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TREATMENT OF HYDROCARBON OILS

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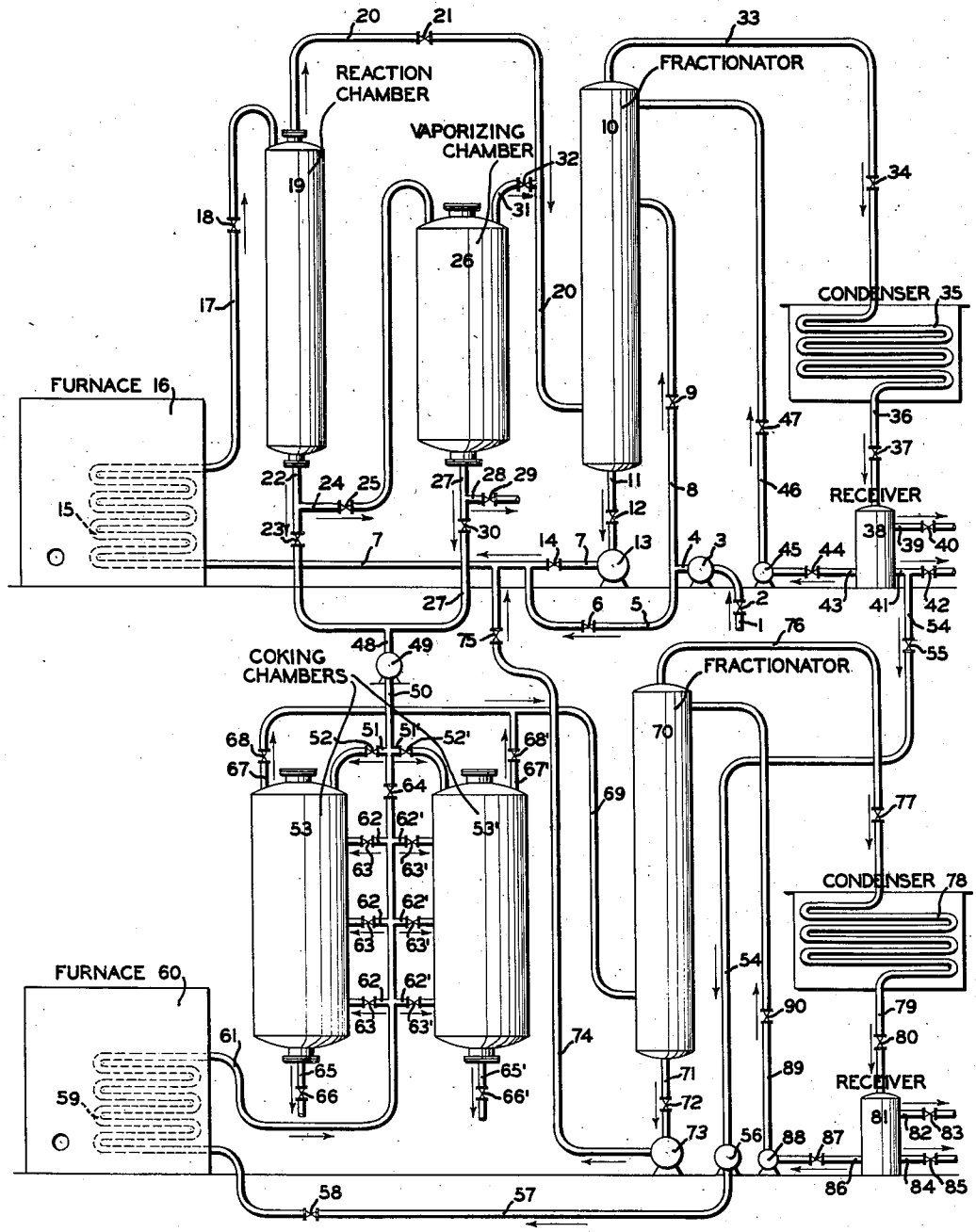

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TREATMENT OF HYDROCARBON OILS

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This invention relates to the treatment of hydrocarbon oils and more particularly refers to an improved process for the reduction of the non-vaporized products of cracking to coke in a reduced pressure zone outside of the main cracking zone and simultaneously reforming gasoline or pressure distillate. This in effect produces non-residuum operation outside of the main cracking zone and permits lengthening the operating cycle.

The principles of the invention may be applied to practically any type of cracking system. As an example, one approved form of cracking process to which the principles of the invention are readily adaptable is the type employing a reaction chamber operated at substantial super-atmospheric pressure wherein the total heated materials introduced thereto from the heating element of the system are subjected to continued conversion, the vapors from the reaction chamber passing to fractionation while non-vaporous residual oil is separately removed from the chamber. Another suitable form of cracking process employs a reaction chamber operated at substantial super-atmospheric pressure wherein continued conversion, particularly of the vaporous conversion products from the heating element of the system, may continue following which both liquid and vaporous products are introduced into a reduced pressure vaporizing chamber to effect further vaporization and cooling of the residual oil and its separation from the vapors, said vapors passing to fractionation while the residual oil is separately withdrawn from the chamber.

According to the principles of the present invention, the residual oil resulting from cracking whether separated from the vaporous conversion products under relatively high or relatively low pressure conditions, is directed to a separate zone preferably maintained at substantially atmospheric or relatively low super-atmospheric pressure wherein said residual oil is reduced to coke or substantially dry carbonaceous material, assisted by the introduction into said coking zone of reheated distillate from the cracking system.

One specific embodiment of the invention may comprise subjecting a hydrocarbon oil to conversion conditions in a heating element, introducing the heated materials into an enlarged reaction zone, operating both the heating element and the reaction zone at substantial super-atmospheric pressure, withdrawing both liquid and vaporous products from said reaction zone to a reduced pressure vaporizing zone wherein vaporous and non-vaporous conversion products are separated, subjecting the vapors to fractionation whereby their relatively heavy components are condensed to be returned to said heating element for further conversion, subjecting the relatively light components of the vapors to condensation and cooling and collecting the resulting distillate and gas, withdrawing non-vaporous residual oil from said reduced pressure vaporizing zone and introducing it into a coking zone preferably operated at substantially atmospheric or relatively low super-atmospheric pressure, subjecting a portion or all of said distillate resulting from the aforementioned cracking and fractionating operations to reheating under any desired temperature and pressure conditions in a separate heating element and introducing the reheated material into said coking zone wherein it assists reduction of said residual oil to coke or substantially dry carbonaceous residue, subjecting vapors from said coking zone to fractionation to effect separation of their relatively light and relatively heavy components, returning said relatively heavy components to the first mentioned heating element for further conversion, subjecting said relatively light components, preferably comprising materials of substantially motor fuel boiling range and gas, to condensation and cooling and collecting the resulting products.

The attached diagrammatic drawing illustrates one form of apparatus embodying the principles of the present invention. The following description of the drawing includes a description of the process of the invention as it may be practiced in the apparatus illustrated. Raw oil charging stock for the system may be supplied through line 1 and valve 2 to pump 3 from which it is fed through line 4 and may pass, all or in part, through line 5, valve 6 and line 7 to heating element 15 or, if desired, all or any portion of the raw oil may pass from line 4 through line 8 and valve 9 into fractionator 10. The raw oil supplied to fractionator 10 is preheated by direct contact with the relatively hot vapors in this zone, serving to assist their fractionation and passing, together with their relatively heavy components which are condensed in the fractionator, through line 11 and valve 12 to pump 13. Pump 13 supplies the reflux condensate or reflux condensate and preheated raw oil, through line 7 and valve 14 to heating element 15.

Heating element 15 is located in a furnace 16 of any suitable form and the oil supplied to this zone is heated to the desired conversion temperature preferably at a substantial super-atmos-

pheric pressure. The heated oil is discharged from the heating element through line 17 and valve 18 to reaction chamber 19.

Chamber 19 is also preferably maintained at a substantial super-atmospheric pressure and, as here illustrated, this zone may be operated in either of two manners. By one mode of operation the materials entering chamber 19 from heating element 15 are substantially separated into vaporous and non-vaporous components. The vapors, after subjection to continued conversion in the reaction chamber pass through line 20 and valve 21 to fractionation in fractionator 10. Residual liquid products are withdrawn from the chamber through line 22 and may pass either through valve 23 to further treatment, as will be later more fully described, or through line 24 and valve 25 to further vaporization in chamber 26. The time to which non-vaporous conversion products are subjected to further conversion in chamber 19 will depend primarily upon the level of residual oil maintained in this zone, a substantial level being maintained when prolonged conversion of residual material is desired while little or substantially no level of residual oil is maintained in the chamber when it is desired to subject said residual oil to relatively short conversion time in this zone. The other mode of operation possible with the arrangement of apparatus illustrated in the drawing comprises withdrawing both vaporous and non-vaporous products from reaction chamber 19 through line 22, line 24 and valve 25 into reduced pressure vaporizing chamber 26. In this manner the vaporous products are subjected to continued conversion for a predetermined time as they pass through chamber 19 while the heavier non-vaporous products gravitate more rapidly to the bottom of the chamber and are removed from the reaction zone substantially as fast as they collect, thereby preventing any substantial further conversion of these products.

In case chamber 26 is employed it is preferably maintained under a substantially reduced pressure relative to that employed in chamber 19 and the non-vaporous products introduced into this zone are subjected to further vaporization and cooled by the liberation of heat effected by the reduction in pressure. Residual oil remaining unvaporized in chamber 26 is withdrawn therefrom through line 27 and may be removed, in part, from the system to cooling and storage or elsewhere, as desired, through line 28 and valve 29. A portion or all of the residual oil, however, passes through valve 30, in line 27, to further treatment as will be later more fully described. Vapors from chamber 26 pass through line 31, valve 32 and line 20 to fractionation in fractionator 10.

The vapors introduced into fractionator 10, coming either from reaction chamber 19 or reduced pressure vaporizing chamber 26 or in part from both, as previously described, are separated into relatively light and relatively heavy components by fractionation in this zone. The relatively heavy components of the vapors, which are condensed in fractionator 10 pass, as already described, to heating element 15 for further conversion. The relatively light components of the vapors which may, for example, comprise cracked materials of motor fuel boiling range, together with gas produced by the system, may be withdrawn from the upper portion of the fractionator through line 33 and valve 34 to be subjected to condensation and cooling in condenser 35, distillate and uncondensable gas from which may pass through line 36 and valve 37 to be collected in receiver 38. Uncondensable gas may be released from receiver 38 through line 39 and valve 40. A portion of the distillate may be withdrawn from the receiver and from the system through line 41 and valve 42. A portion of the distillate collecting in receiver 38 may, if desired, be withdrawn through line 43 and valve 44 to be recirculated by means of pump 45 through line 46 and valve 47 to the upper portion of fractionator 10 to assist fractionation of the vapors and to maintain the desired vapor outlet temperature from the fractionator.

Residual oil produced by the cracking system which, depending upon the operation employed, may be withdrawn either from chamber 19 through line 22 and valve 23 or from chamber 26 through line 27 and valve 30, as already described, passes through line 48 to pump 49 from which it is fed through line 50 and may pass either through line 51 and valve 52 into coking chamber 53 or through line 51′ and valve 52′ into coking chamber 53′ or the residual oil may, if desired, be directed to both coking chambers simultaneously. Chambers 53 and 53′ are similar coking zones which may be operated either alternately or simultaneously. It will be understood that it is also within the concepts of the present invention to employ a single coking zone or any number of a plurality of such zones although only two are illustrated in the drawing.

A portion or all of the distillate from receiver 38 is withdrawn through line 54 and valve 55 to pump 56 from which it is fed through line 57 and valve 58 to heating element 59 being therein subjected to the desired temperature under any desired pressure conditions. A furnace 60 of any suitable form supplies the required heat to heating element 59. The reheated distillate is discharged from heating element 59 through line 61 and may pass through any or all of a plurality of lines 62 controlled by valves 63 into coking chamber 53 or through similar lines 62′ controlled by valves 63′ into coking chamber 53′. If desired, by use of valve 64 connecting lines 50 and 61, the residual oil and the reheated distillate may be commingled prior to their introduction into the chambers 53 and 53′ in which case the commingled materials may enter the chambers through any or all of the lines 62, 62′, 51 and 51′. In any case the reheated distillate is intimately contacted in chambers 53 and 53′ with the residual oil, materially assisting its reduction to coke or substantially dry carbonaceous material in the coking zones. Chambers 53 and 53′ are provided with drain lines 65 and 65′ respectively, controlled respectively by valves 66 and 66′. Vapors are removed from chamber 53 through line 67 and valve 68 while vapors are withdrawn from chamber 53′ through line 67′ and valve 68′, either or both streams of vapors passing through line 69 to fractionation in the fractionator 70.

Vapors supplied to fractionator 70 are separated into relatively light and relatively heavy components; the latter, which are condensed in the fractionator, being withdrawn therefrom through line 71 and valve 72 to pump 73 from which they are fed through line 74 and valve 75 into line 7 and thence to heating element 15 for further conversion. The relatively light desirable components of the vapors supplied to fractionator 70, preferably comprising materials of substantially motor fuel boiling range, are removed together with uncondensable gas from

fractionator 70 through line 76 and valve 77, are subjected to condensation and cooling in condenser 78 from which distillate and uncondensable gas are withdrawn through line 79 and valve 80 to be collected in receiver 81. Uncondensable gas may be released from the receiver through line 82 and valve 83 while the distillate may be withdrawn through line 84 and valve 85. A portion of the distillate collecting in receiver 81 may, if desired, be withdrawn therefrom through line 86 and valve 87 to be recirculated by means of pump 88 through line 89 and valve 90 to the upper portion of fractionator 70 for the purpose of assisting fractionation in this zone and maintaining the desired vapor outlet temperature therefrom.

Pressures employed within the system may range from substantially atmospheric to super-atmospheric pressures as high as 2000 pounds or more per sq. in. Conversion temperatures employed may range from 800 to 1600° F., more or less. Preferably temperatures of the order of 850 to 950° F. or thereabouts are employed in the primary heating element, wherein the raw oil charging stock and reflux condensates are treated, while this heating element and the succeeding reaction chamber preferably employ substantial super-atmospheric pressures which may range, for example, from 100 to 500 pounds, more or less, per sq. in. The vaporizing chamber, when employed, preferably utilizes a substantially reduced pressure relative to that employed in the reaction chamber and ranging, for example, from substantially atmospheric to 100 pounds or thereabouts per sq. in. Pressures employed in the fractionating, condensing and collecting portions of the primary cracking system may be substantially equalized with that employed in the vaporizing chamber or when the vaporizing chamber is not used may be either substantially equalized with or somewhat lower than those employed in the reaction chamber.

Temperatures employed in the secondary heating element, utilized for reheating of the distillate, may vary, depending primarily upon the type of operation desired, over a relatively wide range, for example, from 800 to 1600° F., more or less, and the pressures employed in this zone may also vary over a range of from substantially atmospheric to 500 pounds or more super-atmospheric pressure per sq. in. Preferably substantially atmospheric pressure or relatively low superatmospheric pressures are employed in this zone when temperatures above 1000° F. or thereabouts are employed. The coking chambers and the succeeding fractionating, condensing and collecting portions of the coking system preferably employ substantially atmospheric or relatively low super-atmospheric pressures, although pressures up to 500 pounds, or more, per sq. in. may be employed, if desired, when such pressures are employed in the secondary heating element.

As a specific example of the operation of the process of the present invention, a 23° A. P. I. gravity mid-continent fuel oil is the charging stock supplied to the cracking system, it is subjected in the primary heating element together with reflux condensates from both fractionators of the system to a temperature of about 885° F. A superatmospheric pressure of approximately 275 pounds per sq. in. is maintained in this heating element and is substantially equalized in the reaction chamber. The vapors are removed from the reaction chamber to fractionation and little or substantially no level of residual liquid is permitted to accumulate in the reaction chamber. Cracked distillate from the fractionator, having an end-boiling point of approximately 550° F., is subjected in a separate heating element to a temperature of approximately 950° F. under a pressure of approximately 600 pounds per sq. in. The heated materials are introduced into alternate coking chambers maintained at a pressure of about 100 pounds per sq. in. wherein they assist reduction of the residual oil from the reaction chamber to coke. This operation may yield approximately 70 percent of 400° F. end-point motor fuel having an antiknock value approximately equivalent to a blend of 80 percent octane and 20 percent normal heptane. The additional products of the system are about 1200 cubic ft. of gas and about 85 pounds of coke per barrel of charging stock. By reducing the pressure in the coking chambers the yield and the volatility of the coke may be reduced, the yield of motor fuel being also somewhat reduced and the production of gas somewhat increased.

As an example of another operation within the scope of the present invention, a 36° A. P. I. gravity Pennsylvania crude oil containing approximately 30 percent of straight-run gasoline is the charging stock to be treated. This material is supplied to the fractionator of the cracking system wherein straight-run gasoline is separated from the crude, to be collected, together with the cracked motor fuel produced by this portion of the system. The topped crude, together with intermediate conversion products from the fractionator of the cracking system and reflux condensate from the fractionator of the coking system, are subjected in the heating element of the cracking system to a temperature of approximately 910° F. A substantially equalized super-atmospheric pressure of approximately 400 pounds per sq. in. is maintained in the heating element and reaction chamber. Both liquid and vaporous products from the reaction chamber are introduced into the vaporizing chamber at a reduced pressure of approximately 50 pounds per sq. in. Residual liquid from the vaporizing chamber is introduced into alternately operated coking chambers. Distillate from the receiver of the cracking system comprising straight-run gasoline and cracked products of substantially gasoline boiling range, are heated in a separate heating element to a temperature of approximately 950° F. under a super-atmospheric pressure of approximately 500 pounds per sq. in. and are thence commingled with the residual oil undergoing coking in the coking chambers. The coking chambers and subsequent portions of the system are maintained under a super-atmospheric pressure of about 30 pounds per sq. in. This operation may yield a total motor fuel product amounting to approximately 84 percent of the crude and having an antiknock value approximately equivalent to an octane number of 75. In addition about 32 pounds of relatively low volatile coke and about 1400 cu. ft. of uncondensable gas of high calorific value may be produced per barrel of charging stock.

As a specific example of another possible operation, utilizing a 38° A. P. I. gravity Muskegon crude containing approximately 33 percent of bad knocking gasoline: this charging stock, including its gasoline components, is subjected in the heating element of the cracking system to a temperature of approximately 900° F. under a super-atmospheric pressure of approximately 400 pounds per sq. in. A pressure of approxi-

mately 65 pounds per sq. in. is maintained in the vaporizing chamber, the pressure in the reaction chamber being substantially equalized with that in the heating element. Distillate of substantially motor fuel boiling range from the receiver of the cracking system is subjected in a separate heating element to a temperature of approximately 1600° F. under substantially atmospheric pressure. Substantially atmospheric pressure conditions are also maintained in the alternate coking chambers where residual oil from the vaporizing chamber of the cracking system is reduced to a substantially dry carbonaceous residue by contact with the products resulting from the high temperature retreatment of the distillate. This operation may produce about 7500 cubic feet of uncondensable gas of high calorific value and containing a substantial amount of hydrogen. In addition about 15 gallons of a relatively light distillate having an antiknock value approximately equivalent to that of benzol and suitable for blending with inferior motor fuel to improve its antiknock value and lower its boiling point may be produced. The coke produced may amount to approximately 28 pounds per barrel of charging stock and may have a volatile content of less than 6 percent.

We claim as our invention:

1. A hydrocarbon oil cracking process which comprises heating the oil to cracking temperature under pressure in a heating zone and separating the same into vapors and unvaporized oil in a separating zone maintained under pressure, reducing the unvaporized oil to coke in a coking zone maintained under lower pressure than the separating zone, dephlegmating said vapors to condense fractions thereof heavier than gasoline, separately condensing the gasoline vapors uncondensed by the dephlegmation and collecting the resultant distillate, passing a gasoline-containing portion of said distillate, without contact with said vapors undergoing dephlegmation, through a second heating zone and heating the same therein sufficiently to increase its antiknock value, introducing the thus heated distillate to said coking zone to assist the coking of the unvaporized oil therein, and removing the vapors from the coking zone and subjecting the same to dephlegmation and condensation.

2. The process as defined in claim 1 further characterized in that said portion of the distillate is heated to higher temperature in said second heating zone than is the oil in the first-mentioned heating zone.

3. A hydrocarbon oil cracking process which comprises subjecting the oil to cracking conditions of temperature and pressure in a cracking zone, removing vapors and unvaporized oil from the cracking zone, dephlegmating the vapors in direct contact with crude oil containing natural gasoline to condense fractions of the vapors heavier than gasoline and thereby distilling the natural gasoline from the crude, supplying the topped crude admixed with the condensed heavier fractions to the cracking zone, finally condensing the mixed vapors of natural gasoline and cracked gasoline and collecting the resultant distillate, introducing said unvaporized oil while still hot into a distillation zone and further distilling the same therein, passing a gasoline-containing portion of said distillate, without contact with said vapors undergoing dephlegmation, through an independent heating zone and heating the same therein sufficiently to enhance its anti-knock value, introducing the thus heated distillate to said distillation zone to assist the distillation of the unvaporized oil therein, and removing the vapors from the distillation zone and subjecting the same to dephlegmation and condensation.

4. A hydrocarbon oil cracking process which comprises subjecting the oil to cracking conditions of temperature and pressure in a cracking zone, removing vapors and unvaporized oil from the cracking zone, dephlegmating the vapors to condense fractions thereof heavier than gasoline, separately condensing the dephlegmated gasoline vapors and collecting the resultant distillate, introducing said unvaporized oil while still hot into a distillation zone and further distilling the same therein, passing a gasoline-containing portion of said distillate, without contact with said vapors undergoing dephlegmation, through an independent heating zone and heating the same therein sufficiently to enhance its antiknock value, introducing the thus heated distillate to said distillation zone to assist the distillation of the unvaporized oil therein, and removing the vapors from the distillation zone and subjecting the same to dephlegmation and condensation.

5. A hydrocarbon oil cracking process which comprises heating the oil to cracking temperature under pressure in a heating zone and separating the same into vapors and unvaporized oil, reducing the unvaporized oil to coke in a coking zone, dephlegmating said vapors to condense fractions thereof heavier than gasoline in direct contact with crude oil containing natural gasoline thereby vaporizing the natural gasoline from the crude, supplying the topped crude and admixed reflux condensate to the heating zone, finally condensing the mixed vapors of natural gasoline and cracked gasoline and collecting the resultant distillate, passing a gasoline-containing portion of said distillate, without contact with said vapors undergoing dephlegmation, through a second heating zone and heating the same therein sufficiently to increase its anti-knock value, introducing the thus heated distillate to said coking zone to assist the coking of the unvaporized oil therein, and removing the vapors from the coking zone and subjecting the same to dephlegmation and condensation.

6. A hydrocarbon oil cracking process which comprises subjecting the oil to cracking conditions of temperature and pressure in a cracking zone, removing vapors and unvaporized oil from the cracking zone, dephlegmating the vapors to condense fractions thereof heavier than gasoline and to form a gasoline-containing distillate, introducing said unvaporized oil while still hot into a distillation zone and further distilling the same therein, passing a gasoline-containing portion of said distillate, without contact with said vapors undergoing dephlegmation, through an independent heating zone and heating the same therein sufficiently to enhance its anti-knock value, introducing the thus heated distillate to said distillation zone to assist the distillation of the unvaporized oil therein, and removing the vapors from the distillation zone and subjecting the same to dephlegmation and condensation.

7. A hydrocarbon oil cracking process which comprises subjecting the oil to cracking conditions of temperature and pressure in a cracking zone, removing vapors and unvaporized oil from the cracking zone, dephlegmating the vapors to condense fractions thereof heavier than gasoline, topping crude oil containing natural gasoline by introducing the same into direct contact with the vapors undergoing dephlegmation, removing from

the dephlegmating step a mixed natural gasoline and cracked gasoline-containing distillate, introducing said unvaporized oil while still hot into a distillation zone and further distilling the same therein, passing a gasoline-containing portion of said distillate, without contact with said vapors undergoing dephlegmation, through an independent heating zone and heating the same therein sufficiently to enhance its anti-knock value, introducing the thus heated distillate to said distillation zone to assist the distillation of the unvaporized oil therein, and removing the vapors from the distillation zone and subjecting the same to dephlegmation and condensation.

8. A hydrocarbon oil cracking process which comprises subjecting the oil to cracking conditions of temperature and pressure in a cracking zone, removing vapors and unvaporized oil from the cracking zone, dephlegmating and condensing the vapors to form a reflux condensate heavier than gasoline and a lighter condensate containing a substantial quantity of hydrocarbons boiling within the gasoline range, introducing said unvaporized oil into a distillation zone maintained under lower pressure than the cracking zone and distilling the same therein by pressure reduction, passing at least a portion of said lighter condensate containing gasoline boiling hydrocarbons, without contact with said vapors undergoing dephlegmation, through an independent heating zone and heating the same therein sufficiently to enhance its anti-knock value, introducing the thus heated condensate to said distillation zone to assist the distillation of the unvaporized oil therein, and removing the vapors from the distillation zone and subjecting the same to dephlegmation and condensation.

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