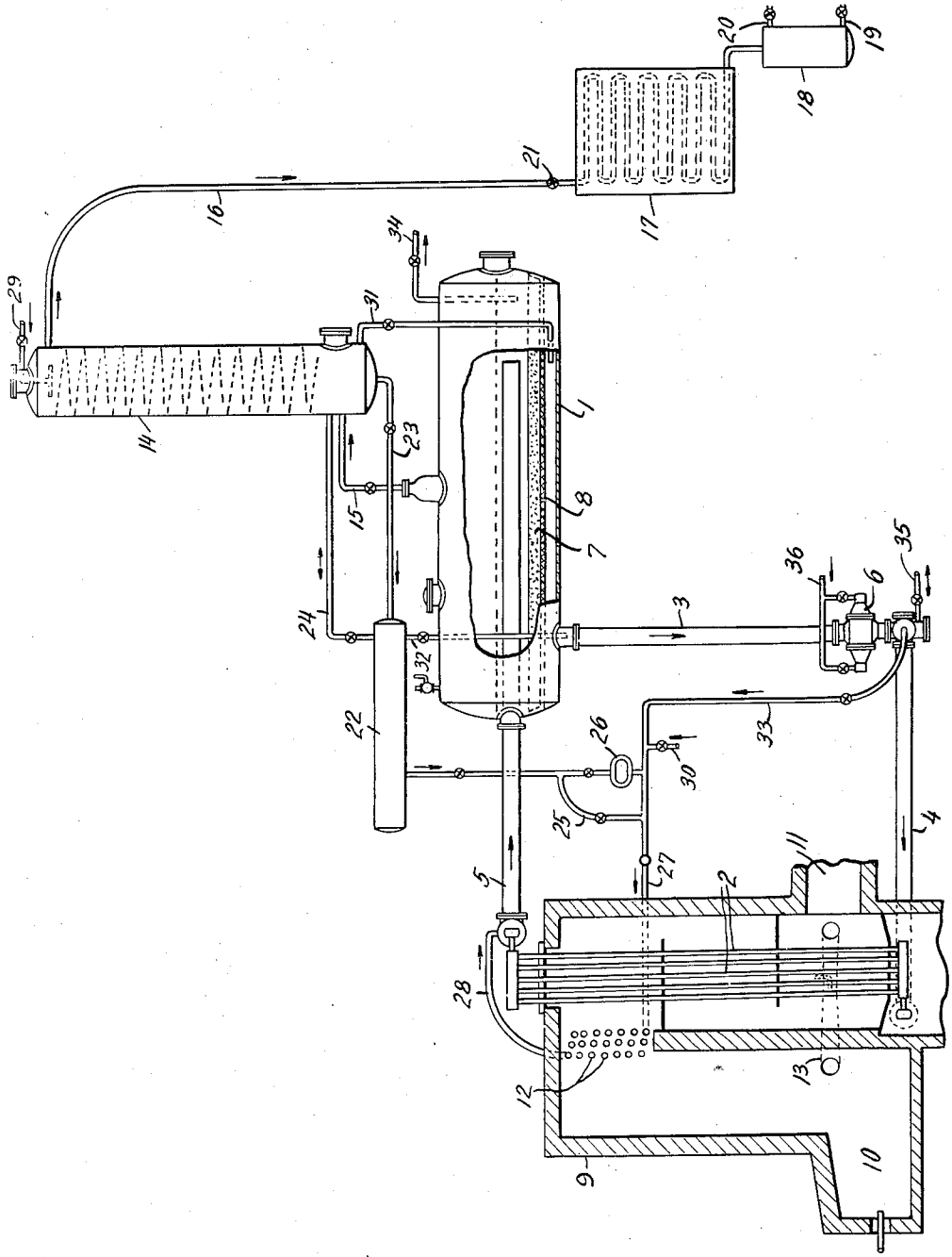
Jan. 6, 1931. E. C. HERTHEL ET AL 1,787,981

ART OF CRACKING HYDROCARBONS

Filed June 11, 1927



INVENTORS
Eugene C. Herthel
Harry L. Pelzer
BY
Fecto, Hibben, Dain & Macauley
ATTORNEYS

Patented Jan. 6, 1931

1,787,981

UNITED STATES PATENT OFFICE

EUGENE C. HERTHEL, OF CHICAGO, ILLINOIS, AND HARRY L. PELZER, OF HIGHLAND, INDIANA, ASSIGNORS TO SINCLAIR REFINING COMPANY, OF NEW YORK, N. Y., A CORPORATION OF MAINE

ART OF CRACKING HYDROCARBONS

Application filed June 11, 1927. Serial No. 198,248.

This invention relates to improvements in the cracking of heavier and higher boiling hydrocarbon oils, such as gas oil, to produce therefrom lighter and lower boiling hydrocarbon oils, such as gasoline and gasoline-containing pressure distillates. This invention relates particularly to improvements in the operation and arrangement of externally heated pressure cracking stills, that is pressure cracking stills in which the heat for the cracking operation is supplied by heating gases passed externally over the heating surfaces of the still from a firebox in which fuel is burned. The invention includes improvements in both method and apparatus.

The products of the cracking reaction include, in addition to the desired lighter and lower boiling hydrocarbon oils, asphaltic and pitch-like constituents which tend to deposit upon the heating surfaces of externally heated pressure stills. Such deposits obstruct heat transfer and tend to cause extreme overheating because of this obstruction of heat transfer, necessitating periodic shut down of the pressure still for cleaning, thus limiting the useful period of operation. As the concentration of such asphaltic and pitch-like constituents in the charge of oil in the pressure still increases, the tendency toward deposition of such materials also increases. This invention provides for reduction in the concentration of asphaltic and pitch-like constituents in the oil in contact with the heating surfaces of the still, and for tempering of the heating gases passing over the heating surfaces through which heat is transferred to that portion of the charge containing the greater concentration of such constituents by a corresponding absorption of heat from the heating gases by heat exchange with oil substantially free from such constituents and of a character such that the tendency toward the formation of such constituents is materially reduced, as well as for particularly advantageous treatment of relatively refractory stocks; thus providing improved continuity of operation with accompanying increase in still capacity and in efficiency of operation.

According to the present invention, a body of oil is maintained at a cracking temperature under pressure in a vaporizing zone, the oil being heated to a cracking temperature in heating tubes through which it is circulated from the body and back to the body, and a bed of finely divided absorbent or filtering material is maintained within the body of oil in the vaporizing zone so that the circulating oil is caused to pass through it. Vapors taken off from the vaporizing zone under pressure are subjected to a refluxing operation and reflux condensate from this refluxing operation is returned to the vaporizing zone through separate heating tubes which are arranged in a common heating furnace with the first mentioned heating tubes so that the heating gases are required to pass first over these separate heating tubes before passing over the heating tubes through which oil from the body in the vaporizing zone is repeatedly circulated. The concentration of asphaltic or pitch-like materials in the oil circulated and recirculated from the vaporizing zone through the first mentioned heating tubes and back to the vaporizing zone is thus reduced by the action of the bed of absorbent or filtering material. At the same time, the heating gases are tempered before they come in contact with these heating tubes over which the heating gases first pass. These separate heating tubes are thus exposed to the heating gases while at highest temperature, but the oil circulated through these heating tubes is substantially free from asphaltic or pitch-like constituents and, this reflux condensate being relatively refractory, the formation of asphaltic or pitch-like constituents in the oil circulated through the separate heating tubes is reduced or retarded while this relatively refractory stock is subjected to particularly advantageous cracking conditions for further production of desired lighter and lower boiling hydrocarbon oils. The oil supplied thereto advantageously is circulated but once or in a single pass through the separate heating tubes.

Fuller's earth, or a similar absorbent earth or clay, is a particularly advantageous absorbent or filtering material. Certain of the asphaltic and pitch-like constituents formed

in the cracking operation, which appear to be relatively small in amount as compared with the total amount of such constituents formed, seem to be particularly objectionable and to have an increased tendency to cause the formation of carbonaceous deposits on the heating surfaces of the pressure cracking still, and among such particularly objectionable constituents certain sulphur-containing compounds appear to be important. Materials other than fuller's earth or the like, for example, pulverized coke, calcined bauxite, and other filtering and desulphurizing materials, are also useful in carrying out the invention, but fuller's earth is particularly efficacious, apparently combining in itself valuable selective absorbent, desulphurizing and other properties which favorably affect and benefit the pressure still operation. For example, fuller's earth seems to have a selective affinity for the more objectionable asphaltic and pitch-like constituents formed by the cracking operation.

In addition to reflux condensate, raw oil may also with advantage be circulated through the separate heating tubes arranged in advance of those through which oil is circulated and recirculated from the vaporizing zone. Such raw oil may be supplied directly to the separate heating tubes in admixture with the returned reflux condensate, or, and this is a particularly advantageous method of operation, the raw oil, or part of it, may be introduced into the refluxing operation for promoting or controlling the refluxing operation and for preheating the raw oil. Admixed reflux condensate and unvaporized raw oil may then be supplied to the separate heating tubes from the refluxing operation. Additional raw oil may also be supplied directly to the charge of oil circulating through the vaporizing zone, and part of the reflux condensate, or admixed raw oil and refluxed condensate, from the refluxing operation may also be supplied directly to the body of oil circulating through the vaporizing zone as required without first being passed through the separate heating tubes.

The present invention thus provides improved protection for all of the externally heated heating surfaces of the pressure still. The heating tubes with which the heating gases first contact and which accordingly are exposed to the heating gases while at highest temperature are protected by circulation therethrough of relatively refractory stock and stock which is substantially free from asphaltic and pitch-like constituents formed in the cracking operation, the stock circulated through these first heating tubes being either reflux condensate or a mixture of reflux condensate and raw oil. The remaining heating tubes are protected in a dual manner; they are protected by the action of the bed of finely divided absorbent or filtering material in reducing the concentration of asphaltic and pitch-like constituents in the oil circulating therethrough, and they are further protected by the tempering of the heating gases effected by heat absorption in the first heating tubes. The reflux condensate circulated through the first heating tubes is also subjected to advantageous cracking conditions, this reflux condensate being relatively refractory with respect to the cracking conditions to which the body of oil circulated and recirculated through the remaining heating tubes is subjected. The several features of the invention thus combine to give a particularly advantageous operation.

The invention will be further described in connection with the accompanying drawings which illustrate, somewhat diagrammatically and conventionally, in elevation and partly in section and with parts broken away, a pressure still system embodying the invention and adapted for the practice of the process of the invention.

Referring to the drawings, the pressure still illustrated comprises a bulk supply drum 1, a battery of heating tubes 2 and circulating connections 3, 4 and 5 including a circulating pump 6 arranged to provide for circulation of oil from the bulk supply drum through the heating tubes 2 and back to the bulk supply drum. Arranged in the bulk supply drum and below the normal liquid level therein is a bed 7 of finely divided absorbent or filtering material. This bed is supported on a suitable support 8 adapted to retain the finely divided solid material but to permit free passage of oil therethrough. The support may consist, for example, of one or more screens arranged between perforated plates or between suitable gratings. The support 8 and the bed of finely divided solid material thereon are arranged in the bulk supply drum 1 extending entirely across the bulk supply drum and between the circulating connections 3 to the circulating tubes 2 and the circulating connections 5 from the heating tubes so that oil circulating and recirculating through the heating tubes 2 is compelled to pass through this bed of finely divided material.

The battery of heating tubes 2 is arranged in a heating flue in the heating furnace 9. A firebox 10 communicates with the upper end of this heating flue and a stack flue 11 with the lower end of this heating flue. A separate bank of heating tubes 12 is arranged in the heating furnace in the flue between the firebox 10 and the heating tubes 2 so that heating gases from the firebox must pass over these heating tubes 12 before contacting with the heating tubes 2. Further to assist in tempering the heating gases passing over the heating tubes, means for circulating over the heating tubes a portion of the escaping waste heating gases in admixture with fresh hot products of com-

bustion from the firebox may be provided, as shown at 13.

Arranged above the bulk supply drum 1 is a reflux tower 14. Vapors from the bulk supply drum enter the lower end of this reflux tower through vapor line 15. Vapors remaining uncondensed escape from the upper end of this reflux tower through vapor line 16 to the condenser 17 arranged to discharge into the receiver 18. The distillate product is discharged from the receiver 18 through the connection 19 and uncondensed vapors and gases through the connection 20. The pressure in the system may be maintained and regulated by means of the valve 21 or by means of suitable valves arranged beyond the condenser or receiver. Reflux condensate from the reflux tower 14 is conveyed to the reservoir 22 through connection 23. A supplemental vaporline between the upper end of the reservoir 22 and a point in the reflux tower above the outlet for reflux condensate is provided at 24. From the reservoir 22, reflux condensate is circulated through the heating tubes 12 by means of connection 25 or pump 26 and connection 27. The hot oil products from the heating tubes 12 are discharged into the bulk supply drum 1 through connections 28 and 5. Feed line 29 is provided for introducing raw oil into the upper end of the reflux tower 14. Raw oil so introduced into the reflux tower 14 passes to the reservoir 22 and continues in admixture with the reflux condensate. Additional raw oil may be supplied directly to the heating tubes 12 through connection 30. An overflow connection for reflux condensate, or reflux condensate and admixed unvaporized raw oil, in excess of that discharged through connection 23 is provided at 31. Oil may also be discharged from the reservoir 22 into the upper end of the circulating connection 3 through connection 32. If for any reason the supply of oil to the heating tubes 12 from reservoir 22 is insufficient, as in starting the operation, a part of the recirculating charge of oil in the pressure still may be supplied thereto through connection 33, or other oil may be supplied through connection 30.

A tar line for discharging tar or pitch-laden oil from the pressure still during operation is provided at 34. A connection for pumping out and for initially charging the still is shown at 35. Oil for cooling and lubricating the bearings of the circulating pump 6 may be supplied through connection 36, or raw oil in excess of the amount required for cooling and lubricating the pump bearings may be supplied to the recirculating still charge through this connection and forced in through the pump bearings.

The bulk supply drum 1, the reservoir 22, and the several hot connections are all advantageously lagged or insulated to prevent or reduce heat loss. Where the refluxing operation is effected by heat exchange with raw oil, as in the apparatus illustrated, it is also advantageous to lag or insulate the reflux tower 14.

In starting operation, the still system is charged with oil and gradually brought to cracking conditions of temperature and pressure in the usual manner. While the still is being brought to cracking conditions, or until an adequate supply of reflux condensate is available, a portion of the oil discharged by the circulating pump 6 may be diverted through the heating tubes 12 by means of connection 33.

In cracking gas oil to produce gasoline, for example, pressures in the neighborhood of 100 to 125 pounds per square inch or higher pressures may be used. The average temperature of the body of oil circulating or recirculating through the heating tubes 2 will in general be the temperature corresponding to the pressure used; but the oil circulating through the heating tubes 12 may be superheated to a considerably higher temperature. For example, if the oil body in the bulk supply drum 1 is at a temperature in the neighborhood of 750° to 775° F., the hot oil products from the heating tubes 12 as discharged through connection 28 may be at a temperature of from 775° to upwards of 825° F. The refluxing operation may be controlled by regulated introduction of raw oil through connection 29; for example, the temperature at which the vapors remaining uncondensed escape from the upper end of the reflux tower may be maintained at some appropriate predetermined temperature by regulating the introduction of raw oil. Additional raw oil supplied to the operation may be introduced through connection 36 or in part through connection 36 or through connection 30 or in part through connection 30.

In a pressure still of the type illustrated in which the bulk supply drum 1 is adapted to contain a normal operating charge in the neighborhood of 10,000 gallons, the bed of finely divided solid material 7 may with advantage consist of from four to seven tons of fuller's earth. It is advantageous to use relatively coarse earth, say from 15 to 30 mesh, although finer earth may be used. The tar line 34 is advantageously arranged, as illustrated, to discharge pitch-laden oil from the body of oil in the bulk supply drum 1 from above the bed of finely divided filtering or absorbent material, although it may be arranged to discharge from beneath the bed of finely divided absorbent or filtering material.

In carrying out the process of the invention in the apparatus illustrated, the oil circulated and recirculated through the battery of heating tubes 2 contains a reduced concentration of asphaltic and pitch-like constituents formed by the cracking operation due to

the repeated passage of the circulating oil through the bed of absorbent or filtering material 7. This bed of filtering or absorbent material is entirely submerged in and directly exposed to the body of oil in the bulk supply drum 1 so as to exert its maximum effect upon the still charge. The concentration of asphaltic and pitch-like constituents in the charge of oil circulating through the bulk supply drum 1 is further controlled by the discharge of tar or pitch-laden oil through connection 34 in conjunction with the supply of raw oil to the operation. During the operation, the oil circulated through the battery of heating tubes 2 will nevertheless contain some asphaltic and pitch-like constituents but these heating tubes are further protected by the tempering of the heating gases effected by the heat absorption by the separate bank of heating tubes 12.

The heating gases including fresh hot products of combustion from the firebox pass first over the separate bank of heating tubes 12 and then over the battery of heating tubes 2 so that the reduction in temperature of the heating gases as they pass over the heating tubes 12 reduces the temperature of the heating gases as they contact with the heating tubes 2. The separate bank of heating tubes 12 are protected by the circulation of oil substantially free from asphaltic and pitch-like constituents therethrough, either reflux condensate from the reflux tower 14 or such reflux condensate admixed with raw oil. The relatively refractory character of the reflux condensate, moreover, assists in further reducing or retarding the formation of asphaltic or pitch-like constituents in the heating tubes 12, that is the heating tubes subjected to highest temperatures.

The hot oil products discharged from the separate bank of heating tubes 12 may assist in heating, internally, the charge of oil in the bulk supply drum 1. Where the hot oil products are heated in the heating tubes 12 to a temperature substantially higher than that prevailing in the bulk supply drum 1, the reduction of temperature of the hot oil products discharged from the separate bank of heating tubes 12 as they are introduced into the body of oil in the bulk supply drum 1 may also assist in arresting any tendency toward overcracking.

We claim:

1. An improved method of cracking hydrocarbon oils, which comprises circulating oil from a body of oil in a vaporizing zone through heating tubes and back to the body and heating it to a cracking temperature in the heating tubes, maintaining a bed of finely divided solid absorbent material within said body of oil so that the circulating oil is caused to pass therethrough, taking off vapors from said vaporizing zone under superatmospheric pressure and subjecting them to a refluxing operation, circulating reflux condensate from said refluxing operation through separate heating tubes into said vaporizing zone, and passing heating gases from a firebox in which fuel is burned for supplying heat to the cracking operation first over said separate heating tubes through which reflux condensate is circulated and then over the first mentioned heating tubes.

2. An improved method of cracking hydrocarbon oils, which comprises circulating oil from a body of oil in a vaporizing zone through heating tubes and back to the body and heating it to a cracking temperature in the heating tubes, maintaining a bed of finely divided solid material within said body of oil so that the circulating oil is caused to pass therethrough, taking off vapors from said vaporizing zone under superatmospheric pressure and subjecting them to a refluxing operation, introducing raw oil into direct contact with the vapors in the refluxing operation, circulating admixed reflux condensate and unvaporized raw oil from said refluxing operation through separate heating tubes into said vaporizing zone, and passing heating gases from a firebox in which fuel is burned for supplying heat to the cracking operation first over said separate heating tubes through which admixed reflux condensate and unvaporized raw oil is circulated and then over the first mentioned heating tubes.

3. An improved method of cracking hydrocarbon oils which comprises circulating oil from a body of oil in a vaporizing zone through heating tubes and back to the body and heating it to a cracking temperature in the heating tubes, maintaining a bed of finely divided solid material within said body of oil so that the circulating oil is caused to pass therethrough, taking off vapors from said vaporizing zone under superatmospheric pressure and subjecting them to a refluxing operation, circulating reflux condensate from said refluxing operation together with raw oil through separate heating tubes into said vaporizing zone, and passing heating gases from a firebox in which fuel is burned for supplying heat to the cracking operation first over said separate heating tubes through which reflux condensate and raw oil are circulated and then over the first mentioned heating tubes.

4. An improved method of cracking hydrocarbon oils which comprises circulating oil from a body of oil in a vaporizing zone through heating tubes and back to the body and heating it to a cracking temperature in the heating tubes, maintaining a bed of finely divided solid material within said body of oil so that the circulating oil is caused to pass therethrough, taking off vapors from said vaporizing zone under superatmospheric pressure and subjecting them to a re-

fluxing operation, circulating reflux condensate from said refluxing operation through separate heating tubes into said vaporizing zone, discharging pitch-laden oil from the body of oil in said vaporizing zone and supplying raw oil, and passing heating gases from a firebox in which fuel is burned for supplying heat to the cracking operation first over said separate heating tubes through which reflux condensate is circulated and then over the first mentioned heating tubes.

5. An improved method of cracking hydrocarbon oils, which comprises circulating oil from a body of oil in a vaporizing zone through heating tubes and back to the body and heating it to a cracking temperature in the heating tubes, maintaining a bed of fuller's earth within said body of oil so that the circulating oil is caused to pass therethrough, taking off vapors from said vaporizing zone under superatmospheric pressure and subjecting them to a refluxing operation, recirculating reflux condensate from said refluxing operation through separate heating tubes into said vaporizing zone, and passing heating gases from a firebox in which fuel is burned for supplying heat to the cracking operation first over said separate heating tubes through which reflux condensate is circulated and then over the first mentioned heating tubes.

6. An improved apparatus for cracking hydrocarbon oils, comprising a heating furnace having a heating flue, a firebox connected to one end thereof and a stack flue to the other, a bulk supply drum and a battery of heating tubes arranged in the heating flue of the heating furnace and circulating connections for circulating oil from the bulk supply drum through the heating tubes and back to the bulk supply drum, a bed of finely divided solid material arranged in the bulk supply drum below the normal liquid level therein and extending entirely across the bulk supply drum between the circulating connection from the said heating tubes and the circulating connection to the said heating tubes, a reflux tower and a vapor line from the bulk supply drum to the reflux tower, a separate bank of heating tubes arranged in the heating flue of the heating furnace between the firebox and the first mentioned bank of heating tubes, and circulating connections for circulating reflux condensate from said reflux tower through said separate bank of heating tubes back to the bulk supply drum.

7. An improved method of cracking hydrocarbon oil which comprises passing the oil through a heating coil wherein it is subjected to a conversion temperature, discharging the heated oil into an enlarged conversion chamber and maintaining a body of oil therein, taking off vapors from said conversion chamber under superatmospheric pressure and subjecting them to a refluxing operation, returning reflux condensate from the refluxing operation to said heating coil, maintaining a bed of finely divided solid material within said body of oil, circulating unvaporized oil in said conversion chamber through the bed of finely divided solid material and thereafter through an independent heating element wherein it is subjected to a lower temperature than the oil in said coil and back to the conversion chamber, and maintaining a superatmospheric pressure on the oil undergoing conversion.

EUGENE C. HERTHEL.
HARRY L. PELZER.