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COMPLETE SPECIFICATION.

Process for the Production of Higher Hydrocarbons.

We, Professor Dr. FRANZ FISCHER, a citizen of the German Republic, and HELMUT PICHLER, citizen of Austria, both residing at 1 and 2, Kaiser-Wilhelm-Platz, Mülheim on the Ruhr, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The invention relates to a process for the production of higher hydrocarbons by heating methane.

The production of hydrocarbons with a higher percentage of carbon than methane by heating methane is known in itself. The general procedure has been to conduct the methane through pipes heated from outside, sometimes under increased pressure, with the use of catalysers and with increased rate of flow for the gas to be treated. But by the application of any of the methods hitherto known it has not been possible to produce economically hydrocarbons with a higher percentage of carbon than methane, especially carbocyclic hydrocarbons, by heating methane. Generally the assumption was, that at temperatures above the red hot state the methane substantially would decompose into its components, viz. carbon and hydrogen.

We now have found, that this decomposition of the methane into its elements may be obviated even at temperatures of about 1000° C. and above, and that especially aromatic hydrocarbons are produced, if the duration of the heating to the said high temperatures is made very short. It has been found that the use of catalysers is of no value especially in the production of unsaturated aliphatic hydrocarbons. An essential feature of the process according to the present invention, however, is that, although the methane or the methane containing gas mixture is heated to a temperature where the methane molecule begins to decompose, this process of decomposition is not allowed sufficient time to proceed to such a degree that all four hydrogen atoms will be split off from the carbon. In this respect it has been found, that it is not admissible to heat longer than one second to temperatures of more than 1000° C., if it is intended to obtain considerable quantities of non-saturated and aromatic hydrocarbons, i.e. quantities as are to be considered in actual practice. The shorter the period of heating, the better generally will be the output of the process. If the time of heating is shorter than one second, the result will be, that at temperatures of 1000° C. and above practically no free carbon is separated out. At temperatures essentially below 1000° C., however, the output, especially of aromatic hydrocarbons, will also be slight.

It has already been proposed to produce unsaturated aliphatic hydrocarbons by passing saturated aliphatic hydrocarbons, such as methane and mixtures containing same at atmospheric or increased pressure over a catalyst heated to temperatures of 700 to 1000° C. or still higher at a sufficient speed to preclude further condensation of the products primarily formed, and this catalytic process is not claimed here. It further has been proposed to produce said unsaturated aliphatic hydrocarbons from methane and the like by passing such gases alone or in a diluted state through a flame. As this flame must be produced by means of gases containing oxygen, either by burning a suitable combustible gas in the presence of oxygen or by burning a branched-off portion of the gas to be treated in the presence of oxygen, so in any case a considerable admixture of diluted or undiluted oxygen with the gas to be converted will take place. Such a dilution with oxygen does not take place in the present process, and this known process is not claimed in the present specification.

According to our present invention the methane or the methane-containing gases are to be heated at a temperature of at least 1000° C. during a period not exceeding one second only, the use of catalysts and the simultaneous introduction of oxygen or oxygen-containing gases being avoided.

The process according to the present invention will be described in the following by way of example in one form of execution.

Methane is conducted through narrow pipes of 3 to 5 millimeters width at a temperature of 1000 to 1100° C. with such a velocity as to make the period of heating at this high temperature last only 1/5 to 1/20 of one second. Thick mists of white or slight yellowish brown colour then pass out from the outlet openings of the pipes, from which mists benzene and other aromatic hydrocarbons with higher boiling point may easily be separated out. By one passage of the gases through the heated pipes 10 to 20% by weight of the methane is converted into these aromatic hydrocarbons. In this process practically no free carbon is separated.

When the temperature in this process is increased considerably over 1200° C., a strong separation of carbon is to be observed even if very high flowing velocities are used, suppose that pure methane is employed. When, however, the employed methane is diluted by considerable quantities of inert gases, the temperature may yet be increased correspondingly.

Generally not all the methane passed through the apparatus is decomposed, but free hydrogen and slight quantities of unsaturated, gaseous hydrocarbons are also formed. The mixture of methane and hydrogen thus produced as a by-product may now be subjected several times to the same converting process.

There is, however, also the possibility of binding the free hydrogen produced at the same time with the formation of the higher hydrocarbons again to carbon, i.e. to transform the hydrogen wholly or partly into methane again, for instance by admixing carbon monoxide or carbonic acid or water gas to the reaction gases of the described process after they will have been freed from the formed higher hydrocarbons, and by then using the hydrogen for hydrogenating the oxides of carbon by way of catalysis. For instance methane may thus be produced by means of a nickel catalyser, and said methane may then be subjected to the thermal methane decomposition again in the manner above described, and so on. It is further possible, provided the necessary conditions, to follow up the mineral oil synthesis by way of catalysis when using other catalysers, and to subject the final gas, rich in methane, resulting herefrom again to the thermal decomposition of methane according to the present invention, and so on.

As in the thermal methane decomposition above described unsaturated and aromatic hydrocarbons will be produced, the hydrogen bearing reaction-gas may also be used to hydrogenate for instance aromatic hydrocarbons, the above mentioned reaction-gas becoming poorer of hydrogen and therefore relatively richer of methane in this hydrogenating process, so that it thereby becomes better adapted for a further thermal decomposition by the process of the present invention.

The raw material to be used in the process according to the present invention may be pure methane or methane diluted with other gases or vapours, e.g. coke gas; the best material for this purpose, however, is pure methane.

The novel process may be performed at ordinary or also at reduced pressure.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of producing higher, especially unsaturated and aromatic hydrocarbons by thermal decomposition of methane in the pure state or diluted with other gases, in which the said gas or gas mixtures are heated at high temperatures during a short time, characterised by the fact that the methane or the methane-containing gases are heated at a temperature of at least 1000° C. during a period not exceeding one second only, the use of catalysts and the simultaneous introduction of oxygen or oxygen-containing gases being avoided.

2. A process according to claim 1, characterised by the fact that the free hydrogen formed in the decomposition of the methane is partly or completely bound again to carbon for freshly forming methane, the methane thus obtained being subjected again to the thermal decomposition.

3. A process according to claim 1, characterised by the fact that the remaining hydrogen bearing reaction-gas is mixed with oxides of carbon or gases containing same and is then subjected at elevated temperatures to the action of catalysers for forming mineral oils from carbon oxides and hydrogen, the remaining final gas freed from the formed mineral oils and richer of methane being subjected again to the thermal decomposition of methane, and so on.

4. A process according to claim 1, characterised by the fact that the free hydrogen produced by the decomposition of methane being used wholly or partly for hydrogenating the higher hydrocarbons produced before in the thermal decomposition of the methane.

Dated this 14th day of December, 1928.
MARKS & CLERK.

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