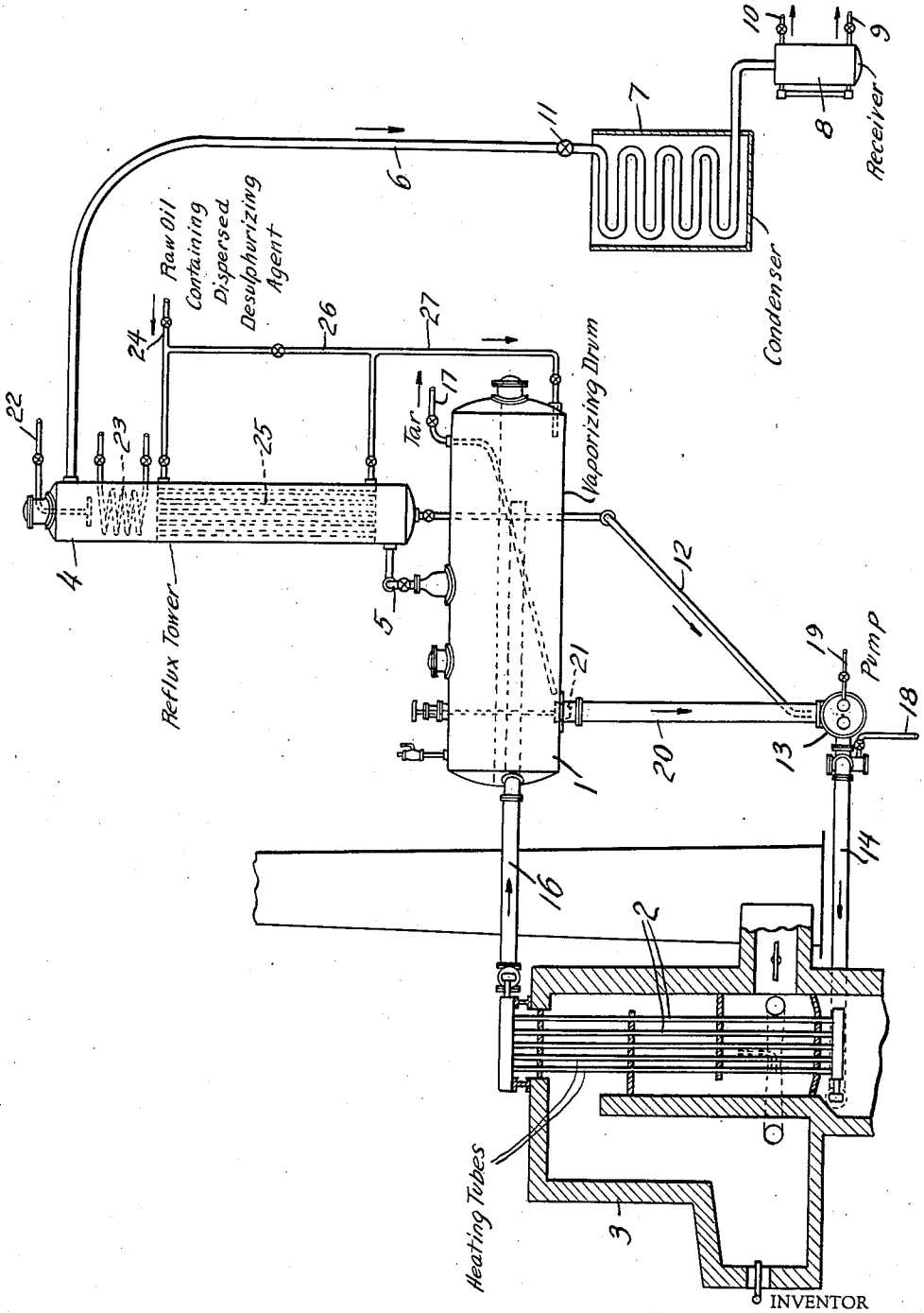
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ART OF CRACKING HYDROCARBON OILS

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# UNITED STATES PATENT OFFICE

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## ART OF CRACKING HYDROCARBON OILS

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Petroleum oils as they come from the ground, probably without exception, contain sulphur. The amount of sulphur and the form in which the sulphur is present varies in different oils. The amount of sulphur may vary, for example, from a fraction of one per cent to several per cent on the oil. Sometimes the sulphur is present in a form such that its removal offers no particular difficulties, sometimes in a very refractory form. The removal of sulphur or the conversion of sulphur to an unobjectionable form is one of the important purposes of most refining treatments to which petroleum oil products are usually subjected. In this aspect the sulphur is objectionable because it impairs the quality of the product. Frequently the sulphur is objectionable in another aspect, namely as a cause of corrosion. Cracking operations as commonly carried out usually involve the maintenance of high temperatures and high pressures, and in this latter aspect the presence of sulphur in stocks subjected to cracking operations consequently involves special difficulties because high temperatures tend to accelerate corrosion and high pressures increase the element of danger resulting from corrosion.

This invention relates to improvements in the cracking of heavy sulphur-containing hydrocarbon oils, such as gas oil, crude oil, topped crude oil, fuel oil, by distillation under superatmospheric pressure to produce lighter hydrocarbon oils, such as gasoline.

According to this invention, a desulphurizing agent is supplied to the cracking operation dispersed in raw oil supplied to the cracking operation in a manner such that circulation of the desulphurizing agent through zones in which the oil is externally heated is avoided and such that a contact between the oil and the desulphurizing agent particularly effective to combat corrosion is effected. In carrying out the invention, oil vapors are taken off from a vaporizing zone under superatmospheric pressure and subjected to a refluxing operation in which constituents of the vapors heavier than suitable as components of the desired product are condensed, reflux condensate from this refluxing operation is circulated through a heating zone in which it is heated to a cracking temperature to the vaporizing zone without permitting circulation of unvaporized oil from the vaporizing zone through the heating zone, raw oil is supplied to the vaporizing zone and the desulphurizing agent is also supplied to the vaporizing zone dispersed in this raw oil, and unvaporized oil including any unconsumed desulphurizing agent and any heavy products of the desulphurization is discharged from the vaporizing zone. Raw oil including the dispersed desulphurizing agent is with advantage passed in indirect heat exchanging relation with the vapors in the refluxing operation before introduction into the vaporizing zone.

Thus, all constituents of the raw oil supplied to the vaporizing zone circulated through the heating zone must first be vaporized in the vaporizing zone and condensed in the refluxing operation, and any unconsumed desulphurizing agent and any heavy products of the desulphurization remain in the vaporizing zone to be discharged therefrom with the unvaporized oil without being circulated through the heating zone. At the same time, all of the raw oil so supplied to the vaporizing zone is brought into intimate contact with the desulphurizing agent at elevated temperature. Corrosion difficulties seem to be more severe on surfaces in contact with oil vapors than on surfaces in contact with liquid oil, at the same temperature. This invention however insures intimate contact between the desulphurizing agent and vaporized constituents as well as unvaporized constituents of the raw oil so supplied to the operation. The maximum effect of the desulphurizing agent may be secured by maintaining a substantial body of oil in the vaporizing zone. By passing the raw oil containing the dispersed desulphurizing agent in indirect heat exchanging relation with the vapors in the refluxing operation, the oil is preheated and thus maintained in contact with the desulphurizing agent at elevated temperature for a prolonged period and for a period preceding introduction into the vaporizing zone. These several factors cooperate to make the desulphurizing agent more effective. By avoiding circulation of the desulphurizing agent or heavy

products of the desulphurization through the heating zone, any tendency of such materials to cause or to accelerate the formation of carbonaceous deposits in the heating zone impeding heat transfer and tending to cause overheating of that part of the apparatus is avoided.

The desulphurizing agents useful in carrying out this invention include lime, copper oxide or copper silicate gels, finely divided absorbent materials such as fuller's earth carrying dispersed copper salts such as copper chloride, alcoholic solutions of caustic alkali. The invention is particularly adapted to utilize finely divided solid desulphurizing agents supplied in suspension in raw oil. The invention is also adapted to utilize liquid or semi-liquid desulphurizing agents supplied in emulsion in raw oil. The invention is particularly adapted to utilize lime as the desulphurizing agent and lime is a particularly advantageous desulphurizing agent to use in carrying out this invention.

This invention thus provides an advantageous method of combatting corrosion in the cracking of sulphur-containing hydrocarbon oils by distillation under superatmospheric pressure and is also effective in reducing the sulphur content of the oil products of such operations.

The invention will be further described in connection with the accompanying drawings which illustrate, diagrammatically and conventionally, in elevation and partly in section and with parts broken away, one form of apparatus adapted for carrying out the process of the invention. It will be understood that the following more detailed description of the invention in connection with this particular form of apparatus is intended to exemplify the invention and that the invention can be carried out in other and different forms of apparatus.

The pressure still illustrated comprises a vaporizing drum 1 and a battery of heating tubes 2 arranged in the heating flue of a heating furnace 3. A reflux tower 4 is arranged above the vaporizing drum 1. Vapors escape from the vaporizing drum 1 to the lower end of the reflux tower 4 through vapor line 5 and vapors remaining uncondensed escape from the upper end of the reflux tower 4 through vapor line 6 to a condenser 7. Condenser 7 is arranged to discharge into receiver 8 from which the distillate product of the operation is discharged through connection 9 and uncondensed vapors and gases through connection 10. Pressure in the system may be maintained and regulated by means of valve 11 in the vapor line 6 between the reflux tower 4 and the condenser 7 or by means of suitable valves arranged beyond the condenser or receiver. Reflux condensate from the lower end of the reflux tower 4 is discharged through connection 12 to the pump 13 which then forces this oil mixture through connection 14 upwardly through the heating tubes 2 through connection 16 to the vaporizing drum 1. The oil is heated to a cracking temperature in the heating tubes 2. Tar line 17 is provided for discharging unvaporized oil from the vaporizing drum during operation. Connection 18 is provided for initially charging the still and for pumping out the still at the end of a run. Connection 19 is provided for supplying cooling oil to the bearings of the pump 13. Connection 20 with closure valve 21 is provided for use in bringing the still into operation. Connection 22, for direct introduction of a refluxing medium, and cooling coil 23 are provided for effecting or controlling the refluxing operation in tower 4. Raw oil is supplied through connection 24, either around the vapor tubes 25 in the reflux tower 4 or through connection 26, through connection 27 to the vaporizing drum 1.

The particular type of pump illustrated, designated 13, is described in more detail in an application of Thomas d' C. Tifft filed June 7, 1927, Serial No. 197,209. The particular type of closure valve illustrated, designated 21, is described in more detail in my application filed January 12, 1928, Serial No. 246,263.

To bring the still system illustrated to operating conditions of temperature and pressure, with the valve 21 open the still is charged with enough oil to fill the drum 1 say half full, pump 13 is started to maintain circulation of the oil charge from the drum 1 through the heating tubes 2 back to the drum 1, fires are started in the heating furnace 3, drips are taken off, valve 11 is then closed until the desired operating pressure is reached, valve 21 is then closed very gradually and valve 11 is gradually opened and regulated to maintain the desired operating pressure, and the supply of raw oil and discharge of unvaporized oil is begun. For the production of gasoline from gas oil, for example, pressures in the neighborhood of 90–125 pounds per square inch may be employed, or higher pressures up to say 300 pounds per square inch or more may be employed. In general, higher pressures are employed with lighter charging stocks or to produce lighter distillate products. In any particular case the temperature will be determined by the pressure used.

The initial charge of oil may consist of the same stock to be supplied during operation or, particularly if the stock to be supplied during operation contains a large amount of objectionable sulphur, the initial charge may consist of some other stock containing a relatively small amount of objectionable sulphur or, if the stock to be supplied during operation is a crude or topped crude or fuel

oil or contains a large amount of tarry or pitchy constituents, the initial charge may consist of a clean gas oil stock.

In carrying out the present invention in the apparatus illustrated, after the still system has been brought to operating conditions of temperature and pressure, the introduction of raw oil, the sulphur-containing stock, into the vaporizing drum 1 through connections 24 and 27 together with a desulphurizing agent dispersed therein is begun. The raw oil so supplied to the vaporizing drum 1 may contain in suspension, for example, from ¼ to 4 pounds of hydrated lime per barrel (42 gallons). This raw oil containing the dispersed desulphurizing agent may be supplied to the vaporizing drum 1 after passing around the vapor tubes in the reflux tower 4 or may be supplied to the vaporizing drum 1 through connection 26 or may be supplied partly in each way. For example, the refluxing operation carried out in tower 4 may be controlled, in whole or in part, by regulated by-passing of such raw oil through connection 26, the rest passing around the vapor tubes in the reflux tower 4. In the vaporizing drum 1 the constituents of the raw oil to be passed through the heating tubes 2 are vaporized and escape to the reflux tower 4 through vapor line 5; in the reflux tower 4 these vaporized constituents are condensed and supplied as condensate to the heating tubes 2 through connection 12. Any unconsumed desulphurizing agent and heavy products of the desulphurization together with any unvaporized heavy constituents of the raw oil remain as a residue in the vaporizing drum. For example, a gas oil raw stock may be completely vaporized upon introduction into the vaporizing drum 1 or a crude or topped crude stock or fuel oil stock may be vaporized only in part leaving heavy constituents or tarry or pitchy constituents in the residue. The residue collecting in the vaporizing drum 1 also includes heavy constituents discharged from the heating tubes 2. This residue is not permitted to circulate through the heating tubes 2, but is discharged through tar line 17. The reflux condensate collecting in the lower end of tower 4 includes heavy constituents condensed from the cracked vapors of the oil discharged into the vaporizing drum 1 from the heating tubes 2 as well as vaporized then condensed constituents of raw oil introduced into the vaporizing drum 1 through connection 27. The refluxing operation carried out in tower 4 is regulated to condense all constituents of the vapors passing therethrough heavier than suitable as components of the desired distillate product suitable to be supplied to the heating tubes 2 to be heated to a cracking temperature therein. For the production of gasoline, for example, the refluxing operation may be regulated so that the temperature of the vapors escaping through vapor line 6 as they leave the tower 4 is in the neighborhood of 500–570° F. where the system is operated under a pressure in the neighborhood of 125 pounds per square inch. The cooling effected by passage of raw oil around the vapor tubes 25 may be supplemented or closer control of the refluxing operation effected by the regulated introduction of a suitable refluxing medium through connection 22 or by the regulated circulation of a cooling medium, water or cool oil for example, through cooling coil 23. A part of the distillate product may be reintroduced through connection 22 or a clean gas oil stock may be introduced through this connection, for example, as a refluxing medium. Raw oil circulated through the reflux tower 4 around the vapor tubes 25 is thereby preheated and raw oil containing the dispersed desulphurizing agent may thus with advantage be heated to an elevated temperature while in contact with the desulphurizing agent before introduction into the vaporizing drum 1 and before any possibility of escape by vaporization of any of the raw oil constituents.

The apparatus illustrated, including the vaporizing drum 1, the reflux tower 4 and connections 5, 12, 14, 16, 20 and 27, are with advantage lagged or thermally insulated.

The character of the desulphurizing agent used permitting, the residue including any unconsumed desulphurizing agent and any heavy products of the desulphurization discharged from the vaporizing zone may be subjected to treatment for recovery of the desulphurizing agent. Where cupriferous desulphurizing agents are used, for example, the residue discharged from the vaporizing zone, either before or after distillation therefrom of lighter oil constituents, may be cooled and the cooled residue permitted to settle or subjected to a filtering operation for the separation of the metallic values and this separated material roasted or otherwise treated to render it again active to be reused in the process. In general, where lime is used for example, any unconsumed desulphurizing agent and any heavy products of the desulphurization may be separated from the discharged residue by settling or filtration after cooling.

I claim:

1. In cracking sulphur-containing hydrocarbon oils by distillation under superatmospheric pressure, the improvement which comprises taking off oil vapors from a vaporizing zone under superatmospheric pressure and subjecting such oil vapors to a refluxing operation to condense those constituents of the vapors heavier than suitable as components of the desired distillate product, circulating reflux condensate from the said refluxing operation through a heating zone to the said vaporizing zone without permitting cir-

culation of unvaporized oil from the said vaporizing zone through the said heating zone and heating the oil to a cracking temperature in the said heating zone, supplying raw oil to the said vaporizing zone, whereby all constituents of such raw oil circulated through the said heating zone must first be vaporized in the said vaporizing zone and condensed in the said refluxing operation, supplying a desulphurizing agent to the said vaporizing zone dispersed in such raw oil supplied thereto, whereby circulation through the said heating zone of the desulphurizing agent and heavy products of the desulphurization is avoided, and discharging unvaporized oil including any unconsumed desulphurizing agent and such heavy products of the desulphurization from the said vaporizing zone.

2. In cracking sulphur-containing hydrocarbon oils by distillation under superatmospheric pressure, the improvement which comprises taking off oil vapors from a vaporizing zone under superatmospheric pressure and subjecting such oil vapors to a refluxing operation to condense those constituents of the vapors heavier than suitable as components of the desired distillate product, circulating reflux condensate from the said refluxing operation through a heating zone to the said vaporizing zone without permitting circulation of unvaporized oil from the said vaporizing zone through the said heating zone and heating the oil to a cracking temperature in the said heating zone, passing raw oil in indirect heat exchanging relation with the vapors in the said refluxing operation thereby preheating the raw oil and supplying such preheated raw oil to the said vaporizing zone, whereby all constituents of such raw oil circulated through the said heating zone must first be vaporized in the said vaporizing zone and condensed in the said refluxing operation, supplying a desulphurizing agent to the said vaporizing zone dispersed in such raw oil passed in heat exchaning relation with the vapors in the said refluxing operation and then supplied to the said vaporizing zone, whereby the raw oil containing the dispersed desulphurizing agent is preheated before introduction into the vaporizing zone and whereby circulation through the said heating zone of the desulphurizing agent and heavy products of the desulphurization is avoided, and discharging unvaporized oil including any unconsumed desulphurizing agent and such heavy products of the desulphurization from the said vaporizing zone.

3. In cracking sulphur-containing hydrocarbon oils by distillation under superatmospheric pressure, the improvement which comprises taking off oil vapors from a vaporizing zone under superatmospheric pressure and subjecting such oil vapors to a refluxing operation to condense those constituents of the vapors heavier than suitable as components of the desired distillate product, circulating reflux condensate from the said refluxing operation through a heating zone to the said vaporizing zone without permitting circulation of unvaporized oil from the said vaporizing zone through the said heating zone and heating the oil to a cracking temperature in the said heating zone, supplying raw oil to the said vaporizing zone and supplying lime to the vaporizing zone in suspension in such raw oil supplied thereto, and discharging unvaporized oil including suspended lime and lime-containing reaction products from the said vaporizing zone, whereby circulation through the said heating zone of oil including suspended lime or lime-containing reaction products is avoided.

4. In cracking sulphur-containing hydrocarbon oils by distillation under superatmospheric pressure, the improvement which comprises taking off oil vapors from a vaporizing zone under superatmospheric pressure and subjecting such oil vapors to a refluxing operation to condense those constituents of the vapors heavier than suitable as components of the desired distillate product, circulating reflux condensate from the said refluxing operation through a heating zone to the said vaporizing zone without permitting circulation of unvaporized oil from the said vaporizing zone through the said heating zone and heating the oil to a cracking temperature in the said heating zone, passing raw oil in indirect heat exchanging relation with the vapors in the said refluxing operation and supplying such preheated raw oil to the said vaporizing zone, supplying lime to the said vaporizing zone in suspension in such raw oil passed in heat exchanging relation with the vapors in the said refluxing operation and then supplied to the said vaporizing zone, and discharging unvaporized oil including suspended lime and lime-containing reaction products from the said vaporizing zone, whereby circulation through the said heating zone of oil including suspended lime or lime-containing reaction products is avoided.

In testimony whereof, I have subscribed my name.

EUGENE C. HERTHEL.