

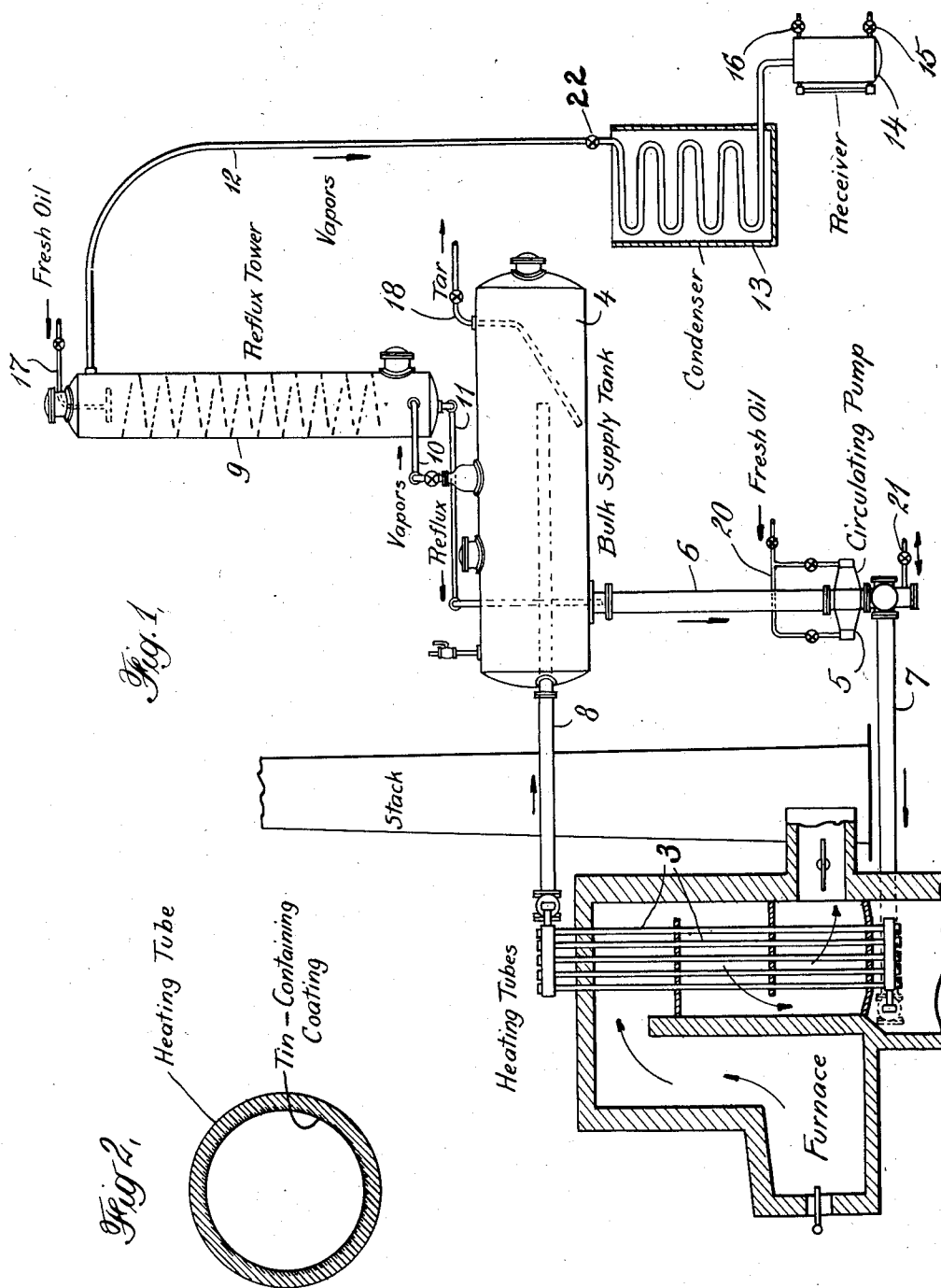
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ART OF CRACKING HYDROCARBONS

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ART OF CRACKING HYDROCARBONS.

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This invention relates to improvements in cracking heavier hydrocarbon oils, such as gas oil, for the production of lighter hydrocarbon oils, such as gasoline or pressure distillate, by distillation under pressure. The invention includes improvements in both method and apparatus.

When a charge of oil, such as gas oil, is subjected to a cracking temperature in a pressure still, cracking takes place in a progressive manner. Lighter constituents produced by the cracking operation are vaporized, and other constituents, such as heavier hydrocarbons formed by the cracking operation, may remain and mix with the charge in the still. An amount of asphaltic or pitch-like constituents is also progressively formed. Initially, these pitch-like constituents may remain more or less completely in solution in the still charge, but, as the cracking operation proceeds and part of the charge is cracked and vaporized and additional amounts of the pitch-like constituents are formed, the concentration of pitch-like constituents in the charge passes saturation and separation and precipitation of these constituents begins.

Externally heated pressure stills having heat transferring walls of iron or steel arranged to transfer heat from heating gases circulated about the exterior of the wall to a body of the oil in contact with the interior of the wall are commonly employed for carrying out the cracking operation. The pitch-like constituents formed by the cracking operation tend to deposit upon the metallic heating walls as they separate from the charge, and in some cases deposits may form upon the heating surfaces even when the general concentration of pitch-like constituents is below saturation in the entire still charge. This is apparently due to a preferential affinity of the pitch-like constituents, or of some component of the pitch-like constituents, possibly sulfur or some sulfur compounds, for the highly heated metal of the heat-transferring wall, or to a local increase in the concentration of pitch-like constituents immediately adjacent the heating wall.

These pitchy deposits, or the coky carbonaceous masses to which they are rapidly converted in contact with the hot heating wall, are not good conductors of heat so that a danger of overheating and failure of the heating walls ensues unless the still is shut down at more or less frequent intervals for clean-

ing. Moreover, this deposit decreases the heat-transferring capacity of the wall and consequently the capacity of the still. The limitation thus imposed upon the period of operation, and the necessity for more or less frequent cleaning of the still, of course decreases the overall efficiency and capacity of the still. The cleaning operation, likewise, is not without its difficulties, particularly as in contact with the hot heat-transferring wall the deposit tends to bake to a hard, compact, dense, carbonaceous mass closely adhering to the wall. The wear due to the cleaning operation and corrosion due to the deposits also necessitates replacement of the heat-transferring walls from time to time.

According to the present invention, the heating surface in contact with the oil is modified to provide a surface inhibiting the tendency of the pitch-like constituents formed by the cracking operation to adhere thereto, whether such constituents are in solution in the still charge or precipitated therefrom, and circulation of the oil over the heating surface is maintained, so that such constituents are swept along with the oil and so that deposit of such pitch-like constituents or formation of closely adhering carbonaceous layers on the heating surfaces is prevented or materially reduced.

According to the present invention, the surfaces of the heating walls of the pressure still which are in contact with the body of oil in the still are coated with tin. Tin in the pure state has a relatively low melting point, but the tin, or a part of the tin, in the coating nevertheless apparently alloys with the iron or steel heat-transferring wall forming a surface layer which is stable at the cracking temperatures ordinarily employed, for example from 650° C. to 750° C., and which modifies the surface so that pitch-like constituents in solution or in suspension in oil in contact therewith do not have the marked tendency to adhere to the surface exhibited in connection with ordinary steel or iron surfaces at the cracking temperature.

The invention is useful in connection with pressure stills of the shell type, in which a body of oil is heated to the cracking temperature by heat transferred through the still shell. The invention is, however, of special value and application in connection with pressure stills in which a circulation of the oil over the heating surfaces is maintained. In

such stills, the tin containing coating on the heating surfaces inhibits the tendency of the pitch-like constituents to adhere thereto and the circulation of the oil over the heating surfaces sweeps the pitch-like constituents along with the oil eliminating or reducing the formation of deposits thereon. Where the invention is employed in connection with a single-pass tubular pressure still, that is a still in which the oil is forced once through one or more externally heated tubes, the tin-containing coating on the surfaces of the heating tubes in contact with the oil reduces the tendency of pitch-like constituents to adhere to the tubes and the circulation of the oil therethrough tends to carry such constituents along with the circulating oil so that they are discharged with the oil from the heating tubes.

The invention is of particular advantage in connection with pressure cracking stills in which the oil charge is circulated and recirculated over the heating surfaces. As compared to a single pass tubular cracking still, for example, the pitch content of the oil in the still is also circulated and recirculated over the heating surfaces. In accordance with the present invention, however, the concentration of pitch-like constituents in the charge may be carried to a greater value before objectionable deposition of pitch and carbon on the heating surfaces begins in stills of this character. Thermosiphonic action may be relied on to maintain the circulation in such stills, or mechanical forcing means, such as a pump, may, with advantage, be employed for maintaining a forced and rapid circulation of the oil over the heating surfaces. Opportunity may also be provided in such stills for the separation, outside of the heater, of pitch-like constituents carried through the heater with the circulating oil so that recirculation of such constituents through the heater may be somewhat reduced.

In carrying out the present invention, the concentration of pitch-like constituents in the pressure still charge may be controlled and maintained below saturation by introducing fresh oil and withdrawing tar in regulated amounts during the progress of the cracking operation, in the manner described in an application of Eugene C. Herthel filed September 24, 1923, Serial No. 664,502. The present invention is of special advantage in connection with an operation of this type; and, by carrying out the cracking operation in a pressure still having heating surfaces with a tin-containing coating while maintaining the concentration of pitch-like constituents in the still charge below saturation by the regulated introduction of fresh oil and withdrawal of tar, the cracking operation may be carried out over a materially prolonged period.

The invention will be further described in connection with the accompanying drawings

which illustrate, in a diagrammatic and conventional way, an apparatus embodying the invention and adapted for practicing the process of the invention. It is intended and will be understood, however, that this further description and illustration are for the purpose of exemplification only and that the invention is not limited thereto but that it may be carried out in a great variety of apparatus.

In the accompanying drawings:

Fig. 1 represents, in elevation and partly in section, a pressure still, and

Fig. 2 is an enlarged transverse section of a tubular heating element embodying the invention.

The pressure still illustrated is of the general construction and operation described in United States Letters Patent No. 1,285,200 granted to the Sinclair Refining Company November 19, 1918, on the application of Edward W. Isom.

The pressure still illustrated comprises a bank of heating tubes 3 arranged in the heating flue of a furnace, a bulk supply tank 4 located away from the furnace, a circulating pump 5, and circulating connections 6, 7 and 8 connecting successively the bulk supply tank, the circulating pump, the lower end of the heating tubes, and the upper end of the heating tubes and the bulk supply tank. Arranged above the bulk supply tank is a reflux tower 9 having baffles therein. The vapors from the bulk supply tank are discharged into the lower end of the reflux tower through the vapor line 10 and reflux, together with any admixed fresh oil, is returned to the circulating connection 6 through the overflow reflux line 11. The vapors from the upper end of the reflux tower escape through the vapor line 12 to the condenser 13 which is arranged to discharge into the receiver 14. The condensed distillate is discharged through the valved outlet 15 and the uncondensed vapors and gases through the valved outlet 16. A feed line 17 is arranged for introducing fresh oil into the upper end of the reflux tower into direct contact with the vapors therein, and a tar line 18 is arranged for withdrawing tar during the progress of the cracking operation. A connection 20 is provided for introducing fresh oil through the bearings of the circulating pump, and a connection 21 is arranged for initially charging and for pumping out the still. The pressure may be reduced and regulated by a regulating valve 22 arranged between the reflux tower and the condenser or by valves located beyond the condenser.

Each of the heating tubes 3 is provided internally with a tin-containing coating as is shown more in detail in Fig. 2. In a commercial still of the character illustrated 4" cold-drawn mild-steel tubing may be employed. The heating tubes may be prepared by tinning such steel tubes in any usual or suitable manner. For convenience, the tubes may be

5 tinned both inside and out. As the tinned tubes are heated to the cracking temperature, a part of the tin coating may be forced off, running down into and collecting in the lower header, but a part of the tin apparently alloys with the steel on the surface of the heating tube forming a tin-containing coating which modifies the surface of the tube in contact with the oil in the way which has been described.

10 In one way of carrying out the process of the present invention in the apparatus illustrated, the still is charged, for example with gas oil, and brought to the desired cracking temperature and pressure in the usual way. The vapors are then allowed to pass into the condenser and additional fresh charging stock is introduced into the upper end of the reflux tower. Some fresh oil is also introduced through the bearings of the circulating pump while it is in operation to cool and protect them. Before the pitch content of the charge reaches the saturation point, the withdrawal of tar is begun, and the rate of introduction of fresh oil and withdrawal of tar is regulated to maintain the concentration of pitch-like constituents in the still charge below saturation. The invention is also useful in connection with processes in which no tar or only a relatively small amount of tar is withdrawn, and by carrying out such operations in accordance with the present invention, the concentration of pitch-like constituents in the charge may be carried to a materially increased value before objectionable deposition begins.

35 The following example will serve to further illustrate the invention: The still was initially charged with 9,000 gallons of gas oil and brought to a pressure of approximately 105 pounds per square inch. The still was then opened to the condenser, and, as distillate was taken off, fresh charging stock was introduced into the reflux tower in amount corresponding to the amount of distillate off. After the still had been on stream for about 26 hours, about 50% of the total charge, initial charge plus additional charge fed in, had been taken off as distillate; and the withdrawal of tar was begun. At the same time the amount of fresh stock fed to the still was increased to correspond to about 200% of the distillate off and the amount of tar withdrawn was regulated to maintain the total distillate taken off at about 50% of the total charge. As the amount of fresh oil introduced into the still was increased, the amount introduced into the reflux tower was regulated to maintain the desired head temperature therein and the additional fresh oil was introduced through the bearings of the circulating pump. During the operation, 109,975 gallons of additional charging stock were introduced

and 43,050 gallons of tar were withdrawn. The operation was terminated after the still had been on stream 132 hours. 50,950 gallons of pressure distillate containing 69% of 450° F. end-point gasoline were obtained. When the still was opened for cleaning some coke was found in the tubes but it was loose and porous and did not adhere closely to the surfaces of the tubes.

It will thus be seen that this invention provides an improved method and apparatus for cracking hydrocarbon oils by distillation under pressure in which the danger of overheating or burning out the heating surfaces of the still is reduced even though the cracking operation is carried out over a prolonged period. It is another important advantage of the present invention that it enables the cracking operation to be materially prolonged, especially where the invention is practiced in conjunction with methods of operation in which the concentration of pitch-like constituents in the charge is controlled by the regulated introduction of fresh oil and withdrawal of tar.

It will also be apparent that the present invention may be employed in conjunction with a great variety of cracking processes and that existing cracking apparatus may readily be modified in accordance with the present invention.

I claim:

1. In a pressure still for cracking hydrocarbon oils, a tubular heater, connections adapted for circulating and recirculating a liquid body of oil in the still therethrough, and means for circulating heating gases externally about the tubular elements of the heater, the internal surface of the tubular heater elements having a tin-containing coating thereon.

2. In a pressure still for cracking hydrocarbon oils, a tubular heater, connections including a mechanical forcing means adapted for circulating and recirculating a liquid body of oil in the still therethrough, and means for circulating heating gases externally about the tubular elements of the heater, the internal surface of the tubular heater elements having a tin-containing coating thereon.

3. A pressure still for cracking hydrocarbon oils, comprising a bulk supply tank and a heater having a surface with a tin-containing coating adapted for contact with oil in the still, means for externally heating the heater, and connections for circulating oil from the bulk supply tank to and through the heater back to the bulk supply tank.

In testimony whereof I affix my signature

JOHN PERL.