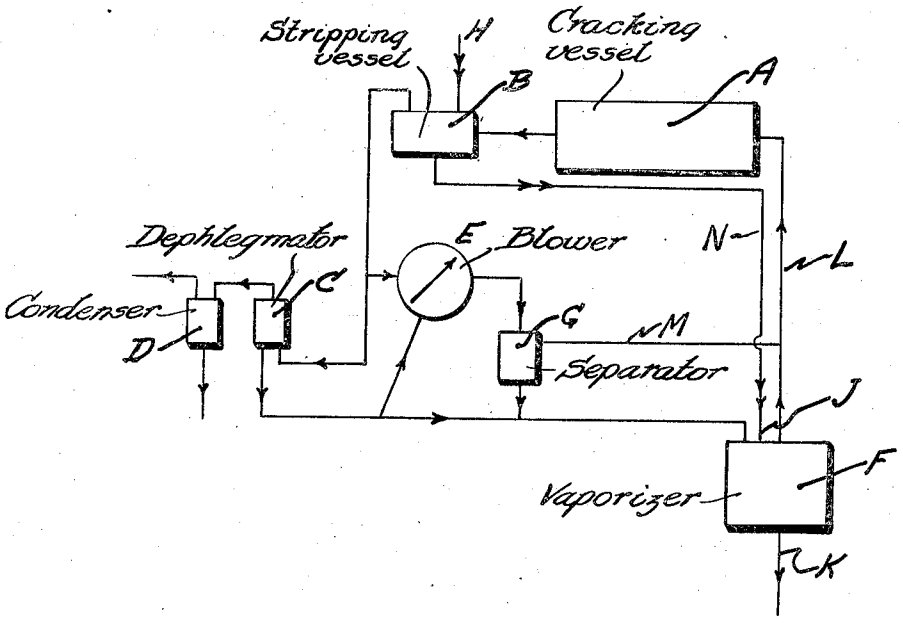
Sept. 28, 1937. G. STERN ET AL 2,094,476

PRODUCTION OF HYDROCARBONS

Filed Feb. 24, 1932



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Patented Sept. 28, 1937

2,094,476

UNITED STATES PATENT OFFICE

2,094,476

PRODUCTION OF HYDROCARBONS

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Application February 24, 1932, Serial No. 594,816
In Germany February 28, 1931

3 Claims. (Cl. 196—61)

The present invention relates to improvements in and apparatus for the manufacture and production of hydrocarbons.

In the preparation of hydrocarbons of low boiling point by the thermal decomposition of hydrocarbon oils, in the vapor phase it has already been proposed to lead the vapors of the initial materials, especially gas oil vapors, which must be as free from very heavy constituents as possible, through the reaction vessel together with steam, cracking gases or permanent gases, to cool the resulting reaction mixture rapidly and to condense the illuminating oil vapors formed separately from the unchanged gas oil and the newly formed heavy oil.

In the said process, the added steam or the gases effect a reduction in the partial pressure of the oil vapors, especially the heavy oil vapors, and thus effect a reduction in the formation of carbon, because, as is well known, the heavy oils are readily partly polymerized to form solid deposits, such as asphaltic or carbonaceous substances. This advantage is attended by several drawbacks, however. The addition of steam results in the necessity of heat being supplied and also withdrawn again during the condensation at temperatures lying below the condensation temperature of the bulk of the light oils and middle oils to be separated. The said oil vapors diluted by steam require for their separation a more extensive and consequently more expensive condensation plant than is necessary for condensing undiluted light and middle oils. Furthermore there is the danger that the steam may have an oxidizing effect on the reaction products. The addition of cracking gases or of permanent gases certainly prevents such an oxidation but the recovery of light oils and middle oils is rendered even more difficult than when adding steam, since also in this event the valuable portions boiling below 100° C. must be recovered from a strongly diluted state.

We have now found that the said drawbacks are to a large extent avoided and that the said process is rendered much more economical by employing as diluting agents oil vapors which only diminish the partial pressure of the heavy oil vapors formed and the main part of which do not condense below the condensation temperature of the vapors of light oils and middle oils, as for example by passing the vapors of oils, boiling between from 100° to 350° C. serving as the initial materials through the reaction chamber together with 1.5 to 20 times the amount of vapors of oils of low boiling point, especially of the vapors of light or middle oils, which have been derived from the thermal decomposition itself and from which the vapors of substances of high boiling point, in particular at least those of a boiling point above 400° C., preferably above 350° C. which tend to form asphaltic deposits formed at the same time have been removed. In any event the average boiling point of the oil vapors added for diminishing the vapor pressure of the heavy constituents of the initial oils is lower than that of said oils. The separation of the vapors of the substances of high boiling point from the vapors of the oils of low boiling point may be effected for example by subjecting the mixture leaving the reaction chamber to a partial condensation by partial refrigeration or to refrigeration and treatment with washing liquids or by refrigeration and an electrical separation. Two or more methods of separation may be used conjointly. By this treatment the substances inclined to polymerization and formation of coke formed in the reaction having a higher boiling point than the upper boiling point limit of the initial material, are separated.

Contrasted with mixing steam with the substances to be split, the process according to the present invention has the advantage, inter alia, that by reason of the higher concentration of the light or middle oil vapors present in the reaction vessel, the resulting heavy oil vapors and substances liable to polymerization are present in a relatively substantially smaller concentration. A lower concentration of the latter substances yields not only less heavy oil and solid deposits, such as asphaltic or carbonaceous substances, but also a better heavy oil because in the said case the polymerization cannot proceed to the formation of such high molecular compounds as when the heavy oil content is high. Moreover, the expenditure of heat is small because the vapors leaving the reaction vessel need only be cooled by about 150° to 200° C., for example without condensing the bulk thereof. The economy of the process is still further increased by using the heat carried away by the vaporous reaction mixture for the evaporation of the fresh oil to be employed.

Contrasted with the addition of steam, cracking gases or permanent gases, the process according to the present invention has the great advantage that it requires a much smaller condensation plant.

It has further been found that when the reaction vessels are of the same size and when the period of time within which the reaction mate-

rials remain in the reaction vessels is the same, a greater amount of the desired cleavage products, such as light oils, is obtained according to the present invention than by splitting the unmixed vapors of the initial materials.

The following example given with reference to the accompanying diagrammatic drawing which illustrates an arrangement of apparatus suitable for carrying out the process according to the present invention, witll further illustrate the nature of this invention, but the invention is not restricted to this example or to the particular arrangement shown. The apparatus may be employed with similar results for treating other hydrocarbon products than those specified in the said example.

Example

The vapors of a gas oil obtained from brown coal low temperature carbonization tar boiling between about 260° and 360° C. are led from vaporizer F by way of pipe L through a reaction vessel A which is heated to 600° C. and the walls of which may be made of catalytically active material, such as iron, nickel, copper, chromium or other active metals or alloys of these metals. After leaving the vessel A, the vapors are cooled in B to such an extent by spraying fresh oil at H into B that a small part of the vapors consisting of constituents of a boiling point of above 360° C. is condensed, or the vapors are washed with a heavy oil at a temperature of about 350° C. which absorbs the heavy constituents. A part of the not condensed oil vapors issuing from B is then branched off; this part is dephlegmated in C and condensed in D for the recovery of light oil boiling between from 50° to 250° C., while the constituents of still lower boiling point are led away from D for further working up. The greater part of the oil vapors issuing from B is led to E and G and then supplied by way of pipes M and L to the reaction vessel A again. For pumping the vapors it is preferable to use a blower E which may be arranged at any convenient place in the cycle, advantageously behind the separator B. In order completely to separate any heavy oil vapors carried away, fresh oil or unconverted oil recovered in the dephlegmator C may be sprayed into the blower E, the mixture of the sprayed-in oil and the heavy oil vapors being separated in G. If the heavy oil obtained in B is to be further worked up for example by cracking or hydrogenation in a separate reaction vessel, it is advantageous first to lead it by way of pipe N through the vaporizer F in order to vaporize the constituents boiling below 350° C. of the fresh oil sprayed into B which are contained therein and to return them to vessel A, and then to pass the non-vaporized parts of said heavy oil to a phase at which it is to be further worked up. A similar procedure is followed with the oils collected in the blower E or the separator G, while the vapors leaving the latter are supplied directly to vessel A. The vaporizer F is provided with an inlet J and an outlet K for the non-vaporized constituents of high boiling point collected therein. Instead of the said gas oil from brown coal low temperature carbonization tar, gas oil or middle oil obtained by cracking or destructively hydrogenating the heavy oil may be used as the initial material for the process according to the present invention.

The separation of the heavy oil vapors formed in the reaction vessel may also be effected by cooling the vaporous reaction mixture by means of fresh initial oil or fresh oil and water to from about 400° to 500° C., the constituents thereby condensed and finely dispersed in the mixture being precipitated therefrom electrically. By trickling the electrodes with cold heavy oil, the condensed constituents may be diluted and brought to a temperature of about 350° C. at which the formation of carbon from condensed heavy oil no longer takes place.

Instead of leading the liquid constituents separated in different parts of the cycle into a single vaporizer, it is preferable in many cases to employ several vaporizers maintained each at a temperature sufficient for vaporizing the particular liquid constituents introduced thereinto. Furthermore, several apparatus working in cycles may be connected parallel to each other by tubular conduits, for example by causing the non-converted initial oil obtained from one cycle to serve as the fresh oil for another cycle.

The process according to the present invention has various advantages compared with a cracking process in which only the waste gases containing no condensable constituents are recycled to the reaction vessel while fresh oil is cracked without admixture of recycled diluting oils. From a gas oil obtained from brown coal tar and boiling from 300° to 360° C., in an apparatus having a heating surface of 6 square meters at an operating temperature of 520° C. according to the process of the present invention a yield of light oil of 3 kilograms per hour is obtained while according to the cracking process without recycling diluting oil in the same apparatus and at the same temperature only 1.5 kilograms of light oil can be obtained, the light oils arising from the two processes having equal anti-knocking qualities. A further advantage of the present process is that the waste gases contain very high percentages of olefines, as for example 65 per cent in the above mentioned cracking of brown coal tar gas oil. In the comparative cracking process the waste gases contain only 43 per cent of olefines.

If a fraction boiling between 100° and 300° C. of a crude German mineral oil is treated at a temperature of about 520° C. in an apparatus having a heating surface of 10 square meters 5 kilograms of a light oil having good knocking properties are obtained per hour. Similarly a non-knocking benzine may be successfully prepared from a light oil boiling between 100° and 200° C. obtained by destructive hydrogenation of a paraffinic crude oil.

What we claim is:—

1. A process for the conversion of hydrocarbon oils into lower boiling normally liquid hydrocarbons which comprises heating fresh oil in a distilling zone to a distillation temperature, removing the vapors and heating them to a cracking temperature, condensing from the cracked vapors the constituents boiling above 400° C. and tending to form asphaltic deposits under cracking conditions without condensing substantial parts of the vapors of normally liquid hydrocarbons of the boiling point range of the initial hydrocarbon oils and of the light oils formed in the said vapor phase cracking, adding part of the uncondensed portion of the cracked vapors mainly consisting of normally liquid hydrocarbons condensing within the boiling point range of the light oils and the initial hydrocarbon oils, while still in the vaporous state, to vapors of fresh hydrocarbon oils to be cracked in an amount of between 1.5 to 20 times the amount of

said vapors of fresh hydrocarbon oils, passing the combined vapors without intermediate condensation into the cracking chamber and collecting the other part of the said uncondensed portion of the cracked vapors by further condensation.

2. A process for the conversion of hydrocarbon oils into lower boiling normally liquid hydrocarbons which comprises heating fresh oil in a distilling zone to a distillation temperature, removing the vapors and heating them in the vapor phase in a cracking zone to a cracking temperature, condensing from the cracked vapors the constituents boiling above 400° C. and tending to form asphaltic deposits under cracking conditions without condensing substantial parts of the vapors of normally liquid hydrocarbons of the boiling point range of the initial hydrocarbon oils and of the light oils formed in the said vapor phase cracking, adding part of the uncondensed portion of the cracked vapors mainly consisting of normally liquid hydrocarbons condensing within the boiling point range of the light oils and the initial hydrocarbon oils, while still in the vaporous state, to vapors of fresh hydrocarbon oils to be cracked in an amount of between 1.5 to 20 times the amount of said vapors of fresh hydrocarbon oils, passing the combined vapors without intermediate condensation into the cracking zone and collecting the other part of the said uncondensed portion of the cracked vapors by further condensation.

3. A process for the conversion of hydrocarbon oils into lower boiling normally liquid hydrocarbons which comprises heating fresh oil in a distilling zone to a distillation temperature, removing the vapors and heating them in the vapor phase in a cracking zone to a cracking temperature, condensing from the cracked vapors the constituents boiling above 400° C. and tending to form asphaltic deposits under cracking conditions without condensing substantial parts of the vapors of normally liquid hydrocarbons of the boiling point range of the initial hydrocarbon oils and of the light oils formed in the said vapor phase cracking, returning the condensate to the initial vaporizing zone, adding part of the uncondensed portion of the cracked vapors mainly consisting of normally liquid hydrocarbons condensing within the boiling point range of the light oils and the initial hydrocarbon oils, while still in the vaporous state, to vapors of fresh hydrocarbon oils to be cracked in an amount of between 1.5 to 20 times the amount of said vapors of fresh hydrocarbon oils, passing the combined vapors without intermediate condensation into the cracking zone and collecting the other part of the said uncondensed portion of the cracked vapors by further condensation.

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