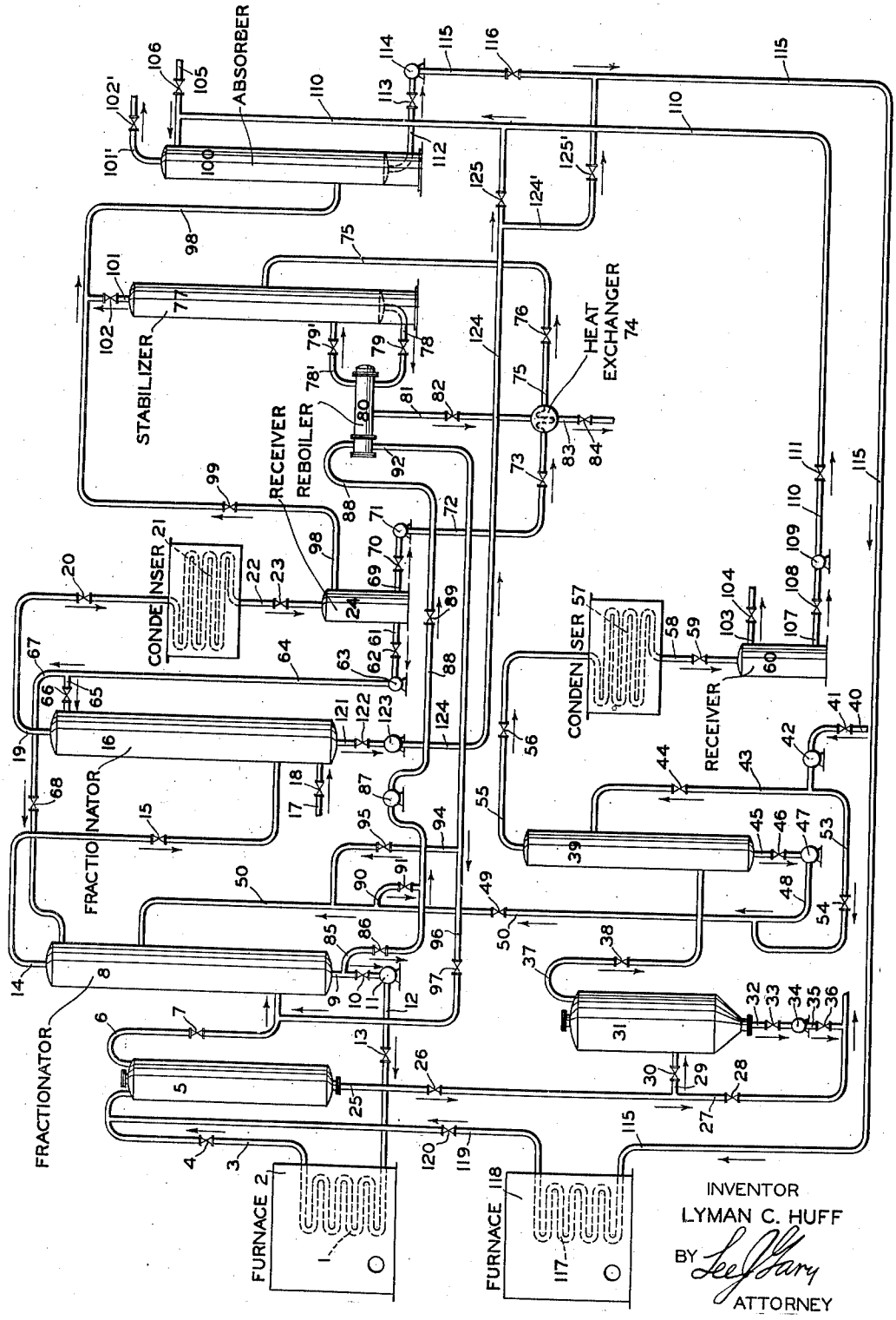
April 8, 1941. L. C. HUFF 2,237,432

CONVERSION OF HYDROCARBON OILS

Filed March 21, 1938



Patented Apr. 8, 1941

2,237,432

UNITED STATES PATENT OFFICE

2,237,432

CONVERSION OF HYDROCARBON OILS

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Application March 21, 1938, Serial No. 197,090

6 Claims. (Cl. 196—48)

This is, in part, a continuation of my co-pending application Serial Number 98,669, filed August 31, 1936, which, in turn, is a continuation-in-part of my now abandoned application Serial Number 6,987, filed February 18, 1935.

My previous applications, above referred to, disclose a cracking operation of the type wherein relatively light and relatively heavy hydrocarbon oils are cracked under independently controlled conversion conditions, with provision for absorbing desirable high-boiling components of normally gaseous conversion products of the process in a suitable relatively light absorber oil and supplying the resulting enriched absorber oil to the light oil cracking step of the system. The present process embodies a similar type of operation which includes the additional cooperative features of topping crude petroleum charging stock for the system by intimate contact with hot vaporous products resulting from the flash distillation of residual liquid conversion products of the process, said topping being effected in a fractionating step of the flash distilling system wherefrom light distillate, including gasoline components of the crude, is recovered and utilized as at least a portion of the absorber oil, the resulting enriched absorber oil being returned, as in the process of the previous applications, to the light oil cracking step of the system whereto other low-boiling intermediate liquid conversion products of the process are also supplied for cracking treatment.

The above described and other features of the process will be apparent from the accompanying diagrammatic drawing and the following description thereof. The drawing illustrates one specific form of apparatus embodying the features of the invention and in which the process of the invention may be conducted.

Referring to the drawing, heating coil 1 to which relatively heavy hydrocarbon oil is supplied, in the manner later described, for cracking, is located within a furnace 2, by means of which heat is supplied to the oil passing through the heating coil to bring it to the desired cracking temperature, preferably at a substantial superatmospheric pressure. The resulting stream of heated products is discharged from coil 1 through line 3 and valve 4 into reaction chamber 5.

Chamber 5 is preferably maintained at a substantial superatmospheric pressure, which may be substantially the same or somewhat lower than that employed at the outlet of heating coil 1. Vaporous conversion products separate from residual liquid conversion products in this zone and are withdrawn from the upper portion of the chamber and supplied through line 6 and valve 7 to fractionator 8.

Fractionator 8 is preferably also maintained at a substantial superatmospheric pressure, which may be substantially the same or somewhat lower than that employed in reaction chamber 5. The fractionator may employ any desired type of fractionating means such as, for example, perforated pans, bubble trays, packing or the like, whereby the vaporous conversion products supplied from reaction chamber 5 to this zone are fractionated for the separation therefrom of high-boiling components which are condensed as reflux condensate. Reflux condensate formed in fractionator 8, high-boiling fractions of the heavy oil charging stock, and other heavy oils, which are supplied to this zone as will be later described, are directed from the lower portion of the fractionator through line 9 and valve 10 to hot oil pump 11 by means of which they are fed through line 12 and valve 13 to heating coil 1 for conversion therein as previously described.

Fractionated vapors of the desired end boiling point, which remain uncondensed in fractionator 8, are directed from the upper portion thereof through line 14 and valve 15 to fractionator 16. Fractionator 16 is preferably operated at a low superatmospheric pressure, relative to that employed in fractionator 8, and may employ any desired type of fractionating means such as, for example, perforated pans, bubble trays, packing or the like, whereby the vaporous conversion products supplied from fractionator 8 to this zone are separated into reflux condensate, comprising their high-boiling components and a fractionated vaporous stream preferably having an end-boiling point within the range of gasoline. To assist in the proper rectification of the reflux condensate formed in fractionator 16, a suitable vaporizing or heating medium, such as steam, heated hydrocarbon vapors or gases, etc., may be introduced into the fractionator through line 17 and valve 18 below the level of reflux condensate maintained in this zone. When desired, any other suitable method of reboiling the reflux condensate may be employed, such as, for example, indirect heat exchange with relatively hot vapor or liquid from within the system or from an external source.

Fractionated vapors and gases, which remain uncondensed in fractionator 16, are directed from the upper portion thereof through line 19

and valve 20 to cooling and condensation in condenser 21, the resulting distillate and uncondensed gases passing through line 22 and valve 23 to collection and separation in receiver 24.

The residual liquid conversion products remaining unvaporized in reaction chamber 5 are removed from the lower portion of this zone through line 25 and valve 26 and may be directed, all or in part, to storage or any desired further treatment, not shown, through line 27 and valve 28. Preferably, however, all or a regulated portion of this material is supplied through line 29 and valve 30 to flash distilling chamber 31.

Chamber 31 is preferably maintained at a substantially reduced pressure relative to that employed in the reaction chamber, by means of which substantial further vaporization of the liquid conversion products supplied to this zone is accomplished. When desired, any suitable fractionating means may be employed in the upper portion of this chamber 31 to assist the separation of mist and entrained heavy liquid particles from the vapors. The residual liquid conversion products remaining unvaporized in chamber 31 are withdrawn therefrom through line 32 and valve 33 to pump 34 by means of which they may be supplied through line 35 and valve 36 to storage or elsewhere as desired. When desired, the residual liquid remaining unvaporized in chamber 31 may be reduced to substantially dry coke therein or external thereto, by any well known means, not illustrated.

Vapors evolved in chamber 31 are withdrawn from the upper portion thereof through line 37 and valve 38 and are supplied to fractionator 39, wherein they may be directly commingled with hydrocarbon oil charging stock supplied to this zone and wherein the commingled materials are fractionated for the formation of reflux condensate, comprising their high-boiling components. Any desired type of fractionating means may be employed in this zone, such as, for example, perforated pans, bubble trays, packing or the like.

Charging stock supplied through line 40 and valve 41 to pump 42 may comprise any desired type of hydrocarbon oil but preferably is an oil of relatively wide boiling range, such as crude petroleum, topped crude or the like.

When the charging stock contain a substantial quantity of low-boiling components, such as poor antiknock gasoline or gasoline fractions, it is preferably supplied from pump 42 through line 43 and valve 44 into fractionator 39. In this zone the charging stock intimately contacts and commingles with the vaporous products supplied thereto from chamber 31. The charging stock is thus at least partially vaporized and the commingled vapors are fractionated in this zone. The reflux condensate formed in fractionator 39 and any unvaporized, high-boiling fractions of the charging stock supplied thereto are withdrawn in a commingled state from the lower portion of this zone through line 45 and valve 46 to pump 47 by means of which they may be supplied through line 48, valve 49 and line 50 to fractionator 8, to commingle therein and undergo fractionation with the vaporous conversion products supplied thereto from reaction chamber 5.

When the charging stock does not contain a substantial quantity of low-boiling components, such as poor antiknock gasoline or gasoline fractions, it may be directed, all or in part, when desired, from pump 42 through line 53 and valve 54 into line 48 and thence to fractionator 8.

The fractionated vapors which remain uncondensed in fractionator 39 are directed from the upper portion of this zone through line 55 and valve 56 to cooling and condensation in condenser 57. The resulting distillate and uncondensed gases pass through line 58 and valve 59 to collection and separation in receiver 60.

A regulated portion of the distillate collected in receiver 24 may be recirculated through line 61, valve 62, pump 63, line 64, line 65 and valve 66 to the upper portion of fractionator 16, and/or through line 67 and valve 68 to the upper portion of fractionator 8 to serve as a cooling and refluxing medium in one or both of these zones. That portion of the distillate collected in receiver 24 which is not required as a cooling and refluxing medium may be withdrawn to storage or any desired further treatment, by well known means, not illustrated. Preferably, however, the distillate is first subjected to stabilization for the purpose of liberating therefrom regulated quantities of dissolved normally gaseous products, whereby to reduce its vapor pressure to the desired degree. To accomplish this, distillate is directed from receiver 24 through line 69 and valve 70 to pump 71 and thence through line 72 and valve 73 to heat exchanger 74, wherein it is heated, by indirect heat exchange with the final stabilized product of the process, as will later be more fully described, sufficiently to effect its substantial vaporization in stabilizer 77 to which it is directed through line 75 and valve 76.

Stabilizer 77 may be any conventional type of stabilizing equipment employing suitable fractionating means and capable of effecting rectification of the distillate to the desired vapor pressure. In the case here illustrated, unvaporized distillate is withdrawn from the lower portion of stabilizer 77 through line 78 and valve 79 to reboiler 80 wherein it is maintained at a substantially constant temperature, sufficient to reboil the same, by means of its indirect heat exchange in the reboiler with any suitable heating medium which, in the case here illustrated, comprises a regulated portion of the reflux condensate withdrawn from fractionator 8 and supplied to the reboiler as will be later described. The vapors and/or gases evolved in reboiler 80 are returned therefrom through line 78' and valve 79' to stabilizer 77. The stabilized and reboiler distillate is withdrawn from reboiler 80 through line 81 and valve 82 to heat exchanger 74, wherein it is passed in indirect heat exchange with and supplies heat to the unstabilized distillate passing from receiver 24 to stabilizer 77, as previously mentioned, and is removed through line 83 and valve 84 to further cooling and storage or to any desired further treatment, not illustrated.

In the case here illustrated, a regulated portion of the reflux condensate withdrawn from fractionator 3 is utilized as a heating medium in reboiler 80, to assist vaporization of the material undergoing stabilization in stabilizer 77, and may be directed from the lower portion of fractionator 8 through line 9 and thence through line 85 and valve 86 to pump 87 by means of which it is supplied through line 88 and valve 89 into reboiler 80, through which it passes in indirect heat exchange with the distillate from stabilizer 77. It is also within the scope of the invention to utilize regulated quantities of the commingled heavy oils withdrawn from the lower portion of fractionator 39 as a heating medium in reboiler

80. To accomplish this regulated quantities of this material are diverted from line 50 through line 90 and valve 91 into line 85 leading to pump 87 and reboiler 80. The partially cooled heating medium having passed through reboiler 80 is directed therefrom through line 92 and may be supplied, all or in part, to fractionator 8 by means of line 94, valve 95 and line 50, or it may be supplied, all or in part, through line 96 and valve 97 into line 6, to commingle with and partially cool the vaporous conversion products passing from reaction chamber 5 to fractionator 8.

Gaseous products separated from the distillate in receiver 24 may be directed therefrom to storage or elsewhere as desired, by well known means not shown, but preferably are supplied through line 98 and valve 99 to absorber 100. Normally gaseous products liberated from the distillate in stabilizer 77 and released from the upper portion of this zone through line 101 and valve 102 are supplied through line 98 to absorber 100, either alone or together with gases previously separated from the unstabilized distillate in receiver 24. The gaseous products released in receiver 60 through line 103 and valve 104 may also be supplied to absorber 100, by well known means not shown, or they may be withdrawn from the system to storage or elsewhere, as desired.

The normally gaseous products supplied to absorber 100 are passed in direct counter-current contact with a suitable absorber oil, which serves to absorb desired high-boiling components of the gases, consisting principally of gases having 3 and more carbon atoms to the molecule. The lower boiling, unabsorbed gases are released from the upper portion of the absorber through line 101' and valve 102'.

When desired a selected absorber oil from an external source may be supplied to absorber 100 through line 105 and valve 106. Preferably, however, the low-boiling oil recovered as the overhead distillate product from fractionator 39 is utilized, either alone or in conjunction with other low-boiling oils, as the absorption medium in absorber 100. Distillate may be directed from receiver 60 through line 107 and valve 108 to pump 109 by means of which it may be supplied through line 110 and valve 111 to the upper portion of absorber 100. Light reflux condensate from fractionator 16 may also be employed as absorber oil, when desired, regulated quantities of this material being directed from fractionator 16 through line 121 and valve 122 to pump 123 and thence through line 124, valve 125 and line 110 into absorber 100. Preferably when light reflux condensate from fractionator 16 is thus utilized it is cooled, by well known means not shown, prior to its introduction into absorber 100.

The enriched absorber oil is withdrawn from the lower portion of absorber 100 through line 112 and valve 113 to pump 114 by means of which it is supplied through line 115 and valve 116 for conversion in heating coil 117. Light reflux condensate from fractionator 16, or that portion thereof not supplied to absorber 100, is directed from line 124 through line 124' and valve 125' into line 115 and thence to further cracking in heating coil 117.

Coil 117 is disposed in a furnace 118, of suitable form, by means of which heat is supplied to the relatively low-boiling oils and normally gaseous products passing through the heating coil to bring the same to the desired cracking temperature, preferably at a substantial superatmospheric pressure. Although illustrated conventionally in the drawing, coil 117 and furnace 118 preferably comprise one of the well known types of heaters wherein the materials passing through this zone, after being heated therein to the desired cracking temperature, are maintained in a final "soaking" section of the heating coil for a predetermined time at a substantially constant temperature relatively close to the maximum temperature previously attained in the coil, whereby conversion of the oils and gases into high yields of good antiknock gasoline is accomplished.

Preferably, the material undergoing conversion in heating coil 117 is subjected therein to more severe cracking conditions than those employed in coil 1. The conditions of temperature, pressure and time employed in this zone are preferably within the range of the so-called "reforming" conditions, whereby the antiknock qualities of the gasoline or gasoline fractions supplied to coil 117 are materially improved without excessively altering their boiling range. Such conditions are also maintained within the range suitable for converting any higher boiling oils supplied to coil 117, as well as the olefinic gases supplied to and formed in this zone, into substantial yields of liquid products boiling within the range of gasoline and of good antiknock value. The stream of heated products discharged from heating coil 117 are supplied through line 119 and valve 120 into reaction chamber 5, wherein these relatively hot products commingle with the less highly heated products supplied to this zone from heating coil 1 and wherein the commingled materials are subjected to continued conversion at their attained temperature.

The preferred range of operating conditions which may be employed, in an apparatus such as is illustrated and above described, to produce the desired results, are approximately as follows: Heating coil 1 may employ an outlet conversion temperature ranging, for example, from 825° F. to 950° F., preferably with a superatmospheric pressure at this point in the system of from 100 to 500 pounds, or thereabouts, per square inch. Reaction chamber 5 may utilize the same or somewhat lower pressure than that employed in heating coil 1, and substantially the same or somewhat lower pressure may be utilized in fractionator 8.

Fractionator 16 is preferably operated at a substantially reduced pressure relative to that employed in the preceding portion of the system and this reduced pressure may range, for example, from substantially atmospheric to 150 pounds, or more, per square inch, superatmospheric pressure. Substantially the same or somewhat lower pressure may be employed in the succeeding condensing and collecting equipment.

Flash chamber 31 is preferably operated at a substantially reduced pressure relative to that employed in reaction chamber 5 and this reduced pressure may range, for example, from substantially atmospheric to 150 pounds, or thereabouts, per square inch, superatmospheric pressure. Fractionator 39 and the succeeding condensing, and collecting portions of the system may employ substantially the same or somewhat lower pressure than that utilized in chamber 31.

The conversion temperature employed at the outlet of coil 117 will depend upon the composition of the materials supplied to this zone, and may range from 900° F. to 1200° F. with a superatmospheric pressure at this point in the

system ranging, for example, from 300 to 1200 pounds, or thereabouts, per square inch. The pressure employed in the stabilizing zone may range, for example, from 100 to 300 pounds, or thereabouts, per square inch. Any desired pressure within substantially the same range may be utilized in the absorption zone.

As an example of one specific operation which may be conducted in accordance with the features of the invention and in an apparatus such as illustrated and above described: The charging stock is a Montana Cut Bank crude oil of approximately 34.7° A. P. I. gravity having an initial boiling point of approximately 160° F. and containing approximately 35% of materials boiling up to 400° F. The straight run gasoline which is of poor antiknock value, is separated from heavier components of the crude in fractionator 39 and collected in receiver 60, together with the relatively small quantity of cracked products of similar end-boiling point supplied to fractionator 39 from chamber 31. The topped crude and heavier condensed components of the vapors supplied to fractionator 39 from chamber 31 are supplied to fractionator 8, wherefrom the reflux condensate formed in this zone and the heavy components of the topped crude are supplied to heating coil 1. A cracking temperature of approximately 900° F. and a superatmospheric pressure of approximately 300 pounds per square inch are employed at the outlet of heating coil 1 and this pressure is substantially equalized in reaction chamber 5 and fractionator 8. The distillate from receiver 60 is utilized as absorber oil in absorber 100 and the enriched absorber oil from this zone is subjected to heating coil 117 to a cracking temperature of approximately 1000° F. at a superatmospheric pressure, measured at the outlet of the coil, of approximately 800 pounds per square inch. Light reflux condensate from fractionator 16 is supplied directly to coil 117.

An operation such as above outlined will produce, per barrel of charging stock, approximately 58% of good quality gasoline, having an end-boiling point of approximately 400° F. and an octane number of approximately 70 by the motor method. Approximately 8%, based on the charging stock, of relatively low-boiling reflux condensate is recovered from fractionator 16 as a final product of the process. This product has a gravity of approximately 32° A. P. I. and a boiling range of approximately 400° F. to 560° F. The other products of the process are approximately 27% of residual liquid having a gravity of about 8° A. P. I. and suitable for use as fuel oil, and approximately 7% of light gases.

I claim as my invention:

1. In a process wherein a light hydrocarbon oil is cracked at cracking temperature and superatmospheric pressure in a light oil cracking step, a heavier hydrocarbon oil cracked at cracking temperature and superatmospheric pressure in a heavy oil cracking step, resultant hot conversion products from both cracking steps separated into vaporous and liquid components at substantial superatmospheric pressure, said vaporous components fractionated to form light and heavy reflux condensates which are returned, respectively, to the light oil and heavy oil cracking steps, fractionated vapors of the desired end-boiling point, comprising gasoline and normally gaseous conversion products, subjected to condensation and the resulting distillate separated from normally gaseous products which include polymerizable olefins such as propene and butenes, the improvement which comprises flash distilling said liquid components of the conversion products at a substantially reduced pressure relative to that at which they are separated from said vaporous components, fractionating the resulting evolved vapors out of contact with said vaporous components and in commingled state with uncracked hydrocarbon oil from an external source, recovering from the last mentioned fractionating step an overhead distillate consisting of relatively low-boiling fractions of said uncracked oil and relatively low-boiling fractions of the vapors evolved by said flash distillation, contacting distillate thus recovered with said olefin-containing gases to absorb desirable high-boiling components of the latter, such as propene and butenes, and supplying the resulting enriched absorber oil to the light oil cracking step of the system for treatment therein in commingled state with said light reflux condensate.

2. A process such as defined in claim 1 wherein condensate recovered from the last mentioned fractionating step, which includes relatively high-boiling fractions of the uncracked oil and relatively high-boiling fractions of the vapors evolved by said flash distillation, is supplied for cracking treatment to the heavy oil cracking step of the system.

3. A process such as defined in claim 1 wherein condensate resulting from the last mentioned fractionating step, which includes relatively high-boiling components of the uncracked oil and relatively high-boiling components of the vapors evolved by said flash distillation, is directly supplied to the fractionating step of the system wherein said heavy reflux condensate is formed and fractionated therein in commingled state with said vaporous components of the conversion products supplied to this zone.

4. A process such as defined in claim 1 wherein condensate formed in the last mentioned fractionating step and comprising components of the uncracked oil and the vapors evolved by said flash distillation which boil above the range of said overhead distillate is further separated into light and heavy fractions which are returned, respectively, to the light oil and heavy oil cracking step, said separation being effected by commingling said condensate with said vaporous components of the conversion products in the first mentioned fractionating step.

5. A process for the pyrolytic conversion of hydrocarbon oils which comprises heating an oil of relatively high-boiling characteristics to cracking temperature at superatmospheric pressure in a heating coil, heating an oil of lower boiling characteristics to an independently controlled higher cracking temperature at superatmospheric pressure in a separate heating coil, supplying resultant conversion products from both heating coils to an enlarged reaction chamber also maintained at substantial superatmospheric pressure, separately removing vaporous and liquid conversion products from the reaction chamber, fractionating the vapors to form a heavy reflux condensate and a light reflux condensate, returning the heavy reflux condensate to the first mentioned heating coil for further cracking, returning the light reflux condensate to said separate heating coil for further cracking, subjecting resultant fractionated vapors of the desired end-boiling point to condensation, recovering as the resulting distillate cracked gasoline containing dissolved normally gaseous conversion products of the process, stabilizing the

distillate to reduce its vapor pressure to the desired degree by liberating therefrom regulated quantities of the dissolved normally gaseous products, supplying gases liberated from the distillate by said stabilization to an absorber, contacting the same therein with an absorber oil derived as subsequently described and thereby absorbing desirable high-boiling components including propene and butenes from the gases, supplying the resulting enriched absorber oil to said separate heating coil, supplying said liquid conversion products removed from said reaction chamber to a zone of substantially reduced pressure, therein appreciably vaporizing the same, recovering the resulting non-vaporous residue, supplying the evolved vapors to a separate fractionating zone, contacting the same therein with a virgin oil of relatively wide boiling range and thereby fractionally distilling the latter in commingled state with said evolved vapors, removing condensate, comprising selected high-boiling components of the virgin oil and of the evolved vapors, from the last mentioned fractionating zone and supplying the same to the first mentioned fractionating zone, removing fractionated vapors of the desired end-boiling point, comprising selected low-boiling fractions of the virgin oil and of said evolved vapors, from the last described fractionating step, subjecting the same to condensation, and supplying resultant condensate as absorber oil to the absorber.

6. A conversion process which comprises subjecting hydrocarbon oil heavier than gasoline to cracking conditions of temperature and pressure in a heating coil and separating the same into vaporous and liquid conversion products in an enlarged chamber, removing the vaporous products and recovering therefrom a gasoline distillate and normally incondensible gases formed by the cracking, separately removing unvaporized oil from the chamber and flash distilling the same by pressure reduction, fractionating resultant flashed vapors in contact with crude petroleum, thereby vaporizing the low anti-knock gasoline fractions of the crude, condensing the uncondensed vapors from the fractionating step to form a condensate containing the low anti-knock gasoline fractions of the crude, supplying to said heating coil liquid products of said fractionating step comprising portions of the crude and of the flashed vapors heavier than gasoline, scrubbing cracked normally incondensible gases separated as aforesaid with at least a portion of said condensate to absorb in the latter polymerizable olefinic components of the gases, subjecting the thus enriched condensate to reforming conditions of temperature and pressure in a second heating coil and discharging the resultant products into said chamber.

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