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CONVERSION OF METHANE INTO LIQUID HYDROCARBONS

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The present invention relates to the conversion of methane into liquid hydrocarbons, and has particular reference to the constructional materials of the vessels employed in this process.

It is already known that methane or gases containing the same, such as natural gas, coke oven gas or fractions of such gases can be converted into liquid hydrocarbons, especially into aromatic hydrocarbons such as benzene and its homologues, by a thermal treatment at temperatures of about 800° to 1200° C. To the industrial application of this process there is the great objection that the constructional materials hitherto proposed are not sufficiently resistant at the necessary temperatures or give rise to undesirable side reactions, especially to the deposition of carbon black. The materials used in laboratories, such as quartz or porcelain, cannot be used on an industrial scale. Similarly iron and the usual special steels, such as V2A-steel or WT2-steel, are useless since they have the effect of promoting catalytically the decomposition of the methane into carbon black and hydrogen.

I have now found that the metals chromium, tungsten and molybdenum as such or in the form of alloys of these metals with each other, or graphite constitute constructional materials which are to a large extent free from the said drawbacks. These materials are very resistant at temperatures of from 800° to 1200° C., that is to say, they are neither deformed nor are they chemically attacked by the materials with which they come into contact, nor do they become permeable to certain substances, such as hydrogen. Furthermore, the said constructional materials promote the conversion of methane into liquid hydrocarbons to a large extent but influence the decomposition of methane into carbon and hydrogen no more, and in some cases even less, than quartz or porcelain. The said materials may also be employed as coatings on other refractory materials, such as steels of high melting point. When the coatings are suitably prepared, for example by applying them electrolytically or by thermal diffusion to the material of which the apparatus is constructed, they adhere so well that they do not scale off even after use for long periods of time. Any lustrous carbon which may separate after working for long periods of time and which also exerts a favorable catalytic effect may be removed mechanically or by burning with air from time to time.

The construction of the graphite apparatus is preferably carried out by subjecting graphite powder, as for example, oil coke to strong pressure and thereupon cutting slabs or producing tubes from the block thus produced. Also parts of the apparatus may be pressed directly from graphite powder.

The following examples will further illustrate the nature of this invention, but the invention is not restricted to these examples.

Example 1

15 liters of 90 per cent methane are passed per hour at 1050° C. through an electrolytically chromed steel tube having an internal diameter of 16 millimeters and a length of 60 centimeters. By one passage of each cubic meter of methane 60 grams of a liquid product are obtained of which 50 per cent consists of benzene the remainder being a thinly liquid brown tar.

From time to time any lustrous carbon which may have been deposited is burnt off with a current of air at a somewhat lower temperature, methane then being led through again at 1050° C. The yields after this treatment are the same as before and do not vary even after working for long periods of time. The reaction tube is not attacked.

The same result is obtained if the reaction tube consists of a steel-tube which has been internally coated with chromium, for example by diffusion of chromium powder by the action of heat, or of a steel-tube which has been coated with an alloy of chromium and molybdenum, for example by applying chromium electrolytically onto the inner surface of said steel-tube and then allowing molybdenum thermally to diffuse into the layer of chromium until the desired composition is obtained.

Example 2

63 liters of a gas mixture consisting of 86.4 per cent of methane, 6.6 per cent of hydrogen and 7 per cent of nitrogen is passed through a graphite tube 1 meter in length and 15 millimeters in internal diameter, which is embedded in a tube of quartz or chamotte and which is externally heated by an electric furnace over a length of 60 centimeters to a temperature of from 1000° to 1020° C. 68 liters of a gas consisting of 64.5 per cent of methane, 26.8 per cent of hydrogen, 6.5 per cent of nitrogen and 2.2 per cent of unsaturated hydrocarbons consisting mainly of acetylene are obtained after stripping off the liquid constituents from the products leaving the reaction space. 4.1 grams of liquid products of which 95 per cent boil up to 110° C. are obtained per hour. From 1000 liters of methane therefore 70 grams of liquid hydrocarbons boiling below 110° C. are obtained. It is preferable to suck off continuously or after definite periods the gas which has diffused through the graphite into the space between the tube of quartz or chamotte and that of graphite in order to avoid an accumulation of hydrocarbons in the graphite which may cause a deposition of carbon. A diffusion of the hydrocarbons into the graphite may also be prevented by filling the space between the quartz-tube and the graphite-tube with an inert gas in such a manner that a higher pressure prevails on the outer surface of the graphite-tube than on the inner surface of this tube.

A deposition of carbon or a decrease of the yield of the desired products does not take place even after working for a long time.

What I claim is:

1. In the production of liquid hydrocarbons by heating a gas comprising methane to a temperature between about 800° and 1200° C., the step which comprises confining said gas by means of a surface consisting of an element selected from the group consisting of chromium, tungsten, molybdenum and carbon in the form of graphite.

2. In the production of liquid hydrocarbons by heating methane to a temperature between about 800° and 1200° C., the step which comprises confining said gas by means of a surface consisting of an element selected from the group consisting of chromium, tungsten, molybdenum and carbon in the form of graphite.

In testimony whereof I have hereunto set my hand.

CHRISTIAN STEIGERWALD.