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TREATMENT OF HYDROCARBON OILS

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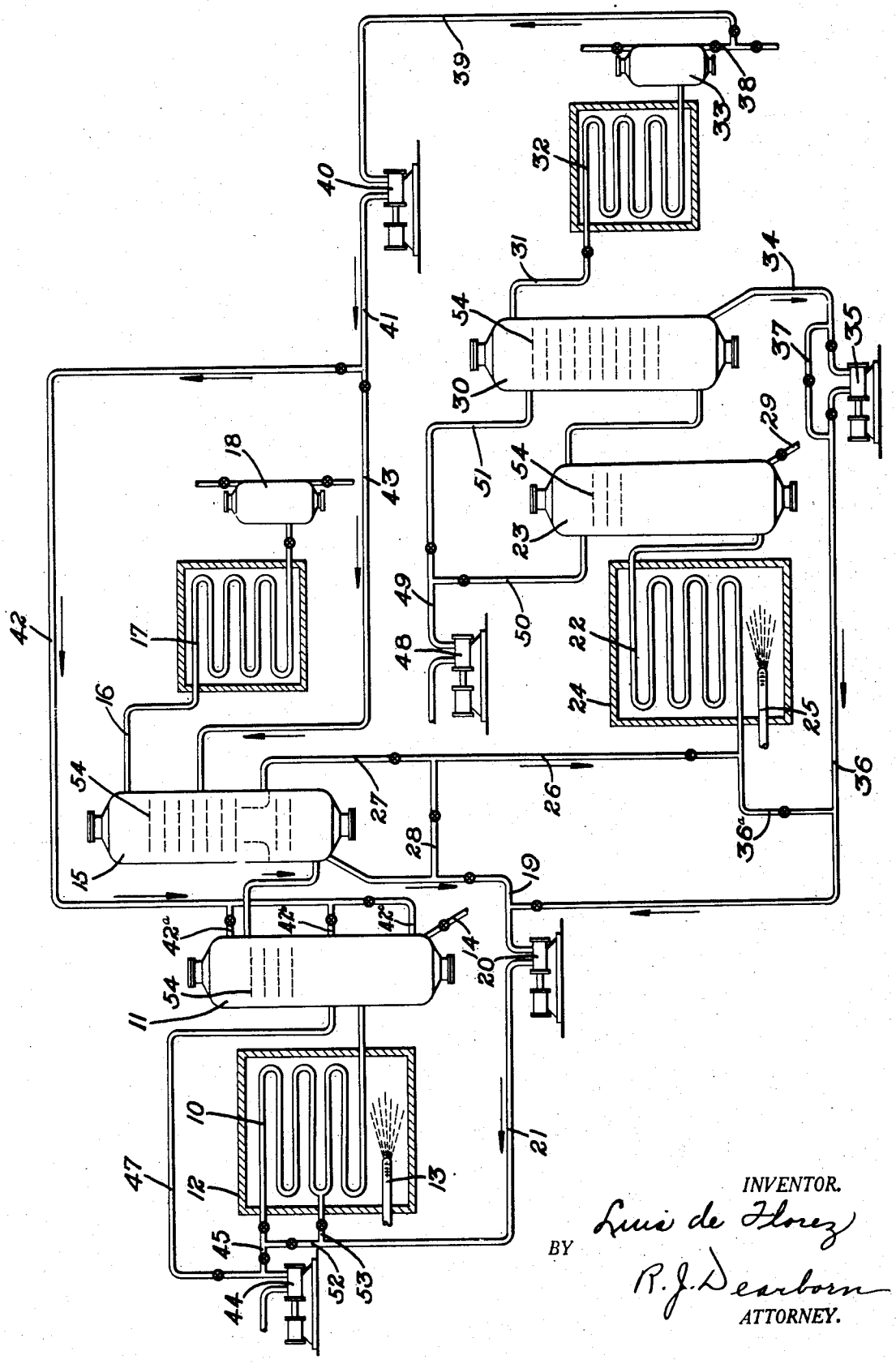

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TREATMENT OF HYDROCARBON OILS

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10 Claims. (Cl. 196—49)

This invention relates to certain novel improvements in the cracking of hydrocarbon oils for the production of gasoline and the like.

The invention contemplates a method in which oil is subjected to cracking under relatively high pressure conditions and a condensate derived from such cracking operation is then subjected to cracking under a relatively lower pressure. Thus, in accordance with the invention, the oil may be subjected to cracking and vaporization, the evolved vapors dephlegmated to form a reflux condensate and this condensate directed into a lower pressure cracking system without the intervention of a pump, the pressure differential between the two cracking elements being relied upon to force the condensate through the lower pressure cracking system.

In one method of operation contemplated by the invention oil in a primary cracking operation is subjected to cracking under given temperature and pressure conditions and a condensate derived from this operation is subjected to cracking in a secondary cracking operation at higher temperatures but under lower pressures than those obtaining in the primary cracking zone.

When a cracking stock is subjected to a cracking operation there is a limit to the amount of cracking which can be carried on largely on account of the decomposition of polymers or high carbon-forming hydrocarbons which are formed in the cracking reaction and which, as the reaction is continued, are converted to coke. In accordance with my invention, an original charging stock may be subjected to a given amount of cracking in a primary cracking zone under conditions avoiding any excessive production of coke, evolved vapors subjected to fractionation and a clean condensate fraction thus obtained which may then be subjected to further cracking, preferably at higher temperatures than that to which the original charging stock was subjected, so as to thus not only increase the yield of gasoline but by reason of the higher temperature employed in the secondary cracking operation to effect an increase in the anti-knock or anti-detonating value of the gasoline product produced.

One aspect of the invention has in view a method of operation in which a condensate derived from the secondary or lower pressure cracking system is conducted to the primary cracking zone or introduced into contact with vapors evolved in the primary cracking zone.

In order to more fully disclose the invention, reference will now be had to the accompanying drawing which is a diagrammatic sectional elevation of the apparatus constructed in accordance with the invention and constituting an embodiment thereof.

In the apparatus thus illustrated a primary cracking apparatus is shown which includes a heating coil 10 and a cracking still 11. The heating coil is shown mounted in a furnace 12 having a burner indicated at 13 and the still 11 is provided with suitable heating means or with heat insulating means. Liquid or residue is withdrawn from the still 11 through a line 14 and the evolved vapors are dephlegmated or fractionated in a tower 15. The overhead vapor fraction is removed from the tower through a line 16 to a condenser 17 and the distillate is collected in a receiver 18. A line 19 is shown extending from the tower 15 to a hot oil pump 20 provided with a discharge line 21 so that reflux condensate formed in the tower may be cyclically conducted to the coil 10.

A secondary cracking apparatus is shown which includes a heating coil 22 and a cracking still 23. The coil 22 is shown mounted in a furnace 24 with a burner indicated at 25 and the still 23 is provided with suitable heating means or with heat insulating means.

A transfer line 26 serves to introduce the charging stock to the secondary cracking apparatus and is shown provided with a branch line 27 extending to an intermediate point in the tower 15 and another branch line 28 communicating with the line 19. Thus by appropriate manipulation of the valves in these lines reflux condensates formed in the tower 15 may be handled in various ways. Thus, for example, all of the heavier condensate which collects in the bottom of the tower may be removed by the line 19 and cycled back to the primary cracking zone by the hot oil pump 20, while an intermediate cut may be withdrawn from an intermediate point in the tower and directed by the lines 27 and 26 to the lower pressure cracking zone; or, if desired, a portion of the heavier condensate fraction may be combined with the intermediate cut passing to the lower pressure cracking zone. In one alternative method of operation all of the condensate collected in the tower 15 may be withdrawn through lines 19 and 28 and passed through line 26 to the lower pressure cracking zone. The disposition of the various condensates formed in the tower may be varied in any suitable manner, but in general it is preferable to employ the heavier or higher boiling condensate as cycle stock for returning to the primary cracking zone while

using a lighter or lower boiling condensate for introduction to the lower pressure cracking zone.

The still 23 is provided with a residue draw-off line 29. The vapors evolved in the still 23 are passed to a dephlegmator or fractionating tower 30. The overhead vapor fraction from the tower 30 is removed by a vapor line 31 to a condenser 32 and a distillate receiver 33 is provided for collecting the distillate. Reflux condensate is removed from the tower 30 by a line 34 extending to a hot oil pump 35 provided with a discharge line 36. The discharge line is shown extending to the intake line 19 of the pump 20 and as provided with a branch line 36A extending to the coil 22. It is generally preferable to cycle the condensate from the tower 30 back thru the branch line 36A and coil 22, altho at times a portion or all of this condensate may be routed to the coil 10. A by-pass line 37 is indicated for by-passing the pump 35 but as a rule it is preferable to employ the pump; when the condensate is cycled to the coil 22 the hot oil pump or analogous pumping means is required and even in case the condensate is conducted to the coil 10 it is desirable to employ the pump 37 to thus take some of the load off the pump 20.

The receiving drum 33 is shown provided with a liquid draw-off line 38 with which communicates a line 39 extending to a distillate pump 40. The discharge line 41 of the pump 40 has a branch line 42 which is shown in communication with the still 11 by means of branch lines 42*a*, 42*b* and 42*c*. Another branch line 43 is provided which extends to the fractionating tower 15. Thus a portion or all of the distillate collected in the receiver 33 may be passed into either the high pressure cracking still 11 or the high pressure fractionating tower 15 or into both the cracking still and the tower.

In some cases it may be desirable to introduce a portion or all of the fresh charging stock into the lower pressure portion of the apparatus, and to accomplish this end a charging pump 48 may be provided having a discharge line 49 with a branch line 50 extending to the still 23 and another branch line 51 extending to the fractionating tower 30. Thus a charging stock containing light constituents may be stripped in either the still 23 or tower 30. The introduction of charging stock through the line 50 into the still 23 has the advantage that a dirty stock such, for example, as crude or crude residuum may be thus introduced into the still 23, the residual products formed in the cracking and vaporization withdrawn through the line 29 and the evolved vapors consisting of cracked products from the coil 22 as well as vaporized charging stock that has been introduced through the line 50 may be subjected to fractionation in the tower 30 to thus form the gasoline distillate fraction, which is withdrawn through the vapor line 31, and a clean reflux condensate which is withdrawn through the line 34 and which may be passed through the line 36 to the hot oil pump 20, to thus constitute charging stock for the high pressure cracking system embodying the coil 10 and still 11. In this way the heat made available by reason of the high temperature applied in the coil 22 may be utilized in the preparation of a clean charging stock for the high pressure cracking system and at the same time the introduction of the fresh charging stock into the cracking still 23 produces a digesting effect therein promoting increased yields of gasoline without a corresponding increase in gas production.

In one method contemplated by the invention different types of charging stock may be introduced by the respective charging pumps 44 and 48, the least refractory charging stock being introduced by the pump 44 and the more refractory charging stock being introduced by the pump 48. Thus for example, a virgin stock may be charged by the pump 44 and a cycle stock (that is, a stock which has previously been subjected to a cracking reaction) may be introduced by the pump 48. When operating in this manner it is preferable to conduct the reflux condensate produced in the tower 30, or at least the major portion of it, to the coil 22, which is subjected to the maximum temperature. When introducing a relatively clean stock by the pump 48 it is advantageous to introduce a portion or all of the stock through the branch line 51 directly to the tower 30, although if desired the charge may be distributed between the still 23 and fractionating tower 30. It is desired to have cracking as well as vaporization take place in the still 23 so that it is not advisable to introduce a sufficient quantity of charging stock through the line 50 as to unduly reduce the cracking rate in that still. It may be pointed out however that while the charging stock introduced to the still 23 through the line 50 may be subjected to some cracking in the still 23, that so far as this fresh charging stock is concerned the effect on it will ordinarily be largely one of vaporization with only a limited cracking, so that constituents which are vaporized from the charging stock introduced by the line 50 and which are collected as a condensate in the bottom of the tower 30 may be subjected to a more complete cracking in the coil 22 or in some cases in the higher pressure cracking system composed of coil 10 and still 11.

The original charging stock to the system may be introduced by a pump 44 through a charging line 45 directly to the coil 10. If desired a by-pass line 47 may be provided so that the charge introduced by the pump 44 may, instead of being routed through the heating coil 10, be passed directly to the still 11. One advantageous method of operation is to interpose a heating coil in the line 47 heated by hot products obtained in the process, such as the residue withdrawn from the still through the line 14, or such coil may be heated in an economizer section of the furnace 12 to thus utilize waste flue gases that have been employed in heating the coil 10. Thus in using the line 47 the charge introduced by the pump 44 may be heated to a certain degree, which may not be a cracking temperature, before being introduced into the still 11.

When fresh charging stock is being introduced by the pump 44 to the coil 10 it is desirable to admit the cycle stock being handled by the pump 20 to an intermediate point in the coil 10, the branch line 53 being provided for this purpose. It is generally preferable to admit the condensate from the line 21 to the coil 10 at a point therein wherein the temperature of the stream of oil with which the condensate is combined approximates that of such condensate.

The fractionating towers 15 and 30 may be of any suitable type, being equipped with suitable bubble trays or other elements adapted for liquid-vapor contact as indicated by 54. While the stills 11 and 23 are cracking stills it is often advantageous to employ the upper portions of the stills as fractionating or dephlegmating zones

and for this purpose trays or contact elements 54 are shown for these stills. Thus, for example, when charging into still 23 it is advantageous to have baffles or trays to receive the charge and similarly when introducing distillate from the receiver 33 to the upper or intermediate portions of the still 11 the baffles or trays are of advantage. A cooling reflux may be supplied to the tower 15 in addition to that furnished by the distillate from the receiver 33. Thus a portion of the final distillate collected in the receiver 18 may be refluxed to the top of the tower 15. Similarly distillate from the receiver 33 may be used as reflux for the tower 30.

The invention contemplates that any suitable range of temperature and pressure conditions may obtain, respectively, in the high pressure and low pressure cracking zones, but preferably with a differential in pressure sufficient to insure the delivery of condensate from the high pressure tower 15 to the heating coil 22 and to maintain a sufficiently high velocity through the coil 22 to insure satisfactory results. By way of example, it may be stated that with 400–600 lbs. pressure in the fractionating tower 15, the still 23 may be held under about 100–200 lbs. pressure.

If desired, the cracking in the high pressure still 11 may be carried on substantially in the liquid phase, as by maintaining a relatively high level of liquid in the still, to thus maintain a body of oil undergoing cracking and vaporization. If desired, however, the liquid precipitating in the still 11 may be rapidly withdrawn through the line 14 so that a large body of vapor is maintained in the still 11 and cracking carried on in the vapor phase. Similarly, cracking conditions in the still 23 may be maintained under either liquid or the vapor phase, preferably, however, under vapor phase conditions.

In one method of operation contemplated by the invention cracking is carried on in the still 11 under relatively high pressures and under essentially liquid phase conditions, under, for example, 400 lbs. pressure at temperatures of the order of 800° F., while cracking is carried on in the still 23 under essentially vapor phase conditions under pressures of the order of 100 lbs. and at temperatures of the order of 900° to 1000° F.

The distillate as collected in the receiver 18 is of the boiling point desired for the final gasoline or other light distillate it is intended to produce, and the distillate collected in the receiver 33 may be of the same endpoint as that of the distillate collected in the receiver 18. When, however, the distillate from the receiver 33 is returned to the higher pressure cracking zone or dephlegmator, this distillate may advantageously be collected at a somewhat higher endpoint than that of the distillate in the receiver 18. By taking this distillate from the receiver 33, which is derived from a relatively low pressure cracking operation, and by conducting this distillate to the high pressure tower 15, the distillate not only serves as a cooling reflux medium for the tower 15, but this distillate by being subjected to dephlegmation and redistillation in the higher pressure tower, may be subjected to a polymerizing action in the tower, tending to produce its stabilization. If the distillate be admitted to the cracking still 11, it may be subjected not merely to polymerization, but by being treated to further cracking heat its anti-knock value may be increased.

Although the methods of heating the oil, as in the coils 10 and 22, may be varied, one method of operation contemplated is to pass the charging stock introduced to the coil 10 through the coil substantially in countercurrent to the flow of the furnace gases so that the oil is progressively raised in temperature in transit through the coil and reaches the maximum temperature approximately at the end of the coil, while the oil passed through the coil 22 may flow substantially concurrent with the furnace gases so that the maximum temperature is reached at an intermediate point in the coil, after which the temperature of the oil is substantially maintained at a desired cracking temperature. The stock introduced to the coil 22 will in ordinary practice be a cleaner stock than that admitted to the coil 10, and consequently the oil passing through the coil 22 may advantageously be subjected to soaking with cracking carried on to a considerable extent before oil is discharged into the still 23. This soaking effect may be accomplished in a known manner by properly regulating the furnace temperature and the time of passage of the oil through the coil.

Certain aspects of the complete process described herein are claimed in the copending application of W. M. Stratford, Serial No. 515,189, filed February 12, 1931.

In one method of operation contemplated by the invention residue may be withdrawn, as thru the line 14, from the high pressure cracking still 11 and directed into the lower pressure cracking still 23, since the lower boiling constituents may be more readily separated from the residue in the lower pressure still. In this method of operation it is preferable to carry a low liquid level in both stills 11 and 23 so as not to prolong unduly the time of subjection of the residue to cracking conditions which would tend to increase coke production. In some cases, however, the lower pressure cracking still may be operated as a pressure coke still running to a coke residue.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The process of treating hydrocarbon oil which comprises passing relatively heavy oil in a stream of restricted cross section through a heating zone wherein said oil is raised to a cracking temperature, transferring the heated oil into an enlarged zone of substantially constant temperature wherein conversion of said oil occurs and vapors are separated, fractionating said vapors in a first fractionating zone to separate therefrom a final light distillate, a relatively heavy reflux condensate and a relatively light reflux condensate, introducing said heavy condensate into said stream first mentioned, passing said lighter condensate through a second zone of restricted cross section wherein the said lighter condensate attains a cracking temperature in excess of that first mentioned, introducing the resulting heated condensate into a second enlarged zone of substantially constant temperature, wherein conversion of the condensate occurs and vapors are separated, passing said vapors through a second fractionating zone wherein separation thereof into relatively light vapors and a reflux condensate occurs, condensing said light vapors and introducing the resulting condensate, free from said reflux condensate last

mentioned into said enlarged zone first mentioned.

2. A process in accordance with claim 1 wherein a cracked charging stock is introduced into said enlarged zone second mentioned, in quantities so small that the temperature of the said zone is not reduced below a cracking value.

3. A process in accordance with claim 1 wherein said reflux condensate last mentioned is introduced into said stream first mentioned for additional cracking.

4. A process in accordance with claim 1 wherein a cracked charging stock is introduced into said fractionating zone last mentioned and reflux condensate formed in this fractionating zone and unvaporized portions of said cracked charging stock are introduced into said stream first mentioned for additional cracking.

5. In the conversion of higher boiling hydrocarbons into lower boiling ones, the process that comprises subjecting fresh relatively heavy hydrocarbon oil to cracking and vaporization in a primary cracking zone at relatively high superatmospheric pressure, subjecting evolved vapors to fractionation in a first fractionating zone to form overhead gasoline vapors and a reflux condensate, free from cracked residue, removing and condensing said overhead vapors as a desired product, passing said reflux condensate to a secondary cracking zone maintained under a lower pressure than that of the primary cracking zone, subjecting the condensate to cracking and vaporization in the secondary cracking zone, subjecting vapors evolved in the secondary cracking zone to fractionation in a second fractionating zone to segregate gasoline constituents therefrom, and returning said gasoline constituents to a point in said primary cracking zone maintained at a cracking temperature, to thereby subject said gasoline constituents to heat at a pressure higher than that of their pyrogenesis.

6. In the conversion of higher boiling hydrocarbons into lower boiling ones, the process that comprises subjecting fresh relatively heavy hydrocarbon oil to cracking and vaporization in a primary cracking zone at relatively high superatmospheric pressure, subjecting evolved vapors to fractionation in a first fractionating zone to form overhead gasoline vapors and a reflux condensate, free from cracked residue, removing and condensing said overhead vapors as a desired product, passing a clean cracking stock through a secondary cracking zone maintained under a lower pressure than that of the primary cracking zone, subjecting the clean cracking stock to cracking and vaporization in the secondary cracking zone, subjecting vapors evolved in the secondary cracking zone to fractionation in a second fractionating zone to segregate gasoline constituents therefrom, and introducing gasoline constituents so segregated into a point in said primary cracking zone maintained at a cracking temperature, to subject said gasoline constituents to a pressure higher than that of their pyrogenesis and thereby polymerize unstable color and gum-forming constituents thereof.

7. In the conversion of higher boiling hydrocarbons into lower boiling ones, the process that comprises passing hydrocarbon oil through a heating zone in a stream of restricted cross sectional area wherein said oil is raised to a cracking temperature under relatively high superatmospheric pressure, passing the resulting heated oil into an enlarged reaction zone maintained under a substantially constant cracking pressure wherein said oil is subjected to conversion, subjecting resulting cracked vapors to fractionation in a first fractionating zone to form a desired gasoline distillate, subjecting hydrocarbon oil in another cracking zone to cracking and vaporization under a pressure lower than that of said cracking zone first mentioned, subjecting vapors evolved in the lower pressure cracking zone to fractionation in a second fractionating zone to form an overhead vapor fraction comprising mainly products in the gasoline boiling range and a reflux condensate, condensing said overhead vapor fraction and introducing the resulting condensate into said enlarged reaction zone to thereby subject said resulting condensate to heat under a pressure higher than that of its pyrogenesis, whereby beneficial polymerization thereof occurs.

8. The process of treating hydrocarbon oil which comprises passing said oil in a stream of restricted cross section through a heating zone wherein said oil attains a cracking temperature, introducing the resulting heated oil directly into a reaction zone maintained at a substantially constant cracking temperature of the order of 800° F. under a relatively high superatmospheric pressure, wherein additional conversion occurs, passing resulting vapors through a fractionating zone wherein constituents heavier than those desired in the final product are condensed, removing the fractionated vapors and condensing them as a desired product, and introducing directly into said enlarged reaction zone a distillate oil comprising essentially gasoline constituents produced as a result of a cracking operation maintained under a pressure materially below that maintained in said reaction zone, whereby beneficial polymerization of said gasoline constituents takes place.

9. In the conversion of higher boiling hydrocarbons into lower boiling ones, the process that comprises heating a confined stream of hydrocarbon oil to cracking temperature, thereafter passing said heated oil into a separate zone maintained at substantially constant cracking temperature and at relatively high superatmospheric pressure wherein conversion of said oil into lower boiling hydrocarbons is effected, separating said converted products into vapors and residual products, subjecting evolved vapors to fractionation in a first fractionating zone to form overhead gasoline vapors and a reflux condensate free from cracked residue, removing and condensing said overhead vapors as a desired product, passing said reflux condensate to a secondary cracking zone maintained under a lower pressure than that maintained in said first-mentioned cracking zone, subjecting the condensate to cracking and vaporization in the second-mentioned cracking zone in the absence of uncracked oil, subjecting vapors evolved in the secondary cracking zone to fractionation in a second fractionating zone to form an overhead vapor fraction and a reflux condensate, condensing said vapor fraction and conducting it free from said reflux condensate last-mentioned to a point in said separate zone to thereby subject the condensed vapor fraction to heat at a pressure higher than that of its pyrogenesis.

10. The process of treating hydrocarbon oils which comprises subjecting heavy hydrocarbon oil to cracking temperature in a substantially liquid phase cracking zone, under relatively high pressure, separating the resulting vapors, and

withdrawing unvaporized residue from the process, simultaneously subjecting a lighter hydrocarbon oil to cracking temperature in a substantially vapor phase cracking zone, under relatively low pressure, separating resulting cracked products into vapors and a liquid residue, withdrawing said residue from the process, fractionating the resulting vapors from the liquid phase cracking operation and resulting low boiling products from the vapor phase cracking operation in a high pressure fractionating zone, under a pressure substantially equal to that of said liquid phase cracking zone, whereby said low boiling products from said vapor phase cracking operation are subjected to beneficial polymerization, and a vapor fraction, a lighter reflux condensate, and a heavier reflux condensate are formed, removing and condensing said vapor fraction as a desired product, charging said lighter condensate into said vapor phase cracking operation and charging said heavier condensate to said liquid phase cracking operation.

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