

May 29, 1934.

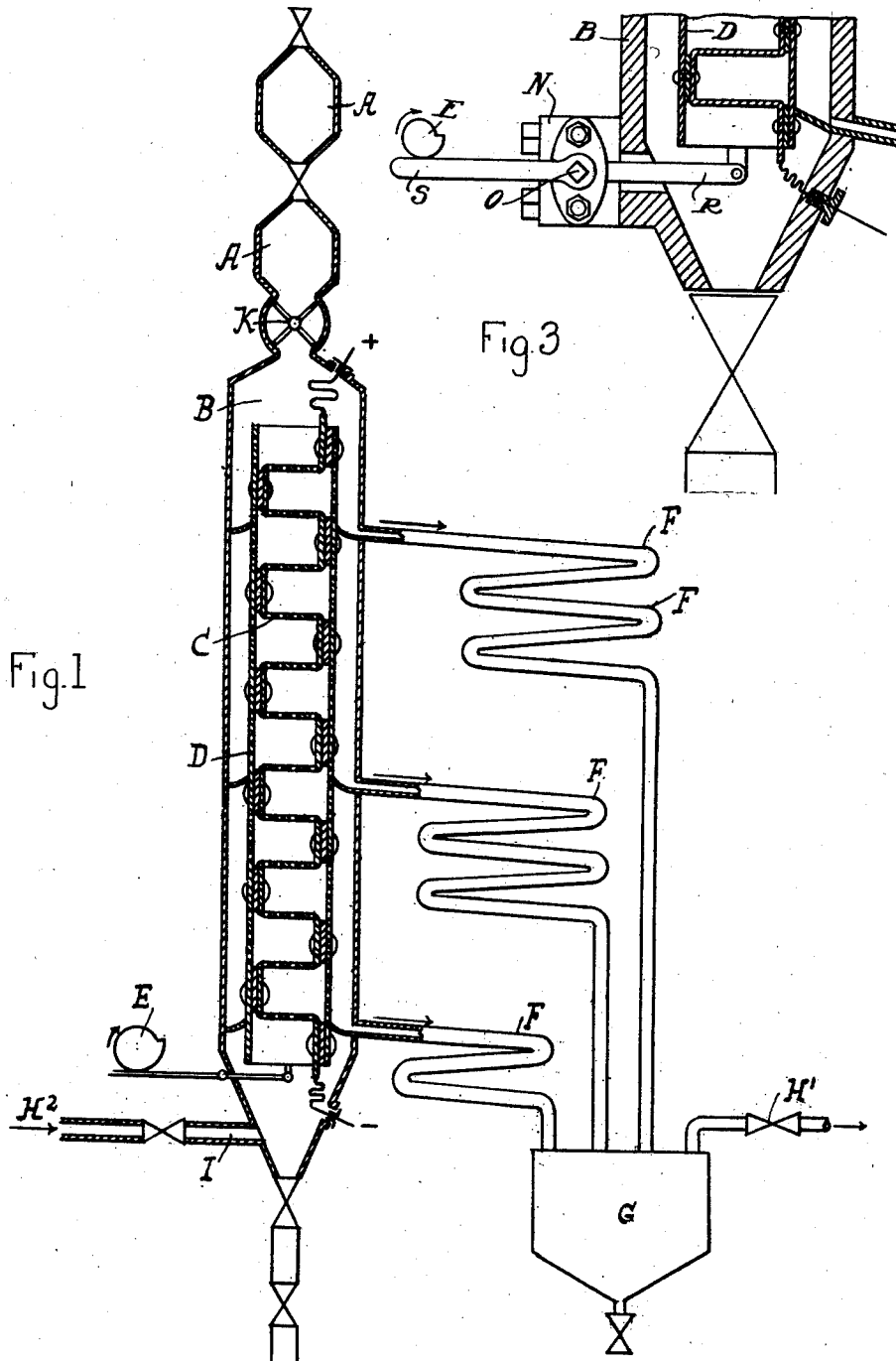
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1,960,972

PRODUCTION OF VALUABLE HYDROCARBONS

Filed July 18, 1930

2 Sheets-Sheet. 1



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Fig. 2.

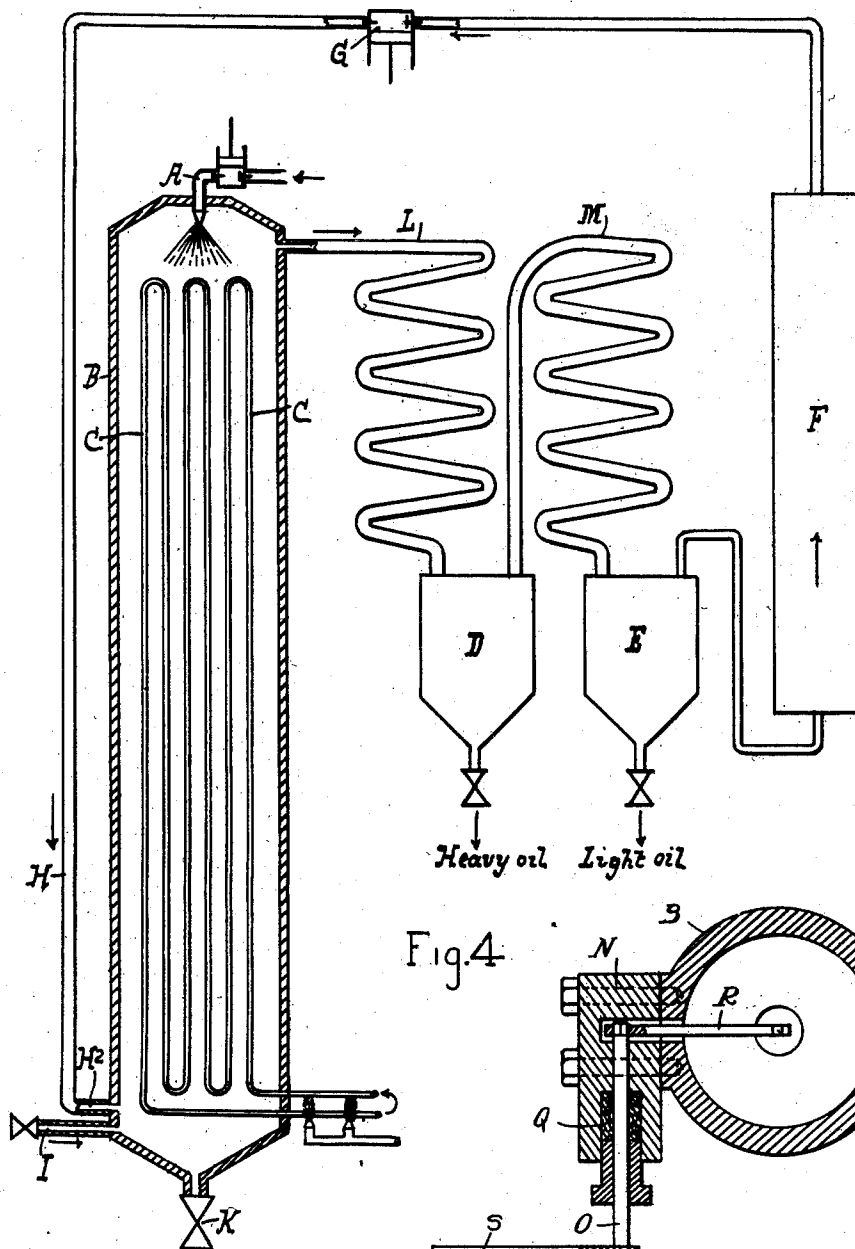
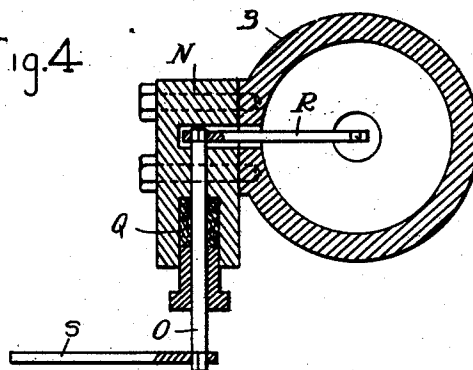


Fig. 4.



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PRODUCTION OF VALUABLE
HYDROCARBONS

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5 Claims. (Cl. 196—53)

This invention relates to improvements in the manufacture and production of valuable hydrocarbons by destructive hydrogenation under pressure.

5 In the processes of the nature of destructive hydrogenations hitherto known for the conversion into liquid hydrocarbons of carbonaceous materials such as coal of all varieties, tars, mineral oils and their distillation and conversion products and residues into hydrocarbons of lower boiling point by a heat treatment under pressure in the presence of hydrogen or of gases containing or supplying hydrogen, the heat to be supplied must be passed from the heat transferer through more or less thick layers of bad heat-conducting carbonaceous initial material, and this is only possible when a marked temperature gradient is set up. This, however, leads to overheating and undesirable chemical reactions, especially the formation of gas owing to a too far reaching splitting and formation of coke, by reason of the fact that the optimum conversion temperature only embraces a comparatively narrow range of temperature. In a lesser degree this is also the case when supplying a part or the whole of the necessary heat by means of the hydrogenating gas. Injurious overheating could hitherto only be repressed by carrying out the heating of the initial materials very slowly, as for example in long heating coils, and while continuously turning the mass and by keeping the mass in motion during the hydrogenation process, or else by working with very thin layers.

Since, in the processes of converting coals into oils and high boiling oils into oils of lower boiling point, not only the addition of hydrogen but also the splitting (partly previously, partly simultaneously and partly subsequently) plays a substantial part, while on the other hand a too far reaching splitting, which is usually accompanied by the formation of coke, is very undesirable, it is important that as far as possible the hydrogen should have access to every carbon molecule, and this could only be effected hitherto to a limited extent by turning the mass, preferably with the simultaneous formation of thin layers, which necessitates troublesome apparatus and much room.

A rapid removal of the valuable hydrocarbons formed from the heating chamber is also of importance because—in the same manner as by overheating—there is the danger of a too far reaching splitting taking place owing to too long a duration of the heating action.

55 We have now found that all these objections

are overcome when the initial materials to be treated are brought into a finely divided form, as for example coal into a finely granular or pulverulent state or oil in the form of drops or droplets, if desired sprayed or in the form of mist, and are allowed to fall freely in the presence of hydrogen or of gases containing or supplying hydrogen continuously through a pressure tight container in which heated heating members are arranged. The gases comprising hydrogen may be led in the same direction as, or in counter current to, the materials to be treated. Hydrogen or gases containing or supplying the same may also be added and withdrawn from time to time in a discontinuous manner. Catalysts, immune from poisoning by sulphur, in a finely divided state may be allowed to fall with the carbonaceous materials under treatment or gaseous or vaporous catalysts may be present.

The heating members may consist of vertically arranged pipes, hollow plates or the like heated by hot gases, vapours or liquids, preferably in circulation, or they may consist of vertically stretched wires or bands heated electrically. The height of the pressure tight container is chosen so that the time of fall of the initial materials is sufficient for the desired conversion.

In order to increase the time of fall or to employ pressure-tight containers of less height, deflecting members which occupy only a small space and are likewise heated to the reaction temperature, may be arranged one above another in the pressure-tight container in such a way that the free fall of the goods to be treated is frequently interrupted. Catalytic materials may be arranged on the said deflecting members. The deflecting members may consist of rods, strips, spirals, gratings, sieves, perforated plates and the like and may either be connected in a heat conducting manner with the vertical heating members or may be constructed as directly heated hollow members, as for example pipes, or they may be heated electrically.

In some cases it is advantageous to increase the temperature of the deflecting members or heating members in the direction of fall or to set up zones of different temperature.

In order to prevent clogging or stoppage of the material to be treated in all cases, especially in the conversion of varieties of coal, it may be advantageous continuously or periodically to cause the deflecting members to be shaken.

The heating members or the heated deflecting members may be surrounded by a cylindrical jacket of smaller diameter than the pressure-

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tight container and provided with holes or slots, preferably inclined upwards, and this offers the further advantage that the pressure-bearing walls may be kept cooler so that they are exposed to smaller mechanical and chemical requirements and may therefore be constructed with smaller thickness and of cheaper material.

The deflecting members may consist of or be coated with catalytic material which promotes the splitting and/or the hydrogenation. Moreover catalytic substances may be previously mixed with the materials to be treated or may be introduced into the container simultaneously or at a lower place therein.

As example of the catalysts immune from poisoning may be mentioned such comprising an element of the sixth group of the periodic system in particular in the form of its oxides, hydroxides, sulphides or carbonates, or any of the other catalysts employed in destructive hydrogenation processes.

During the pressure heat treatment of the materials to be converted in the manner hereinbefore described by allowing them to fall freely or interruptedly through an atmosphere of hydrogen between heating members or over heated deflecting members no formation of layers whatever takes place. The particles of coal or the drops of oil, during their fall, acquire the reaction temperature without the possibility of any injurious overheating since the individual particles offer the largest possible surface to the action of the heat. Similarly the hydrogen may come into contact from all sides with the individual particles without hindrance so that splitting and hydrogenation may be effected simultaneously. The valuable hydrocarbons formed rapidly detach themselves in the form of vapour from the particles by reason of their large surface and their motion so that the unconverted remainder of the particles is continuously set free again for the intensive action of hydrogen and heat.

The vapours of the valuable hydrocarbons formed are preferably withdrawn laterally throughout the whole height of the pressure-tight container, as for example by leading the gas-vapour mixture away from different places in the container into common or separate condensers, the gas being returned into circulation after separation of the hydrocarbons. In some cases the pressure-bearing walls, if desired cooled, may themselves be used as condensing surfaces which may be subdivided by collecting channels at various heights as desired.

The process is preferably carried out at pressures of 10, 20 atmospheres and more, especially at pressures of 50, 100, 200, 300, 800, 1000 atmospheres or more.

The temperatures employed usually range between 300° and 700° C., although preferably temperatures of between 380° and 550° C. are employed.

The following examples and the accompanying drawings will further illustrate the nature of this invention, but the invention is not restricted to these examples, nor to the specific arrangements of apparatus shown in the drawings, of which Figure 1 has reference to Example 1 and Figure 2 to Example 2.

Example 1

Finely ground gas coal, rich in volatile combustible matter, is continuously introduced, as shown in Figure 1, from bunkers A by way of a

conveyer wheel K into a pressure-tight container B several metres in height filled with hydrogen under a pressure of about 200 atmospheres, and containing a system of narrow meshed sieves C arranged one above the other and heated electrically to about 400° C., the said sieves being connected together by a cylindrical jacket D of smaller diameter than the pressure-tight container and provided with slots and insulated from the sieves. The cylindrical jacket D may be shaken by an agitating device E. The coal, during its frequently interrupted fall through the sieve system, is decomposed to the extent of more than 80 per cent. The oils and vapours obtained in a yield of about 60 per cent pass into the condensers F and are collected in the container G. The uncondensable constituents are released by valve H and may be returned to the reaction by way of valve I after being freed from methane.

The mechanism by which the cylindrical jacket D may be shaken is shown in vertical section in Fig. 3 and in horizontal section in Fig. 4. Referring to these Figures in detail, B indicates the high pressure vessel on which is mounted a block N which contains a stuffing box Q through which the shaft O passes. Rigidly connected with the outer end of the shaft O is an arm S upon which the cam surface E rides. Rotation of the cam surface imparts an oscillating movement to the arm S. Rigidly mounted on the other end of the shaft O is the arm R, extending into the reaction vessel and pivotally connected to the lower end of the jacket D. The oscillation of the arm S is transmitted through the shaft O to the arm R which in turn imparts a reciprocating motion to the jacket D.

Example 2

The process according to this example may be carried out in an apparatus as shown in Figure 2. Brown coal low temperature carbonization tar is continuously introduced by means of a nozzle A in an atomized state into the upper end of a pressure-tight reaction vessel B several metres in height filled with hydrogen under a pressure of 200 atmospheres and containing a number of vertically arranged tubes C heated to about 450° centigrade by hot gases in circulation. During their fall, the fine droplets of tar are converted into valuable low boiling hydrocarbons which, after passing through condensers are supplied again to the reaction vessel B by way of nozzle A. The uncondensable gases are passed through a scrubber F, in which the hydrogen is concentrated. This hydrogen may be returned to the reaction vessel B by means of a pump G and pipe H. Fresh hydrogen is supplied by way of valve I. The non-hydrogenated constituents are continuously removed from vessel B through a valve K.

What we claim is:—

1. A process for the destructive hydrogenation in the solid or liquid phase of solid and liquid carbonaceous materials while avoiding hydrogen and coke formation and localized superheating, which comprises continuously dropping said materials in a finely divided state through a space heated to a destructive hydrogenation temperature and containing a hydrogen atmosphere maintained under a pressure of at least 20 atmospheres to thus effect an enveloping of the particles of said materials by the hydrogen gas and uniform heating of said materials, increasing the duration of contact of said particles with the envelop-

- ing hydrogen by baffling at spaced points throughout the reaction zone the flow of said particles without preventing the fall of said particles so that the duration of movement of said materials through said space is that necessary to cause the desired degree of destructive hydrogenation. 80
2. A process for the destructive hydrogenation in the solid or liquid phase of solid and liquid carbonaceous materials while avoiding hydrogen and coke formation and localized superheating, which comprises continuously dropping said materials in a finely divided state through a space internally heated to a destructive hydrogenation temperature and containing a hydrogen atmosphere maintained under a pressure of at least 20 atmospheres to thus effect an enveloping of the particles of said materials by the hydrogen gas and uniform heating of said materials, increasing the duration of contact of said particles with the enveloping hydrogen by baffling at spaced points throughout the reaction zone the flow of said particles without preventing the fall of said particles so that the duration of movement of said materials through said space is that necessary to cause the desired degree of destructive hydrogenation. 85
3. The process as defined in claim 2 wherein the finely divided particles are agitated simultaneously with the baffling of the flow of said particles. 85
4. The process as defined in claim 2 wherein the temperature of the carbonaceous particles is increased during the movement of the particles through the reaction zone.
5. The process as defined in claim 2 wherein a catalyst immune to sulphur poisoning is dropped through the reaction space together with the finely divided carbonaceous material. 90
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