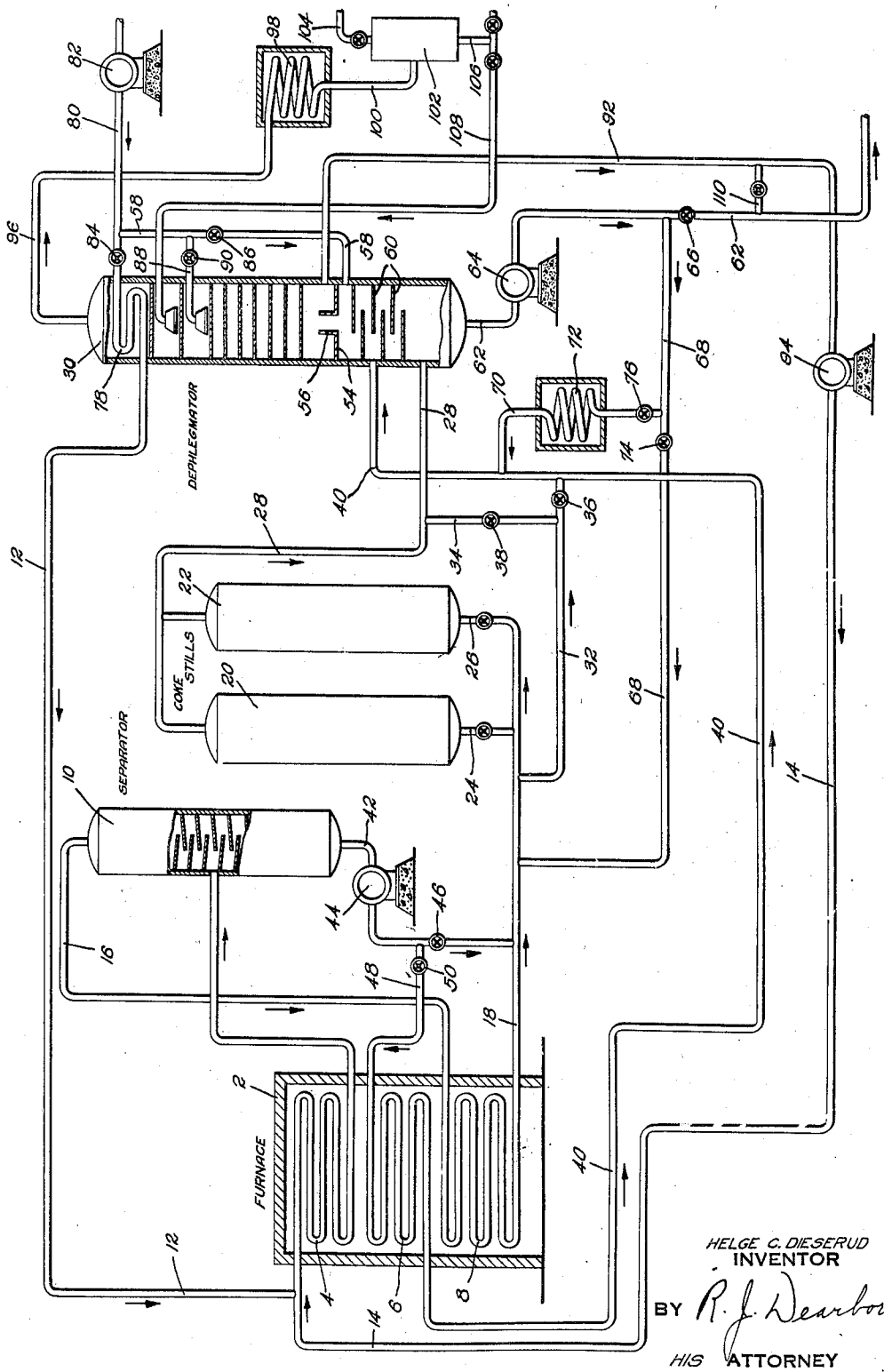
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This invention relates to the conversion of hydrocarbon oils and has to do particularly with a vapor phase cracking process having certain features of novelty which will be described and claimed hereinafter.

In the vapor phase cracking of hydrocarbon oils it has been the practice to simultaneously distill a heavy hydrocarbon oil, such as crude oil, in order to obtain a light fraction which may be easily vaporized and cracked while in vapor form without excessive deposition of coke. The heavy oil has accordingly been contacted with the vapors from the vapor phase cracker to strip the oil of light constituents and simultaneously shock-cool the vapors to retard undesirable reactions and the resulting unvaporized oil and condensates then redistilled to produce a vapor phase cracking stock. This method has certain disadvantages, particularly in that the heat of the hot vapor phase cracked products often produces undesirable amounts of coke and there is then produced from the redistillation step a resulting fuel oil that is undesirable.

Instead of contacting the hot vapors from the vapor phase cracking operation directly with heavy hydrocarbon oil to be stripped, I provide means for cooling the hot cracked vapors prior to contacting with the fresh oil. Thus a relatively cool, heavy or residual oil may be commingled with the hot vapors and the heat sufficiently absorbed by the cool oil, or the heat of the vapors may be dissipated by utilizing such heat to reduce the heavy oil to coke. In this way I am able to use more efficiently the residual oils from the process and at the same time control the reaction so as to retard coke formation at undesirable points in the system and to reduce to coke, in a coking zone, if desired, the heavy oils which cannot be advantageously cracked without harmful deposits of coke in the cracking zone.

In accordance with the invention, a heavy oil is distilled in a pipe still, which may take the form of a tubular heater and a separator, a vapor fraction is removed and subjected to a vapor phase cracking operation, then the residual liquid fraction from the pipe still commingled with the hot cracked products in the vaporizing zone. If it is desirable to further cool the hot cracked products, I provide means for mixing a portion of the cooler heavy oil from the vaporizer therewith, prior to the mixture reaching the vaporizer.

According to the invention, moreover, the residual liquid from the pipe still may be given a separate heat treatment. Therefore, the liquid may be subjected to a cracking operation substantially in the liquid phase and then the cracked products from both the vapor phase and the liquid phase cracking operation commingled in the vaporizing zone. In this method of operation, however, it is preferable to extensively cool the hot cracked products prior to reaching the vaporizer and for this purpose a heavy oil from the vaporizer may be circulated through a cooler and the cool oil then mixed with the hot cracked materials transferred to the vaporizer.

Furthermore, according to one method of operation, it is contemplated that the residual liquids from the system may be reduced to coke by the sensible heat of the hot vapors from the vapor phase cracking operation. Accordingly, the heavy oil from the pipe still, either with or without undergoing a cracking treatment, may be commingled with the hot cracked vapors and the mixture reduced to coke in a coke still. The vapors from the coke still may then be dephlegmated with a heavy oil and the resulting unvaporized liquid from the dephlegmating zone conducted to the coke still or to the pipe still or both.

In any method of operation, according to the invention, it is preferable to preheat the fresh oil charged to the system. Such preheating may be conveniently accomplished in the dephlegmating zone which may comprise a single zone wherein the fresh oil is stripped, the vapors fractionated and the liquids accumulating therein passed all, or in part, to the pipe still or the coking zone; or, the dephlegmating zone may comprise two separate zones, one zone constituting a stripper, wherein the fresh oil is stripped by the hot vapors passed thereto and the resulting unvaporized oil passed to the coking still, and the other zone comprising a fractionating tower where the vapors are subjected to reflux condensation by heat exchange with the charging stock and the liquids collecting therein passed to the pipe still.

The invention may be more clearly understood by reference to the accompanying drawing wherein is shown, for purposes of illustration, one form of apparatus for carrying out the invention.

In the drawing, the reference character 2 represents a furnace in which is located heating coils 4, 6 and 8 for heating the oil. The heating coil 4 and separator 10, comprise a pipe still for distilling the hydrocarbon oil, charged to the coil 4 through the lines 12 and 14. A vapor line 16 connects the top of the separator 10 with a vapor phase cracking coil 8. A line 18 serves to conduct the products from the coil 8 to the coke

stills 20 and 22 through the connecting branches 24 and 26 respectively. A vapor line 28 connects the vapor space of the coke stills to the bottom of the dephlegmator 30. The line 32, branching from the pipe 18, serves as a by-pass to conduct the products from the coil 8 around the coke stills and directly to the dephlegmator 30 via pipe 34 and the line 28. By suitable regulation of valves 36 and 38, in lines 32 and 34 respectively, the products in line 32 may be directed into the line 40, mentioned hereinafter, whereby the vapor phase cracked products may be commingled with the liquid phase cracked products therein and the mixture conducted to the dephlegmator 30.

Referring again to the separator 10, a line 42, in which is interposed a pump 44 and a valve 46, serves to conduct residual liquid from the bottom thereof into line 18 to commingle with the vapor phase cracked products from coil 8. A branch line 48, controlled by valve 50, serves to convey, if desired, the residual liquid, withdrawn through line 42 to the cracking coil 6. The coil 6 in turn is connected by the line 40 with the dephlegmator 30 to conduct oil from the coil to the dephlegmator so as to enter thereto at a point slightly higher than the entrance of the products through vapor pipe 28.

The dephlegmator 30 is shown as an enlarged tower which is divided into two sections by a partition 54 having a vapor riser 56 therein. The lower section of the tower, below the partition or pan 54, constitutes a stripping section wherein oil introduced through pipes 58 and 40 may be stripped of the lighter constituents by contact with the vapors introduced through line 28 while running down over the baffles 60. A line 62, controlled by valve 66, serves to withdraw from the bottom of the tower residual liquid which may be pumped to storage by a pump 64. A branch line 68, communicating with line 18, serves to by-pass the residual liquid to the coke stills 20 and 22. A by-pass line 70, in which is interposed a cooling coil 72, serves to by-pass the oil from the line 68 to the line 40 by suitable regulation of valves 74 and 76 in the lines 68 and 70 respectively.

The upper section of the dephlegmator, above the partition 54, serves as a fractionating or dephlegmating column. A cooling coil 78, located in the top thereof, serves to cool the vapors by conducting therethrough fresh oil from the line 80 through which charged oil is pumped by the pump 82. A branch line 58, referred to hereinbefore, serves to conduct a portion of the charging oil to the stripping section by suitable regulations of valves 84 and 86 in the lines 80 and 58 respectively. A branch pipe 88, controlled by valve 90, serves to introduce fresh oil directly into the fractionator, if desired. A pipe 92, communicating with the bottom of the fractionating section, serves to conduct unvaporized charge and reflux liquid collecting on the pan 54 to the pump 94 which in turn forces the oil through pipe 14 to the pipe still. A vapor line 96 connects the top of the tower 30 to a cooling coil 98 which in turn is connected by line 100 with a receiver 102, the latter having the usual gas release pipe 104 and liquid draw-off line 106. A line 108, connecting with the pipe 106, serves to convey condensate from the receiver 102 to the fractionator to act as a reflux medium.

While the dephlegmating tower 30 is shown in the drawing as a single unit it is to be understood that the lower stripping section and upper fractionating section may comprise separate towers. In some cases it is contemplated that the lower stripping section may be eliminated entirely. Such may well be done when the coking units are in use and in such event, vapors from the coking still would pass directly to the fractionator or, as an alternative, the partition 54 might be eliminated. The lower stripping section is particularly useful when the coking stills are not used and the products from coils 6 and 8 are passed directly to the stripper. The liquids may then be withdrawn from the bottom of the tower and by-passed through line 10 to the pipe still or through line 68 to the cooler 72.

In practicing the invention with an apparatus such as that shown in the drawing, a charging stock such as crude oil or reduced crude is charged by pump 82 through the line 80. In case the oil is reduced crude it may be desirable to pass the oil through coil 78 in indirect heat exchange relation with the vapors in the tower. However, when crude oil containing gasoline constituents is used it is preferable to charge the oil, entirely or in part, directly into the tower through line 88. If the oil is charged directly into the tower it is stripped largely of its gasoline content and the unvaporized portion and condensates collect on the pan 54. The oil, according to the method of operation, is then conducted through line 12 or from the bottom of the fractionator through line 92 to the pipe still. The oil is heated in coil 4 to a temperature insufficient to cause appreciable cracking but sufficient to cause substantial vaporization, say 500–750° F. The oil is separated in separator 10 into a vapor fraction and a residual liquid fraction. The vapor fraction, comprising a wide cut consisting largely of naphtha and gas oil, is subjected to a vapor phase cracking operation. For this purpose the vapors are conducted through heating coil 8 in which the oil is subjected to the highest temperature in the furnace, for example, about 900–1150° F. The hot vapor phase cracked products are then transferred through line 18 to the coke stills, wherein coking of the heavy oil charged thereto takes place as will be more fully explained hereinafter.

The residual liquid fraction from separator 10 is withdrawn through line 42 and may be passed directly into line 18 where it commingles with the hot cracked vapors therein and then the mixture is transferred to the coke stills. As an alternative, the valve 46 in the line 42 may be closed and the valve 50 in line 48 opened and the residual liquid forced through the heating coil 6. It is preferable that cracking, substantially in the liquid phase, takes place in coil 6 and therefore the oil is heated therein to a temperature of about 750–950° F. under a pressure of 200–600 pounds per square inch applied by the pump 44. The cracked products are transferred through line 40 and the by-pass line 32 into line 18 to mix with the vapor phase cracked products and the mixture then transferred to the coke stills. The pressure is preferably reduced at valve 36 to approximately equal to the pressure maintained in the vapor phase cracking operation which may be from atmospheric to 200 pounds per square inch. In the coke stills all volatile products are vaporized and the unvaporizable material reduced to coke. A plurality of coke stills is available so that one may be cleaned of the coke deposited therein while the other is in use. The vapors from the coke still are passed through vapor line 28 to the lower portion of

the stripping section of tower 30. Since the vapors are at a relatively high temperature a heavy oil is usually introduced through line 58 into direct contact with the vapors whereby the heavy oil is partially distilled and the less volatile constituents of the vapors condensed. The liquids collecting in the bottom of the stripper are withdrawn through line 62 and may be passed to storage. It is preferable, however, to bypass these liquids through line 68 back to line 18 where they commingle with the vapor phase cracked products and pass with the mixture to the coke stills.

According to one method of operation, the coke stills are not used but instead the cracked products are passed directly to the tower 30. In this method of operation it is necessary to cool the vapor phase cracked products in order to prevent coking in the tower 30 so that the liquid fuel may be withdrawn from the bottom thereof. This cooling may be done partially by contacting the cooler liquid from the separator 10 directly with the vapor in line 18 by passing the residual liquid therefrom through line 42 instead of to the cracking coil 6. The mixture is then passed through lines 32, 34 and 28 or through lines 32 and 40 directly to the tower 30. Another method of cooling is to contact residual liquid from the bottom of tower 30 with the hot products and to do this residual oil, withdrawn through line 62, may be by-passed through line 70 to the line 40 and in this case the hot materials from line 32 are passed to line 40 instead of pipe 34. The degree of cooling may be regulated, according to this latter method, by controlling the temperature of the liquid in line 70 by use of the cooling coil 72, around which a cooling medium may be circulated. When using the cooler 72 the degree of cooling can be controlled to such an extent that it is possible to crack the residual liquid from separator 10 in the coil 6 and yet have no unduly high temperature in the tower 30. When by-passing the coke stills as just described it is often desirable to eliminate the partition 54 and collect all the liquids from the bottom of tower 30 and for this purpose I have shown bypass line 110, through which a portion of the liquids not used for cooling may be returned to the pipe still.

The vapors rising in the tower 30 are dephlegmated or fractionated preferably in the presence of charging stock, the unvaporized portion of which collects in the lower portion of the tower together with condensates and the mixture returned to the pipe still. Vapors of substantially gasoline boiling range are removed from the top of the tower. These are condensed to produce the desired gasoline distillate. A portion of the distillate may then be returned, if desired, to the top of the tower through line 108 to serve as a reflux medium for controlling the end point of the final distillate.

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 method of converting relatively high boiling hydrocarbon oils into lower boiling oils of the gasoline type which comprises heating in a coil a flowing stream of charging oil to distillation temperature and discharging the heated charging oil into a separating zone wherein the oil separates into vaporous and non-vaporous portions, withdrawing the vapors from said zone and subjecting them to vapor phase cracking, discharging the cracked vaporous products from said vapor phase cracking operation to an enlarged coking still, withdrawing non-vaporous portions from said separating zone and subjecting them in a coil to liquid phase cracking, discharging the resulting cracked products directly into an independent distilling and fractionating zone, withdrawing vaporous products from said coking still and introducing them into said independent distilling and fractionating zone, withdrawing unvaporized residual liquid products from said independent distilling and fractionating zone and discharging them directly into said coking still wherein they are converted to coke by the contained heat of the vaporous cracked products passed thereto from said vapor phase cracking operation, withdrawing reflux condensate from said independent distilling and fractionating zone and passing said condensate to said first named coil for treatment in the system.

2. The method of converting relatively high boiling hydrocarbon oils into lower boiling oils of the gasoline type which comprises heating in a coil a flowing stream of charging oil to distillation temperature and discharging the heated charging oil into a separating zone wherein the oil separates into vaporous and non-vaporous portions, withdrawing the vapors from said zone and subjecting them to vapor phase cracking, discharging the cracked vaporous products from said vapor phase cracking operation to an enlarged coking still, withdrawing non-vaporous portions from said separating zone and independently subjecting them to liquid phase cracking, discharging the resulting cracked products directly into an independent distilling zone, withdrawing vaporous products from said coking still and introducing them into said independent distillation zone, withdrawing cracked unvaporized residual liquid products from said independent distillation zone and discharging them directly into said coking still wherein they are converted to coke by the contained heat of the vaporous cracked products passed thereto from said vapor phase cracking operation, passing the vapors from said independent distilling zone to a fractionating operation wherein they are contacted with relatively cool fresh oil being charged to the system whereby lighter constituents of said fresh oil are vaporized and heavier constituents of said vapors are condensed, and passing the resulting mixture of condensate and unvaporized fresh oil directly to said first-named coil for treatment in the system.

3. The method of converting relatively high boiling hydrocarbon oils into lower boiling oils of the gasoline type which comprises heating in a coil a flowing stream of fresh oil stock to a distillation temperature and discharging the heated oil into a separating zone wherein the oil separates into vaporous and non-vaporous portions, withdrawing the vapors from said zone and passing them to a vapor phase cracking operation wherein they are subjected to vapor phase cracking, discharging the vaporous cracked products from said vapor phase cracking operation to an independent enlarged distilling and fractionating zone, withdrawing non-vaporous products from said separating zone and subjecting them to liquid phase cracking in an independent coil, discharging the resulting cracked products into said independent distilling and fractionating zone and

intimately contacting them therein with the said cracked vaporous products from said vapor phase cracking operation, withdrawing unvaporized residual cracked products from said independent distilling and fractionating zone and discharging them from the system, introducing fresh oil into said independent distilling and fractionating zone and collecting unvaporized portions of said fresh oil in said distilling and fractionating zone separately from said residual cracked products, and separately withdrawing said fresh oil residue and passing it to said first-named coil as charging stock therefor.

4. The method of converting relatively high boiling hydrocarbon oils into lower boiling oils of the gasoline type which comprises heating in a coil a flowing stream of charging oil to distillation temperature and discharging the heated charging oil into a separating zone wherein the oil separates into vaporous and non-vaporous portions, withdrawing the vapors from said zone and subjecting them to vapor phase cracking, discharging the cracked vaporous products from said vapor phase cracking operation to an enlarged coking still, withdrawing non-vaporous portions from said separating zone and independently subjecting them to liquid phase cracking, discharging the resulting cracked products directly into an independent distilling and fractionating zone, withdrawing vaporous products from said coking still and introducing them into said independent distilling and fractionating zone, separately collecting cracked unvaporized residual products in said distilling and fractionating zone, separately withdrawing them and discharging them directly into said coking still wherein they are converted to coke by the contained heat of the vaporous cracked products passed thereto from said vapor phase cracking operation, charging relatively cool fresh charging oil into said independent distilling and fractionating zone and intimately contacting said fresh oil with vaporous products to effect fractional condensation thereof, separately collecting in said distilling and fractionating zone the resulting mixture of reflux condensate and fresh oil, separately withdrawing the said mixture of reflux condensate and unvaporized fresh oil and passing the same directly to said first-named coil for treatment in the system.

5. The method of treating hydrocarbon oils to convert the higher boiling hydrocarbons into lower boiling hydrocarbons which comprises heating the oil in a heating zone and distilling therefrom a substantial vapor fraction leaving a liquid residual fraction, subjecting the vapor fraction to cracking temperatures in a first cracking zone to cause conversion thereof, subjecting the residual fraction to cracking temperature in a second cracking zone to cause conversion thereof, commingling cracked products from said first and second cracking zones and passing the mixture to a separate reaction zone wherein the said mixture is maintained at conversion temperature by the contained heat thereof and separation of vapors from liquids occurs, passing the resultant vapors from the said reaction zone to a dephlegmating zone, contacting the vapors in the dephlegmating zone with a heavy oil to partially vaporize the heavy oil and condense the less volatile constituents of the vapors, passing the resultant unvaporized oil in mixture with condensed constituents of the vapors from the dephlegmating zone directly to said reaction zone, without passage to said second cracking zone, and removing uncondensed vapors from said dephlegmating zone and forming a desired product therefrom.

6. The method of converting relatively high boiling hydrocarbon oils into lower boiling oils of the gasoline type which comprises heating in a coil a flowing stream of charging oil to a distillation temperature and discharging the heated charging oil into a separating zone wherein the oil separates into vaporous and non-vaporous portions, withdrawing the vapors from said zone and passing them through a first cracking zone wherein they are raised to a vapor phase cracking temperature and subjected to cracking, discharging the cracked products from said first cracking zone into an independent enlarged distilling zone and avoiding mixture of any of such cracked products with the said charging oil undergoing said heating and separation, withdrawing non-vaporous products from said separating zone and passing them through a second cracking zone wherein they are raised to a cracking temperature and subjected to liquid phase cracking, discharging the resulting cracked products from said second cracking zone into said independent distilling zone and intimately contacting them therein with the said cracked products from said first cracking zone, withdrawing unvaporized residual oil from said independent distilling zone and admixing it with the cracked products at a point intermediate the said first cracking zone and the said independent distilling zone, and removing uncondensed vapors from said independent distilling zone and forming a desired product therefrom.

7. A process in accordance with claim 6 wherein fresh charging oil is introduced into said independent distilling zone in direct contact with the hot products therein.

8. The method of converting relatively high boiling hydrocarbon oils into lower boiling oils of the gasoline type which comprises heating in a coil a flowing stream of fresh oil stock to a distillation temperature and discharging the heated oil into a separating zone wherein the oil separates into vaporous and non-vaporous portions, withdrawing the vapors from said separating zone and passing them to a vapor phase cracking zone wherein they are raised to a vapor phase cracking temperature and subjected to cracking, discharging the cracked products from said vapor phase cracking zone into an independent enlarged distilling and fractionating zone, withdrawing non-vaporous products from said separating zone and passing them to an independent liquid phase cracking zone wherein they are raised to a liquid phase cracking temperature and subjected to conversion, discharging the resulting cracked products into said independent distilling and fractionating zone and intimately contacting them therein with the said cracked products from said vapor phase cracking zone, withdrawing unvaporized residual cracked products from said independent distilling and fractionating zone and admixing them with the vapor phase cracked products at a point intermediate the said vapor phase cracking zone and the said independent distilling and fractionating zone, introducing fresh oil into said independent distilling and fractionating zone, collecting unvaporized portions of said fresh oil in said distilling and fractionating zone separately from said residual cracked products, and separately withdrawing said unvaporized portions of said fresh oil and passing them to said first-named coil as charging stock therefor.

9. The process of treating hydrocarbon oil which comprises passing fresh relatively heavy hydrocarbon oil through a heating zone wherein it is raised to a distillation temperature, introducing the resulting hot oil into a separating zone wherein vapors separate from liquid residue, separately removing vapors and liquids from said separating zone, passing said vapors through a first cracking zone wherein they are raised to a vapor phase cracking temperature and subjected to conversion, passing said liquid residue through a second cracking zone wherein it is raised to a liquid phase cracking temperature and subjected to conversion, combining the resulting cracked products from said first and second cracking zones and passing them in a stream to a second separating zone wherein vapors separate from liquid residue, separately removing vapors and liquids from said second separating zone, and introducing a portion of the removed liquid from said separating zone last mentioned into said stream to cause cooling thereof.

10. A process in accordance with claim 9 wherein the liquid residue removed from said second mentioned zone is cooled prior to the introduction thereof into said stream.

11. A process in accordance with claim 9 wherein fresh relatively heavy charging stock is introduced into said separating zone second mentioned.

12. The method of treating hydrocarbon oils to convert the higher boiling hydrocarbons into lower boiling hydrocarbons which comprises heating the oil in a heating zone and distilling therefrom a substantial vapor fraction leaving a liquid residual fraction, subjecting the vapor fraction to cracking temperatures in a first cracking zone to cause conversion thereof, subjecting the residual fraction to cracking temperature in a second cracking zone to cause conversion thereof, passing hot cracked products from said first cracking zone into a separate coking zone, removing vapors from said coking zone, passing hot cracked products from said second cracking zone into a separate separating zone wherein vapors separate from liquid residue, subjecting said vapors last mentioned to fractional condensation to form a desired product, and passing liquid residue from said separating zone last mentioned into said coking zone, wherein coke is formed by the contained heat of the cracked products therein.

13. A method in accordance with claim 12 wherein reflux condensate formed by the fractionation of the vapors separated in said separating zone last mentioned, is passed through said heating zone and into said separating zone first mentioned.

14. A method in accordance with claim 12 wherein vapors are removed from said coking zone and introduced into said separating zone last mentioned.

15. An oil-heating system comprising a heating chamber, an oil-conducting heat-absorption structure disposed in said chamber, means connected with said absorption structure for separating the oil therefrom into liquid and vapor components, outlets for separately withdrawing vapors and liquid from said separating means, and other oil-conducting heat-absorption structures disposed in said heating chamber connected to the vapor and liquid outlets, respectively, of said separating means, said last-named heat-absorption structures being connected to a common outlet.

16. A process for treating crude petroleum oil containing natural gasoline which comprises topping the crude and separating therefrom a distillate containing a substantial quantity of the natural gasoline hydrocarbons, passing said distillate through a heating zone and heating the same therein sufficiently to increase the anti-knock value of the gasoline hydrocarbons contained therein, commingling the topped crude with the hot distillate discharged from the heating zone whereby the topped crude is raised to cracking temperature by the heat of the distillate, separating the commingled oils into vapors and residue, and fractionating and condensing the vapors.

17. A process for treating crude petroleum oil containing natural gasoline which comprises topping the crude and separating therefrom a distillate containing a substantial quantity of the natural gasoline hydrocarbons, passing said distillate through a heating zone and heating the same therein sufficiently to increase the anti-knock value of the gasoline hydrocarbons contained therein, discharging the heated distillate into an enlarged reaction zone maintained under cracking conditions of temperature and pressure, introducing the topped crude into said reaction zone and commingling the same therein with the heated distillate, separating the commingled oils into vapors and residue and fractionating the former to condense heavier fractions thereof, heating resulting reflux condensate to cracking temperature and pressure and thence introducing the same to the reaction zone, and finally condensing the fractionated vapors.

18. A process for treating crude petroleum oil containing natural gasoline which comprises topping the crude and separating therefrom a distillate containing a substantial quantity of the natural gasoline hydrocarbons, heating said distillate, while flowing in a restricted stream under pressure through a heating zone, sufficiently to increase the anti-knock value of the gasoline hydrocarbons contained therein and then discharging the same into an enlarged zone, introducing the topped crude into said enlarged zone to be heated therein by contact with the heated distillate and separating the resulting mixture into vapors and residue, fractionating the resultant vapors to condense heavier fractions thereof, heating resultant reflux condensate to cracking temperature under pressure and then discharging the same into said enlarged zone and finally condensing the fractionated vapors.

19. A process according to claim 17 wherein the topped crude is passed through a heating zone and subjected to cracking conditions of temperature and pressure prior to being introduced into said enlarged reaction zone.

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