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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for the Production of Higher Hydrocarbons.

I, Professor Dr. FRANZ FISCHER, citizen of the German Republic, residing at 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 carbocylic 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.

The fact that methane or the methane bearing gases must be heated to temperatures above red hot, is the reason, why the methane should be heated in an apparatus, which makes possible the utmost utilisation and recovery of the heat applied. This object is obtained according to the present invention by using the regenerative working system for this purpose.

For instance a shaft-like furnace built from refractory material and made gas-tight by means of an outer sheet metal casing is first heated by burning gas or also by means of any suitable flue gases. The heat of the gases passing out from the furnace is stored up separately.

If the action of hot blasting has taken place from below upward, it is interrupted at a suitable time, and the methane or methane bearing gas now is passed through the furnace shaft from top downwards. This gas takes heat from the lining or from the filling bodies of the shaft and is heated thereby till it arrives at that hottest zone of temperature, where its decomposition is beginning. This process of passing through and decomposing the methane or methane containing gas in the shaft is continued till the shaft has cooled down too much. The heat of the reaction-mixture passing out of the shaft at its lower end and hereafter conducted into suitable collecting and absorbing devices is preferably stored up in order to utilize it entirely.

After the shaft has become too cool for the further decomposition of the methane, the shaft is hot blasted again in the aforesaid manner, and the heat stored from the decomposition process is now used for preheating the combustion air, or the gas to be burnt, or both of them. The working process is repeated in this manner continually.

It is of high importance that the heat economy in this process is carried to the highest possible degree. In order, however, to carry through this process with full economic effect, further measures are necessary in order to prevent as much as possible the methane decomposing or disintegrating into carbon and hydrogen according to the equation: $CH_4=C+2H_2$, i.e. that all four hydrogen atoms are split off therefrom, but to obtain the result of building up higher hydrocarbons from the radicals produced by splitting off of only a part of the hydrogen atoms from the methane, said radicals then combining with one another or polymerising.

For this purpose arrangements have to be made, on the one hand, that the time of heating the methane in the hottest zone is very short and is not more than one second, preferably not more than a fraction of a second, whereas the time of heating in the range of temperature below red heat is without any importance. The optimum heating duration in the hottest zone will change according to the catalytic behaviour of the material used for the lining or for the filling material.

As the hot-blasted furnace or tower gradually cools down during the passage of the methane or methane containing mixture, it is advisable to increase the duration of the period of highest heating in the same measure as the temperature of the shaft or tower drops, i.e. to reduce the passage velocity of the methane or the like in the measure as the furnace cools down.

For the lining or the filling bodies of the furnace a material may be used which, though it favours the decomposition of methane, on the other hand will prevent as much as possible the separation of free carbon. For this reason iron, nickel, cobalt or other materials containing considerable quantities of such metals should not be used for the present purpose. A very useful material, however, is silicic acid very poor in iron, in the form of silica stones or bricks or of silica gel.

The gaseous, liquid and solid products produced by the decomposition of methane according to the process described may be varied as to their relative quantities within certain limits by suitably adapting or modifying the working conditions. Any suitable method may be applied for separating the single products.

The remainder of methane not transformed may be passed yet several times through the apparatus for further utilisation, or, since it contains hydrogen, it may be used to replace lighting gas or hydrogen. It may, of course, be used also for heating the apparatus.

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. Non-injurious admixtures are hydrogen, nitrogen, carbon monoxide, whereas steam of water, carbonic acid and sulphurous acid will reduce the output in higher hydrocarbons, since the last named admixtures at high temperatures will react with methane in another way, not desirable in the present process. It is evident that the presence of other hydrocarbons than methane does not matter since they will, as is known, split up more easily than methane itself into similar fractions under the influence of heat.

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

A process of producing higher hydrocarbons by thermal decomposition of methane, characterised by the use of an apparatus working according to the regenerative system and which is alternately hot blasted by combustion gases and cooled again by methane or methane containing gases, the time during which the methane has to remain in the hottest zone of the furnace being regulated in such a manner and the material for the lining and the filling bodies of the furnace being such, that the decomposition of the methane will take place whereas the formation of free carbon is prevented as much as possible.

Dated this 15th day of December, 1928.
MARKS & CLERK.

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