) | 0 | 0.13 | 0.23 | 0.37 | 0.45 | 0.47 | 0.42 | 4.0 |
| Contact Time (seconds) | 1.5 | 1.1 | 1.1 | 1.1 | 1.3 | 1.2 | 1.4 | 1.1 |
| Methane Charged (grams) | 8.6 | 4.4 | 4.9 | 3.9 | 4.2 | 4.4 | 3.3 | 7.6 |
| Yield of Fibrous Carbon on Carbon in Methane Chgd.: | | | | | | | | |
| (grams) | 0.20 | 0.13 | 0.19 | 0.42 | 1.14 | 1.24 | 1.03 | 0.79 |
| (percent) | 3 | 4 | 5 | 14 | 37 | 37 | 41 | 14 |

While it is possible to obtain fibrous carbon without using hydrogen sulfide as a catalyst, significantly higher yields are produced, as evidenced by Runs 6 to 13 above, using at least about 0.3% by volume of hydrogen sulfide, on the basis of coke oven gas fed. The hydrogen sulfide may also be added by introducing into the gas, volatile sulfur containing materials, such as carbon disulfide and sulfur dioxide. These react with the hydrogen diluent at elevated temperatures to produce hydrogen sulfide.

The fibrous carbon was obtained principally as intertwined fiber mats having varying degrees of flexibility and as whiskers of roughly parallel fibers. These were collected and agitated in a 40-mesh sieve to remove fines. The yield of fibrous carbon was computed from the weight of the carbon retained in the sieve. By this procedure a certain amount of microscopically fibrous carbon in the form of hard carbon adhering to the collecting surfaces, and in the form of fines was removed from the mats and whiskers and was not computed as part of the yield of fibrous carbon.

Example IV

A series of runs were made using mixtures of pure methane and diluent gases, namely, hydrogen and nitrogen. Hydrogen sulfide was used as a catalyst and the concentration of this constituent also varied. The runs were made at approximately 1350° C. and contact times of 1.0 to 1.4 seconds employed. The apparatus used was that described in Example I and modified in Example III. Yields were determined as in Example III.

| Run No..... | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|--|------|------|------|------|------|------|------|
| Inlet Flow Rate (liter/min.) | 0.43 | 0.46 | 0.45 | 0.45 | 0.45 | 0.44 | 0.45 |
| Inlet Gas Composition: | | | | | | | |
| CH ₄ (Vol. percent) | 30 | 30 | 16 | 29 | 72 | 75 | 99 |
| N ₂ (Vol. percent) | 70 | 70 | | | | | |
| H ₂ (Vol. percent) | | | 84 | 71 | 18 | 25 | |
| H ₂ S (Vol. percent) | 0.30 | 0.31 | 0.32 | 0.32 | 0.57 | 0.20 | 0.89 |
| Contact Time (seconds) | 1.2 | 1.1 | 1.1 | 1.1 | 1.1 | 1.2 | 1.1 |
| Methane Charged (grams) | 4.6 | 4.0 | 2.7 | 4.4 | 11 | 11 | 8.5 |
| Fibrous Yield: | | | | | | | |
| (a) (grams) | 0.06 | 0.06 | 0.08 | 0.97 | 1.38 | 0.14 | 0.11 |
| (b) Percent on carbon in CH ₄ charged | 2 | 2 | 4 | 30 | 16 | 2 | 2 |

As shown above, some fibrous carbon can be obtained using substantially pure, i. e., undiluted, hydrocarbon gas. However, for best results the hydrocarbon gas should be diluted, preferably with hydrogen. Methane concentration in a mixture subjected to pyrolysis is also important with respect to yield and preferably falls within the range of 20 to 80 vol. percent.

While hydrogen and nitrogen have been illustrated above as the diluent gases, other gases such as the carbon oxides, argon and the like may be used.

Example V

The reaction zone of the same apparatus as used previously was filled with rough alundum balls of approximately ¼" diameter. Coke oven gas containing 0.36 percent by volume of hydrogen sulfide was passed through the balls heated to 1350° C. The flow rate was 0.62 liter per minute at room temperature and the contact time was 0.5 second. Within 10 minutes 0.15 gram (18% of the carbon charged as methane) of soft gray mats of fibrous carbon had been deposited on the surface of the balls and the containing tubes. After cooling, the carbon was removed from the balls with an air jet.

Example VI

A mixture of benzene vapor (3.9 percent by volume), hydrogen sulfide (0.29 percent by volume) and hydrogen (95.8 percent by volume) was passed into the same apparatus as for Example III. The overall inlet flow rate was 0.52 liter per minute, the residence time was 1.0 seconds and the temperature was 1350° C. After one

hour 0.18 gram of typical gray carbon mats had been deposited (5% yield on carbon charged as benzene).

One or more inert bodies or surfaces should be placed within the reaction zone, for the purpose of collecting the fibrous carbon and any inert surface may be used for this purpose. Thus, as shown in the foregoing examples, the collecting surface may be the inner walls of the reaction tube itself. As an alternative, alundum pellets or other inert bodies may be positioned within the reaction zone. For example, coke oven gas may be passed through ceramic tubes or ducts heated by blast furnace slag (outlet at 1400° C.) and immediately contacted with a slowly falling bed of ceramic balls. The carbon fiber which builds up on these balls can be separated by a blast of gas or by a water spray after cooling and the carbon thereafter being filtered from the water, or by other physical means apparent to those skilled in the art. Contact time and temperature can be controlled within the ranges referred to above by known gas flow and reactor volume relationships.

For mixtures of hydrogen and methane or other hydrocarbon gas the most favorable concentrations for the formation of fibrous carbon have been found to be in the range of 0.05 to 0.2 grams of carbon (of the gas) per liter at 300° C. With methane mixtures, this corresponds with a methane concentration of 20 to 80 volume percent. When making fibrous carbon from hydrocarbons other than methane and a diluent gas, it is preferred to utilize an equivalent concentration of the hydrocarbon on a weight basis. That is, there is preferably utilized a concentration of the hydrocarbon such that at 300° C. the weight of carbon in the hydrocarbon per liter of diluted gas lies in the range of about 0.05 gram to about 0.2 gram. In producing fibrous carbon from hydrocarbons other than methane, hydrogen sulfide or hydrogen sulfide-producing materials are preferably used in such quantity that the weight of hydrogen sulfide present or formed amounts to more than about 2% of the weight of the carbon present as hydrocarbon. However, fibrous carbon may be formed according to the process of our invention by utilizing concentrations of hydrocarbons and of hydrogen sulfide lying outside these preferred ranges.

As the hydrocarbon gas, paraffinic hydrocarbons such as methane, butane, octanes and dodecanes, olefinic hydrocarbons, such as ethylene, propylene, butylene, heptenes and decenes, acetylenic hydrocarbons, e. g., acetylene; alicyclic hydrocarbons, such as cyclopentane or cyclopentene; and aromatic hydrocarbons, such as benzene may be utilized successfully either singly or as mixtures to make fibrous carbon. Coke oven gas may also be used, as well as other gases containing oxygen. For example, various oxygenated materials, such as isopropanol, may be heated to elevated temperatures below those used in the process of the present invention to give gaseous mixtures containing hydrocarbons in addition to oxygenated compounds. Such gaseous mixtures constitute suitable feed stocks according to the process of our invention.

The product of the invention is obtained in various forms depending on the temperature, the contour of the gas stream, its velocity past the collecting surface, the amount of catalyst and other conditions. Some long single filaments can be obtained as can powdery fines consisting of very short filaments. The carbon also is deposited as whiskers of parallel fibers, as flexible mats or felts of interlaced filaments, and as mats which can be made progressively less flexible until there are obtained rigid, quite hard pieces of carbon of varying bulk density. When carefully broken up and placed under the microscope, each of these microscopic sorts of carbon is shown to be composed principally of filaments or filamentary particles. X-ray examination showed the filaments to be somewhat oriented, partially graphitized carbon.

By the process of our invention one can obtain carbon in the form of filaments which have a wide variety of shapes, for example, straight, crooked, smooth-surfaced,

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rough surfaced, with branches, without branches, of uniform diameter along their length, of non-uniform diameter along their length, similar to other filaments in a mat, dissimilar to other filaments in a mat, filaments joined to microscopic pieces of non-fibrous materials, filaments not so joined, etc. The filaments vary in diameter from a small fraction of a micron to over 100 microns and vary in length from several times the diameter to a number of inches.

The nature of the product can be modified by changing the conditions of formation. Thus, the deposition of springy, gray mats consisting practically entirely of thin, uniform, straight, smooth unbranched filaments is favored by high temperatures, whereas lower temperatures favor the deposition of black, fluffy mats consisting principally of thick, crooked, non-uniform, branched, rough-surfaced filaments. In addition, the fibrous carbon of the invention is a compatible filler for numerous plastics and elastomers, e. g., rubber. The fiber mats possess high heat stability and low bulk density and are therefore excellent high temperature insulation material. The rigid form of fibrous carbon promises to be utility in various electrical applications.

It will be appreciated that various modifications may be made in the invention without deviating therefrom as defined in the appended claims wherein:

We claim:

1. A process for making fibrous carbon comprising the steps of passing through a pyrolysis zone a gas comprising 20 to 80% methane, the balance of the gas primarily being hydrogen, at a temperature between 1150° and 1450° C., using a residence time of between 0.4 second and 15 seconds and collecting the fibrous carbon.

2. The process of claim 1, wherein the fibrous carbon is collected on at least one inert surface in said reaction zone.

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3. A process according to claim 1 wherein there is present 0.3 to 4.0% of hydrogen sulfide as a catalyst.

4. A process according to claim 3 wherein the hydrogen sulfide is formed in situ.

5. A process for making fibrous carbon comprising the steps of passing through a pyrolysis zone coke oven gas at a temperature between 1150° and 1450° C., using a residence time of between 0.4 second and 15 seconds and collecting the fibrous carbon.

6. A process for making fibrous carbon comprising the steps of passing through a pyrolysis zone coke oven gas at a temperature between 1150° and 1450° C., using a residence time of between 0.4 second and 15 seconds in the presence of 0.3 to 4.0% of hydrogen sulfide as a catalyst and collecting the fibrous carbon.

7. A process for making fibrous carbon comprising the steps of passing through a pyrolysis zone a gas consisting of coke oven gas at a temperature between 1250 and 1350° C., using a residence time of between 0.4 second and 15 seconds in the presence of 0.3 to 4.0% of hydrogen sulfide as a catalyst and collecting the fibrous carbon.

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