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PATENT SPECIFICATION

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2217

COMPLETE SPECIFICATION.

Improvements in Processes for the Synthesis of Hydrocarbon Fuels, and for the Cracking and Hydrogenation of Heavy Hydrocarbons.

I, JEAN MERCIER, 15 Rue d'Astorg Paris, France, a citizen of the French Republic, 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 present invention relates to improvements in the known processes for the manufacture of light hydrocarbons starting from heavy hydrocarbons, in which the step of pyrogenation is carried out at a temperature of about 500° C. and is followed by a subsequent treatment carried out at about 180 to 300° C.; the passage from the step of pyrogenation to the subsequent treatment taking place directly without intermediate step and by means of a cooling and expansion as abrupt and energetic as possible.

According to the invention, the mixture subjected to the treatment includes vapors of heavy hydrocarbons, carbon monoxide and hydrogen, said heavy hydrocarbons being either those manufactured in the course of the operation of fresh ones or a mixture of both and the treatment is carried out in the presence of catalysts.

Two plans for carrying out the process according to the invention are diagrammatically shown in the accompanying drawing, which is given solely by way of example.

In this drawing:

Fig. 1 is a diagram showing the process for the synthesis of hydrocarbons, comprising the improvements according to the invention.

Fig. 2 is a diagram showing the combination of said synthetic process with a cracking cycle.

In the form of construction herein represented, the mixture of carbon monoxide and hydrogen, supplied for instance by an independent source of water gas, is admitted into the retort 1, in which the synthesis of the hydrocarbons takes place. The said retort is maintained at about 500° C. and contains the necessary catalysts, which may be the same as are used in the processes for the cracking of hydrocarbons. The catalyst may consist chiefly of metals of the iron group, (iron, nickel, cobalt and the like) in grains, cutting-chips, or in powder, which may be disposed on refractory carriers consisting of oxides such as alumina, lime, magnesia, etc. Certain sulphides such as sulphide of iron, molybdenum, tungsten, etc. can also be used as catalysts.

The resulting hydrocarbons are not slowly cooled, but after they may have been purified at 2 they are abruptly expanded in the deflegmator 3. This apparatus has a large heat-conducting surface, and thus the hydrocarbons are cooled suddenly to a temperature between 180° and 300° C.

After the said deflegmator 3 the plant comprises a vertical container 4 containing a catalyst in the shape of finely divided metal or the like, and the capacity of the deflegmator 3 and the distilling chamber 4 should be such that the hydrocarbons and the gases not yet entirely stabilized and loosened by the sudden expansion and cooling will remain therein for a certain time.

Hydrogen can be advantageously admitted in the apparatus 3, 4, for instance at 5. It is a known fact that the temperatures between 180° and 300° C. are quite favourable to a moderate hydrogenising of unstable hydrocarbons. This increases the output of the plant and improves the quality of the hydrocarbon fuel manufactured.

Low pressures further the formation of synthetic hydrocarbons analogous to petrol. On the contrary, the high pressures further the formation of hydroxides of carbon i.e. organic compounds containing CO. and H. The presence of finely divided metals or other catalysts accelerates the reactions.

The resulting hydrocarbon fuel is circulated into the condenser, 6, from which it descends into the collecting chamber 7. The condensed petrol is withdrawn at 8. The uncondensed gases which are saturated with petrol rise through the bubble plate tower 9, whence they descend

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through the tube 10 to the petrol removal chamber 11. The permanent gases issue therefrom through the pipe 12.

As concerns the heavy liquid hydrocarbons issuing from the circulation, these may be again introduced through the pipe 13, by means of the pump 14, and they may be sent through the heating worm 15 and the evaporating purifier 16.

The heavy hydrocarbons thus introduced into the circulation are subjected in the retort 1 to the cracking operation by pyrogenation, and the cracking is furthered by the temperature of the retort (about 500° C.) and by the above-mentioned catalysts which it contains.

If water vapour is added to the initial gas mixture, the following secondary reaction will take place:

$CO+H^{2}O=CO^{2}+H^{2}+9$ calories.

The resulting nascent hydrogen furthers the production of light hydrocarbons analogous to petrol, whereby the output of the operation will be increased.

Moreover, the presence of such nascent hydrogen offers a considerable advantage. It is known in fact that in all the methods for the cracking of heavy hydrocarbons, the following residues are formed together with the petrol, that is, carbon and very heavy hydrocarbons, light and unstable hydrocarbons which are coloured and have a bad odour, and gaseous hydrocarbons rich in hydrogen.

To counteract the deposit of carbon and the formation of the unstable liquids, the cracking must be performed in the presence of hydrogen.

The invention further consists in combining the aforesaid synthetic process employing a mixture of carbon monoxide, hydrogen and steam, with any suitable hydro- process for the cracking of heavy hydrocarbons, and this permits not only the production of light hydrocarbons by synthesis and by cracking, but also to greatly increase the output of the cracking operation by the energetic action of the nascent hydrogen upon the hydrocarbons during their molecular transformation.

It will be further observed that the reaction which produces the nascent hydrogen is somewhat exothermic, as above indicated, which is a favourable circumstance, and moreover, it can readily take place at temperatures near those of the cracking by pyrogenation, and especially in the presence of catalysts which may be the same as those in use for the cracking and for the synthesis of hydrocarbons.

In practice, it will thus be sufficient to introduce into the retort of a plant adapted for the synthesis of hydrocarbons or for cracking by pyrogenation, or for both these operations, a mixture of hydrogen, steam and carbon monoxide in the proper proportions, in order to obtain the desired result. The gases thus produced in the presence of the hydrocarbons engaged in the cracking operation will combine with these latter, thus forming a somewhat oxidised hydrocarbon and producing a very slightly oxidising atmosphere.

Moreover, Applicant has found that carbon monoxide increases and prolongs for a long time the catalytic activity of various metals, especially of the iron group. The deposits of carbon which usually clog up the cracking apparatus are herein much reduced, so that the plant can be continuously operated for a long period, which would be otherwise impossible.

The finely divided metals or other catalysts which further the cracking operation may thus be used without being rapidly covered with a deposit of carbon by which their activity would be destroyed.

It should be observed that the best catalysts are those which either alone or when mixed together will further the formation of the nascent hydrogen and at the same time the molecular decomposition of the hydrocarbons and the moderate hydrogenising whereby the formation of permanent gases will be obviated. The catalysts above mentioned relatively to the synthesis of hydrocarbons may be herein employed to advantage.

The aforesaid reaction of the carbon monoxide upon the steam is effected without variation of volume, and it will take place during cracking operations effected either in liquid or vapor state. On the contrary, the hydrogenising is furthered by the pressure.

Fig. 2 represents a plant adapted for an improved cycle of cracking operations according to the invention, combined with a cycle for the synthesis of the hydrocarbons shown in Fig. 1.

In the present example, the fresh oil at 17 consisting of heavy hydrocarbons is supplied by the pipe 18 to the vertical bubble plate tower 9 adapted for the superficial removal of petrol or gasoline, and it then descends through the pipe 19 to a sulphur-removing and classing chamber 20 containing metals such as iron and copper. The oil then circulates through the general pipe 18 into the mixing tank 21, whence it is circulated by the pump 14 into the heating worm 15.

The substances which are still liquid are removed by the separating purifier 16, from which the vapour proceeds into the bottom of the retort 1. The hydrogenation by the nascent hydrogen may commence in the worm 15, being then completed in the said cracking retort 1. The substances resulting from the cracking and the hydrogenation are discharged at the top of the retort and transverse the purifier 2, the said substances absorbing the carbon dioxide. However said purifier may be dispensed with.

As above mentioned, the liquid is then abruptly expanded, and for this purpose the temperature is suddenly reduced in the chambers 3 and 4.

When issuing from the said chambers, the slightly oxidised carburant is circulated in the manner above indicated, but it rises through the separating chamber 20 in which it heats the oil employed in the first place.

The said plant is completed by a cycle for the production of the carbon monoxide employed in the process.

In the example herein represented, the carbon monoxide is formed by the high temperature reaction (at 800°—1,100° C.) of the excess of steam upon the whole or a part of the solid, liquid or gaseous residues of the cracking or of the synthesis of the hydrocarbons.

For this purpose, the said residues from the purifier 16 or from the retort 1, are brought together in the two recipients 23 and 24. A cock 26 provides for the circulation of the said residues into the conduits 12 connected to the petrol-removal chamber 11, which admits the aforesaid permanent gases. The excess of the said gases may issue from the circulation through the pipe 22.

A purifying device 27 interposed in the piping 12 serves to remove the carbon dioxide from the permanent gases, which latter are returned to the circuit during the formation of the carbon monoxide. This gas is formed in the chamber 28 into which are introduced the residues of the cracking operation, the permanent gases, the steam admitted into the circuit at 29, and optionally oxygen entering at 30.

The following reaction takes place at the aforesaid temperature:

$$nH^2O + C^nH^m = nCO + (m+2n)H$$

which corresponds to the production of a certain quantity of hydrogen which is employed for the synthetic manufacture of hydrocarbons.

The gas mixture due to this reaction is circulated into the pipe 31, to which steam is added at 32, and hence a mixture of $H^2O + CO + H$ may be supplied at will, through the pipes 33, 34, 35 to the said heating worm 15, to the retort 1, or to the dephlegmator 3, and preferably before cooling, for the purpose of using the heat carried in said mixture for bringing the reagents contained within the retort 1 to the desired temperature.

Obviously, the invention is not limited to this method for the formation of carbon monoxide, and this gas may also be produced by the incomplete combustion of a part of the residue of the high temperature cracking with the optional use of steam.

If a local combustion at a very high temperature is assured, the carbon monoxide can be produced even in the cracking retort 1, by supplying through the pipe 36 small quantities of oxygen or even of air at a sufficiently high temperature, upon porous refractory material. This surface combustion at a very high temperature is quite suitable for the purpose. The amount of heat to be furnished by an external heating of the retort in order to effect the cracking will be reduced or even replaced by the amount of heat furnished by the gases and steam supplied through 34 at a very high temperature or produced by the local combustion and the various exothermic reactions above mentioned.

Obviously, the invention is not limited to the forms of construction herein described and represented, which are given solely by way of example.

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:—

1. In a process for the manufacture of light hydrocarbons, starting from heavy hydrocarbons, in which the step of pyrogenation is carried out at a temperature of about 500° C. and is followed by a subsequent treatment carried out at about 180° to 300° C, the passage from the step of pyrogenation to the subsequent treatment taking place directly without intermediate step and by means of a cooling and expansion as abrupt and energetic as possible, the characteristic feature residing in that the mixture subjected to treatment includes vapors of heavy hydrocarbons, carbon monoxide and hydrogen, said heavy hydrocarbons being either those manufactured in the course of the operation, or fresh ones, or a mixture of both and the treatment being carried out in the presence of catalysts.

2. A process as claimed in claim 1, characterized by the addition of steam to the mixture subjected to treatment in the apparatus of pyrogenation.

3. A process as claimed in claim 1 or 2, characterised in that the step of pyrogenation is carried out in the presence of catalysts adapted to further both the synthesis of hydrocarbons, the cracking of heavy hydrocarbons as well as a moderate

hydrogenation and eventually the formation of nascent hydrogen.

4. A process as claimed in claim 1, 2, or 3, characterized in that the subsequent treatment is carried out in the presence of catalysts adapted to further both the synthesis of hydrocarbons and a moderate hydrogenation and eventually the formation of nascent hydrogen.

5. A process as claimed in claim 3 or 4, characterized in that the catalysts used in the pyrogenation step or in the subsequent treatment or in both comprise, as known per se, metals of the iron class in a divided state.

6. A process as claimed in any of the preceding claims, characterized by the addition to the products subjected to treatment of steam or of a mixture of carbon monoxide and hydrogen, or of a mixture of steam, carbon monoxide and hydrogen, this addition taking place after the step of pyrogenation and either before or after the sudden cooling, for the purpose of avoiding the stabilising of the cracked products before they are subjected to hydrogenation.

7. A process as claimed in any of the preceding claims, characterized in that one at least of the elements, carbon monoxide, hydrogen and eventually steam which are supplied into the pyrogenating apparatus is previously heated up to a high temperature.

8. A process as claimed in claim 1, characterized by the fact that a moderate oxydation is provided within the pyrogenation apparatus of a fraction of the hydrocarbons.

9. A process as claimed in any of the preceding claims, characterized in that the carbon monoxide and hydrogen supplied to the cycle are obtained by action of steam at high temperature on sub-products entailed by the cracking, i.e. either permanent gases or tars or both.

10. A process for the manufacture of light hydrocarbons, starting from heavy hydrocarbons, substantially as described.

Dated this 28th day of May, 1929.

MARKS & CLERK.

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312,916 COMPLETE SPECIFICATION 1 SHEET

2nd Edition

[This Drawing is a reproduction of the Original on a reduced scale.]

Fig.1

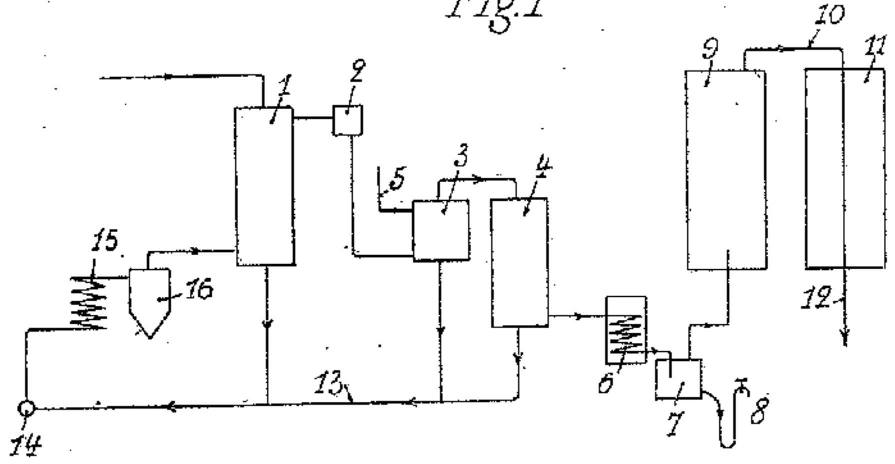
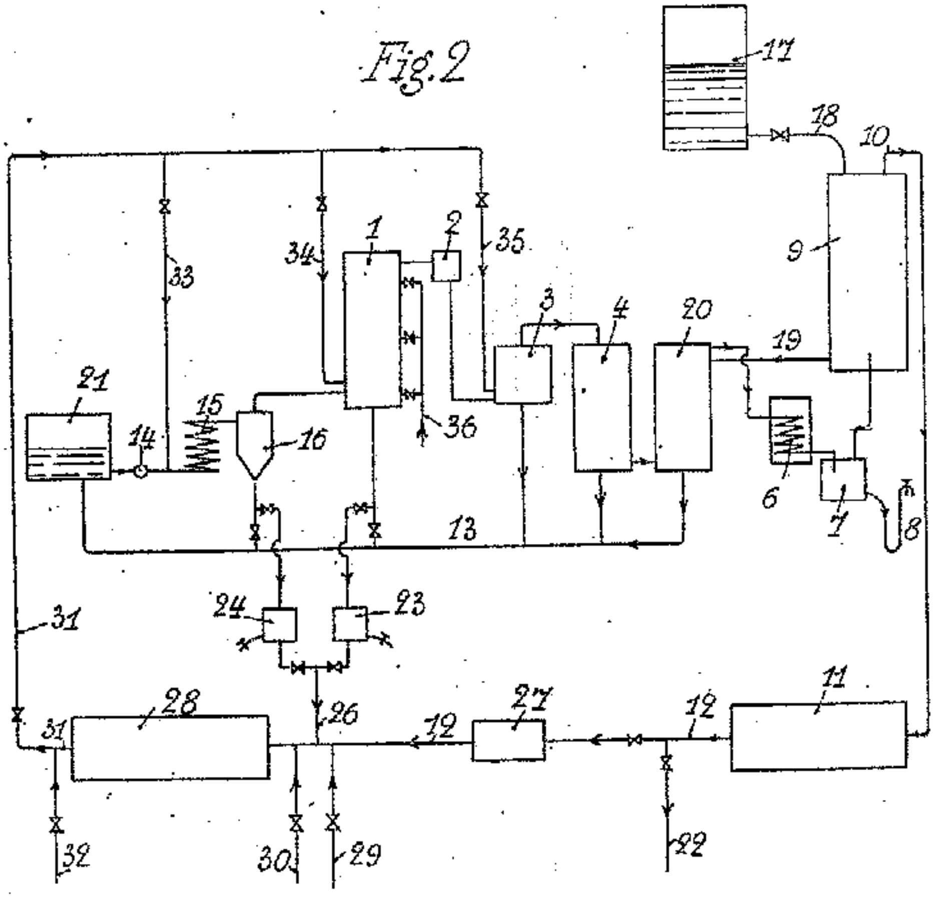


Fig.2



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