UNITED STATES PATENT OFFICE

1.940,209

PROCESS FOR PRODUCING HYDROCAR-BONS HAVING A HIGH CARBON CONTENT FROM HYDROCARBONS HAVING A LOW CARBON CONTENT

Franz Fischer and Helmut Pichler, Mulheim-onthe-Ruhr, Germany

No Drawing. Application July 15, 1931, Serial No. 551,052, and in Germany July 18, 1930

9 Claims. (Cl. 260—170)

It is known to produce hydrocarbons having a high carbon content from hydrocarbons having a low carbon content (that is to say it is known for example to produce acetylene from methane) 5 by heating the hydrocarbons to high temperatures. It is also known that such heating can be effected not only, for example, by electrical means or by an arc, but also that the necessary temperature can be secured by mixing the hydrocarbon to be heated with a small volume of oxygen and thus producing partial combustion, or by passing such a hydrocarbon through a flame produced by chemical reaction.

It has, however, been found that the methods, 15 by which the heating is obtained by partial combustion, produce relatively small quantities, for example, of acetylene from methane. It has been found by others that by the partial combustion of methane in oxygen, a final gas is obtained 20 which contains at most 3.5% of acetylene, and that the increase of the acetylene concentration up to the hitherto maximum of 5% demands such a large addition of oxygen that the process becomes uneconomical. We have found that the 25 low values of acetylene concentration obtained during partial combustion can be increased if certain precautions be taken. The heating period must be of such duration that the maximum volume of acetylene can be produced. The heating 30 period must, however, be so limited that there remains very little time within which the steam first obtained can act upon the hydrocarbons produced, for example acetylene. Accordingly the possible action of the water vapour formed 35 during the reaction is consciously reduced to a minimum. The absence of large volumes of water vapour involves the further practical advantage that it becomes unnecessary to heat large volumes of inert gas to high temperatures.

It has been found that it is necessary, when producing hydrocarbons having a high content of carbon from hydrocarbons poor in carbon by burning the latter with a volume of oxygen, or gases containing oxygen, such as is insufficient to produce complete combustion, to limit the heating periods to 1/100th of a second and less, preferably a few thousands of a second. According to a known process for the partial combustion of hydrocarbons poor in carbon heating pe-50 riods are employed which are over 1/100th of a second and preferably several hundredths of a second in every case. By adhering to heating periods of less than 1/100th of a second a substantial increase in yield is obtained as compared with the yield secured with longer heating pe-

riods. In order to secure the duration of heating needed for producing acetylene in the presence of steam at the temperature prevailing, it is desirable to effect the partial combustion in tubular chambers relatively small in cross-sec- 60 tion. The d'ameter of the tubular chambers lies preferably between 2 mm. and 10 mm., or the necessary cross-sections lie advantageously between approximately 4 square mm. and 100 square mm. It is furthermore important that the tubu- 65 lar chambers should be increased in length according to the increase in cross-section. In the use of tubes their length must be at least 10 times as great as their diameter and preferably considerably longer. The combustion mixture is 70 advantageously heated by the use of the reaction gases in a heat exchanger, preferably by heating the gas containing oxygen separately from the gas containing methane. It is of advantage not to use the waste gas for preheating 75 gas containing oxygen and methane directly after it leaves the heating zone, but first to allow the waste gas to cool by several hundred degrees in order that it can no longer change by the breaking up of acetylene during the transmission of 80 heat, which always needs time. The cooling of the reaction gas hereinbefore referred to is advantageously effected by adding to it at the position where it leaves the actual combustion chamber, a quantity of cold gas, for example, of 85 another cooled reaction gas from which the acetylene has been if necessary removed. Furthermore it is possible to effect the cooling by employing the heat for producing steam. It will be understood that for the last-mentioned pur- 90 pose hot reaction gas should be used, which has been slightly cooled by the addition of the cooled reaction gas. To start the process it is furthermore advantageous to heat the gases first from other sources of heat, for example by electrical 95 means, and it is preferable for safety always to employ a small additional electrical heating apparatus which may be in the form of a spark gap, for the purpose of ensuring the burning of the reaction mixture.

As even where there is a high yield of acetylene of approximately 10% in the reaction gas obviously not all the methane is converted into acetylene, and it means a further increase in the economy of the process, which is in itself already high, 105 as appears from the examples hereinafter appearing, if the process be so conducted that carbon monoxide and hydrogen approach as nearly as possible to the proportions of 1:2 in the reaction gas. In these circumstances, after the 110

acetylene has been removed, the residual gas may be used for the synthesis of benzine, for in the process hereinbefore described the organic sulphur compounds, usually present in raw gases which are unfavourable to catalytic operations, are broken up without further treatment.

The process of the invention enables not only acetylene but also other hydrocarbons to be produced such as ethylene and benzol.

The invention may be carried out in the fol-

lowing manner:

Some of the heat which is necessary for converting hydrocarbons having a low content of carbon into hydrocarbons having a high content 15 of carbon, is transmitted from an already heated heat-carrier and only the remainder of the necessary heat is produced in the manner hereinbefore described by adding oxygen and by direct partial combustion. In this way it is possible to 20 make a considerable saving in oxygen.

In this process a heat carrier is first advantageously heated according to a regenerative system, whereupon the reaction gas is passed through, while at the same time the desired vol-25 ume of oxygen or air is added, partial combustion taking place in the hottest zone. Thereupon the heat carrier is re-heated and the reaction mixture is then once again passed through together with

oxygen in alternation.

Example I

Coke oven gas and oxygen in the proportion of 5:1 are passed through a tube made of Pythagoras composition and of an internal diameter of 35 3 m. m. with a reaction zone of 100 m. m. in length. When the tube has a temperature of 1000° C. the best yield of acetylene obtained is 6.2% in the final gas, the duration of heating according to the invention being 8.5 thousandths 40 of a second. In comparison, half the reaction period produces only 1.8% of acetylene in the reaction gas, while double the period gives 5% of acetylene therein. At a temperature of 1600° C. under the conditions above indicated, the yield of 45 acetylene is at its maximum when the duration of heating is 2.9 thousandths of a second, the yield then being 6.6%. A heating period of 6 thousandths of a second gives more than 4% to 5% of acetylene in the reaction gas. In comparison 50 with these results a heating period of 12 thousandths of a second gives less than 1% of acetylene in the reaction gas.

In the experiment carried out at 1600° C. in which a reaction gas with 6.6% of acetylene is 55 obtained, as the initial gas contains 19.6% of methane, and for producing one volume of acetylene it is necessary to have two volumes of methane 67% of the methane is converted into acetylene in one operation. It will be under-60 stood that the residual gas in this process does not contain carbon monoxide and hydrogen in the proportion of 1:2, but in the proportion of 1:4. If this gas is to be used for the synthesis of benzine, this is effected most 65 advantageously in admixture with water gas.

Summarizing, it may be stated that by correctly determining the duration of heating, that is to say by the correct arrangement of apparatus, it is possible to obtain an economy in the conversion of methane to acetylene to a degree hitherto unknown.

We claim:

1. A process for producing hydrocarbons richer in carbon from gaseous hydrocarbons of the aliphatic series by burning the hydrocarbons in the presence of oxygen in volume insufficient to effect complete combustion, consisting in subjecting the gaseous mixture to a temperature of not less than 1000° C. for a period of less than onehundredth of a second so that any subsequent action of the resulting steam upon the hydrocarbons having a high carbon content that are produced is avoided.

2. A process according to claim 1, wherein the hydrocarbon gas mixture after subjection to heat at a temperature of not less than 1000° C. for the period of less than one hundredth of a second is cooled by the admixture of cold gas immediately on leaving the hottest zone.

3. A process according to claim 1, wherein the oxygen is present in such quantity that the residual gas resulting from the heat treatment contains carbon monoxide and hydrogen approximately in the proportion of 1:2.

4. A process according to claim 1, wherein the hydrocarbon to be subjected to treatment and a 100 gas containing oxygen for the supply of oxygen for combustion are separately heated by transmission of the sensible heat of the reaction gases resulting from the treatment.

5. A process according to claim 1, wherein the 105 hydrocarbon to be subjected to treatment is preliminarily heated by electrical means which serve also to maintain the reaction during the period of heating.

6. A method of carrying out the process ac- 110 cording to claim 1, in which the application of heat for the period less than one hundredth of a second is effected while the gas under treatment is traversing a path, the cross-sectional area of which lies between 4 and 100 sq. mms.

7. A method of carrying out the process according to claim 1, in which the application of heat for a period less than one hundredth of a second is effected while the gas under treatment is traversing a path, the cross-sectional 120 area of which lies between 4 and 100 sq. mms. and in which the length of the zone by which heating is applied is at least ten times as great as the diameter of a circular area representing the cross-sectional area of the passage.

8. A process for producing hydrocarbons richer in carbon from gaseous hydrocarbons of the aliphatic series, consisting in heating the hydrocarbons by heat transmission from a previously heated heat carrier, and supplying the remainder 130 of the heat necessary for converting the hydrocarbon having a low carbon content into a hydrocarbon having a higher carbon content by burning the hydrocarbon in the presence of oxygen in volume insufficient to effect complete com- 135 bustion, the temperature being maintained at not less than 1000° C. for a period of less than onehundredth of a second, so that any subsequent action of the resulting steam upon the hydrocarbons having a high carbon content that are 140 produced is avoided.

9. A process according to claim 8, wherein the heat carrier is heated regeneratively.

> FRANZ FISCHER. HELMUT PICHLER.

145

115