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ART OF CRACKING HYDROCARBON OILS

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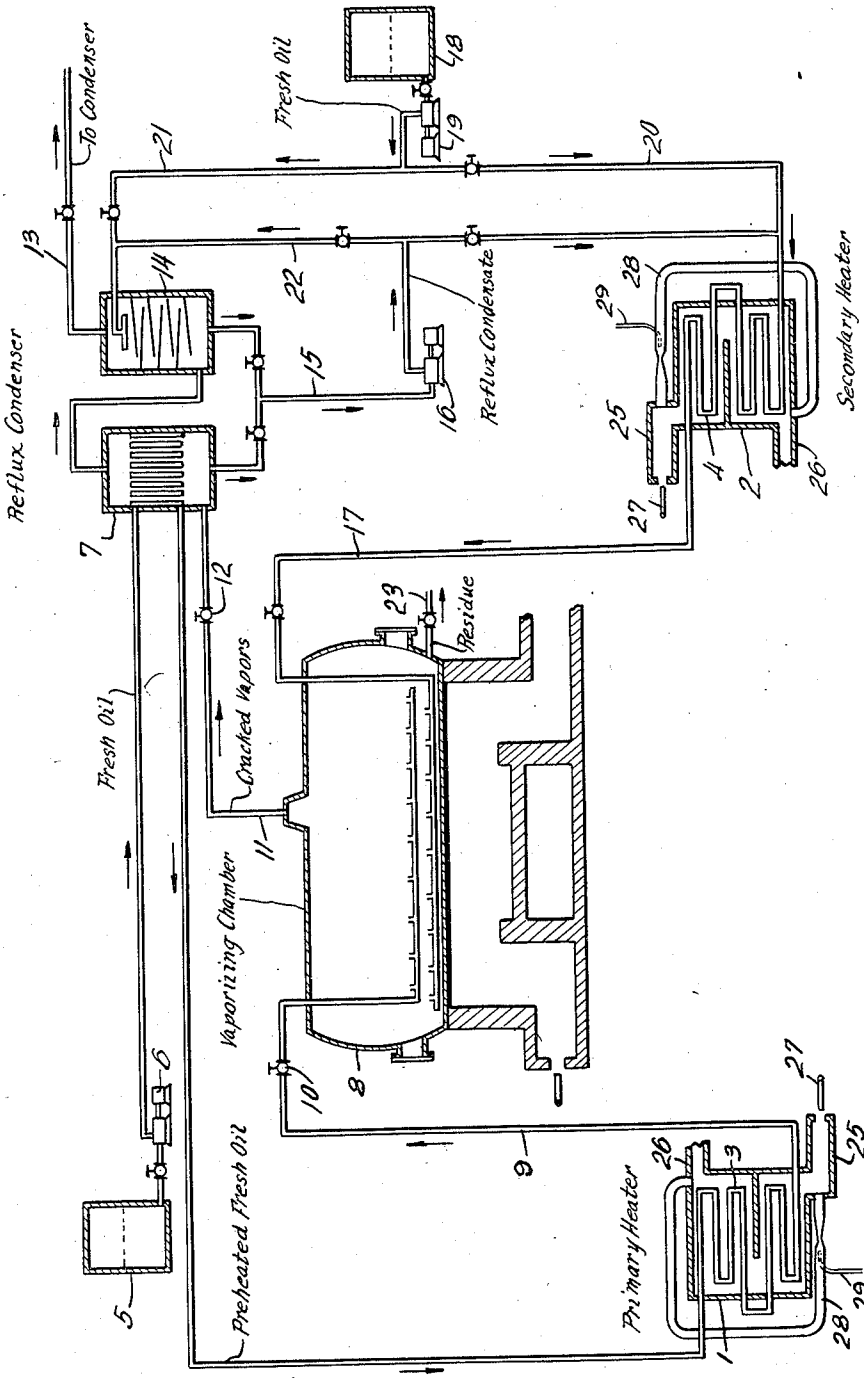

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ART OF CRACKING HYDROCARBON OILS

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1 Claim. (Cl. 196—60)

This invention relates to improvements in the cracking of heavier hydrocarbon oils, such as fuel oil, gas oil or kerosene, to produce lighter hydrocarbon oils such as gasoline or pressure distillates therefrom. This application is in part a continuation of my prior application filed August 28, 1922, Serial No. 584,711.

The present invention relates particularly to improvements in the operation of externally heated tubular single pass oil cracking stills or in the operation of cracking still systems in which externally heated tubular single pass heaters are employed.

When hydrocarbon oils are heated to a cracking temperature, they are decomposed with the formation of lighter hydrocarbon oils. The products of the cracking reaction also include a certain amount of fixed gases and heavy tar, or pitch, or carbon. When the cracking is effected by external heat transferred to the oil through the walls of heating tubes, the carbon or tarry matter tends to deposit on the heating surfaces in contact with the oil and to form an insulating layer thereon which retards heat transfer. Not only does this deposit impede effective transfer of heat to the oil, but it also deprives the walls of the heating tubes of the protective effect of the oil which tends to reduce the temperature of the tube walls by absorbing heat therefrom. The result is a tendency toward increase in the temperature of the tubes themselves as compared to that of the oil passing therethrough, which accelerates the deposition and tends to bake the deposit to a dense, closely adherent mass, further increasing the temperature of the tubes. This imposes a danger of rupture due to overheating, and is usually the limiting factor in the life of the heating tubes as well as in the period over which the operation can be continued in a single run. Heavier oils such as fuel oil or gas oil may be cracked at a lower temperature than lighter and more refractory oils and their decomposition results in the formation of substantially lighter hydrocarbon compounds, such as those suitable as components of gasoline, as well as carbon or tarry matter, and also a substantial proportion of refractory intermediate constituents. These refractory intermediate constituents may advantageously be subjected to a further cracking operation at a higher temperature. However, subjection of the heavier and more readily crackable oils to conditions such as those better suited for the conversion of the more refractory intermediate constituents tends to promote overcracking and also tends to cause excessive formation of carbon or tarry matter with resulting excessive deposition of carbonaceous material on the heating surfaces.

According to the present invention, heavy hydrocarbon oils are subjected to a cracking operation under conditions favorable for the conversion of the more readily crackable constituents of such oils to desired lighter hydrocarbon oils while eliminating or substantially reducing the tendency to deposition of carbonaceous material on the heating surfaces, and the refractory intermediate constituents formed, subsequently separated from heavy tarry matter and the desired lighter products of the cracking reaction, are subjected to a cracking treatment under conditions favorable for the further conversion of these intermediate constituents to desired lighter hydrocarbon oils. Thus further conversion of the intermediate constituents is advantageously effected in a cracking operation carried out in the vapor phase or substantially in the vapor phase. In the present invention, the vapor phase treatment of the refractory intermediate constituents and the treatment of the heavier oils are combined in a particularly advantageous manner. The invention is also of special value and application in connection with the combined treatment of heavier oils such as heavy gas oil or fuel oil and lighter oils of a more refractory nature such as kerosene or rerun pressure distillate bottoms.

According to one particularly advantageous embodiment of the invention a stream of the heavy oil to be treated is caused to flow once through a heating conduit or primary heater and is heated therein to a temperature sufficiently high to produce cracking of only the more readily crackable constituents. Excessive carbon deposition is accordingly avoided as the heavy tarry constituents formed by this relatively mild cracking treatment are not subjected to extreme temperatures and they are not again subjected to the cracking temperature in this primary heater. The hot products from the primary heater are discharged into a vaporizing chamber wherein vaporization of lighter products of this first cracking operation, effected largely in the liquid phase, as well as of the insufficiently cracked and more refractory constituents, takes place. The vapors liberated in the vaporizing chamber are withdrawn therefrom and subjected to a refluxing operation in which vapors heavier than those suitable as components of the desired pressure distillate are condensed. The reflux

condensate, which is of a relatively refractory character, is circulated once through a secondary heating conduit or secondary heater, either alone or together with additional light oils of a relatively refractory character, and subjected therein to a further more intense cracking treatment, substantially in the vapor phase. The hot products from the vapor phase cracking treatment are introduced into and caused to intermingle with the unvaporized oil from the primary cracking treatment in the vaporizing chamber. The temperature and pressure maintained in the vaporizing chamber are such as to permit substantial vaporization of all but the heavy tarry matter which it is not desirable to subject to further cracking treatment and the residual oil which accumulates in the vaporizing chamber is withdrawn therefrom and not again returned to the system. The unvaporized products from the primary cracking treatment, largely effected in the liquid phase, are thus intermingled with the hot vapors from the vapor phase cracking treatment. The excess sensible heat of the products from the latter assists in vaporizing the insufficiently cracked, intermediate constituents not vaporized by the heat contained in the hot products discharged from the primary heater, while the hot products from the secondary heater are scrubbed by the relatively cooler unvaporized products from the primary heater, thereby effectively condensing and separating heavy tarry matter resulting from the vapor phase cracking treatment. Contacting of the highly heated vapor from the vapor phase cracking treatment with the hot unvaporized oil from the primary heater also tends to promote a combination of any unstable, unsaturated constituents of the former to increase the yield of more saturated and more stable compounds.

In addition to the internal heat supplied to the unvaporized oil in the vaporizing chamber by the hot vapors from the vapor phase cracking operation, external heat may be supplied when required to insure substantially complete vaporization of all but the extremely heavy decomposition products of the combined operations. Distillation in the vaporizing chamber may be carried substantially to the point of coking by internal and external heating. The amount of heat supplied externally will in all cases be small and in many cases may be dispensed with altogether and internal heating relied upon entirely. The fresh oil supplied to the primary heater is preheated by indirect heat exchange with the vapors withdrawn from the vaporizing chamber, the cooling action of the fresh oil thereby effecting a preliminary refluxing of the vapors. The vapors remaining uncondensed in the preliminary refluxing operation are subjected to a further refluxing operation, which may be controlled by the introduction of fresh light oil or reflux condensate from the preliminary refluxing.

The invention will be further described in connection with the accompanying drawing which illustrates in a diagrammatic and conventional manner, in elevation and partly in section, an apparatus adapted for the practice of the process of the invention, but it is intended and will be understood that this further description and illustration are for the purpose of exemplification and that the invention is not limited thereto.

In the drawing two single pass externally heated tubular heaters are shown arranged to discharge into a shell or reservoir from which vapors of the cracked oil are taken off. The single pass cracking heaters are shown as of generally similar construction and comprise furnaces 1 and 2 having batteries of heating tubes 3 and 4, respectively, located therein. Fresh oil from the supply tank 5 is forced by the pump 6 through the reflux tower and heat exchanger 7, the battery of heating tubes 3 and thence to the reservoir 8 through pipe 9 provided with valve 10. Vapors are taken off from the reservoir 8 through connection 11 provided with valve 12 and pass successively through reflux towers 7 and 14 and thence to a condenser (not shown) through connection 13. In the reflux tower 7 the vapors are cooled and the heavier constituents refluxed by cool oil pumped about tubes through which the vapors pass. Uncondensed vapors passing from the top of reflux tower 7 are subjected to a further refluxing operation in the baffled reflux tower 14. Reflux condensate from towers 7 and 14, together with fresh unvaporized oil where fresh oil is introduced to the latter, is conveyed through pipe 15 to pump 16 and thence forced through the battery of heating tubes 4 and valved connection 17 to the reservoir 8. Fresh oil (preferably of a lighter character than that supplied to the battery of heating tubes 3) may be supplied from the supply tank 18 by the pump 19 directly to the battery of heating tubes 4 through valved connection 20. However, at least a part of this fresh oil is introduced to reflux tower 14 through valved connection 21. The refluxing operation in the tower 14 may be controlled in this manner, or by the introduction of a portion of the reflux condensate to the top of the tower through valved connection 22.

Each single pass heater is provided with a firebox 25 and a stack flue 26. Burners for gas or liquid fuel are shown at 27. Return connection 28 provided with forcing means 29 are arranged for withdrawing heating gases near the outlet to the stack flues and recycling them over the oil heating tubes. The forcing means shown consist of steam jets 29 but other suitable forcing means may be used. The temperature of the heating gases contacting with the oil heating surfaces may thus be regulated while permitting the firebox temperature to be maintained at the temperature required for the most efficient combustion of the fuel employed.

In beginning operation, fresh oil is forced through both batteries of heating tubes. As soon as reflux begins to accumulate, the circulation of reflux together with the fresh oil through the battery of heating tubes 4 is begun and as the quantity of reflux increases the introduction of fresh oil to heating tubes 4 is reduced. In the vaporizing drum or reservoir 8 the vapors of the cracked oil are separated from any residue. The residue may be reduced to coke or withdrawn as a flux through valved connection 23. The apparatus illustrated is exceptionally flexible as to pressure control. The pressures in the single pass heaters may be controlled independently and maintained at values substantially in excess of that prevailing in the reservoir 8. The reservoir 8 may be operated at atmospheric pressure or at substantially the pressure maintained in one or both heaters or at a pressure intermediate that prevailing in the heaters and atmospheric pressure. When the reservoir 8 is maintained under a pressure substantially in excess of atmospheric pressure, the pressure may be reduced between the reservoir and the reflux

towers or between the reflux towers and the condenser, or the pressure may be maintained through the condenser and reduced at a point beyond the condenser. The actual pressure employed may vary widely. In the primary heater 3 pressures up to from 100 to 300 pounds per square inch or more may be employed, while the pressure in the secondary heater 4 may be reduced to a point just sufficient to maintain flow therethrough at the desired rate.

In one particularly advantageous method of operation, the heater 3 may be maintained under a pressure of from about 90 to 125 pounds per square inch and the oil leaving the heater maintained at a temperature of from about 700 to 1000 degrees F., while the oil supplied to the heater 4 may be maintained therein under a pressure of from about 50 to 100 pounds per square inch and the temperature of the superheated oil vapors discharged therefrom maintained between about 800 to 1200 degrees F. The pressure maintained in the reservoir 8 may advantageously be just sufficient to provide for the discharge of the vapors and heavy unvaporized oil therefrom through the reflux towers and final condenser.

The improved process of the invention is useful in the production of hydrocarbon motor fuels having a relatively high critical compression, or of hydrocarbon distillates capable of increasing the critical compression of other hydrocarbon motor fuels with which they may be blended.

In referring to single pass heaters, reference is intended to heaters in which fresh oil is circulated but once through the oil heating tubes and where vaporized fractions of the oil may be refluxed and the reflux recirculated through the oil heating tubes, as distinguished from heaters in which the fresh oil or any unvaporized portion of the fresh oil is recirculated through the heating tubes.

I claim:

An improved method of cracking hydrocarbon oils which comprises passing fresh oil in a single pass through a heating zone of restricted cross section and thence into an enlarged vapor separating zone, subjecting the oil passing through the said heating zone to a cracking temperature and superatmospheric pressure, maintaining in said vapor separating zone a temperature and pressure sufficient to permit partial vaporization but to preclude complete vaporization of the oil supplied thereto, separating vapors from liquid oil in said vapor separating zone, taking off vapors of the cracked oil from the vapor separating zone and subjecting them successively to a first and second refluxing operation, introducing fresh oil into direct contact with the vapors in the second refluxing operation, passing reflux and preheated fresh oil from the second refluxing operation in a single pass through a separate heating zone and thence into the vapor separating zone, passing fresh oil being supplied to the first mentioned heating zone in indirect heat exchanging relation with the vapors in the first refluxing operation, and subjecting the oil in the second mentioned heating zone to a cracking treatment in the vapor phase under a pressure lower than that maintained in the first mentioned heating zone.

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