March 9, 1937. J. K. ROBERTS ET AL 2,073,073

STABILIZATION OF LOW BOILING HYDROCARBON OILS AND PARTICULARLY CRACKED HYDROCARBON VAPORS

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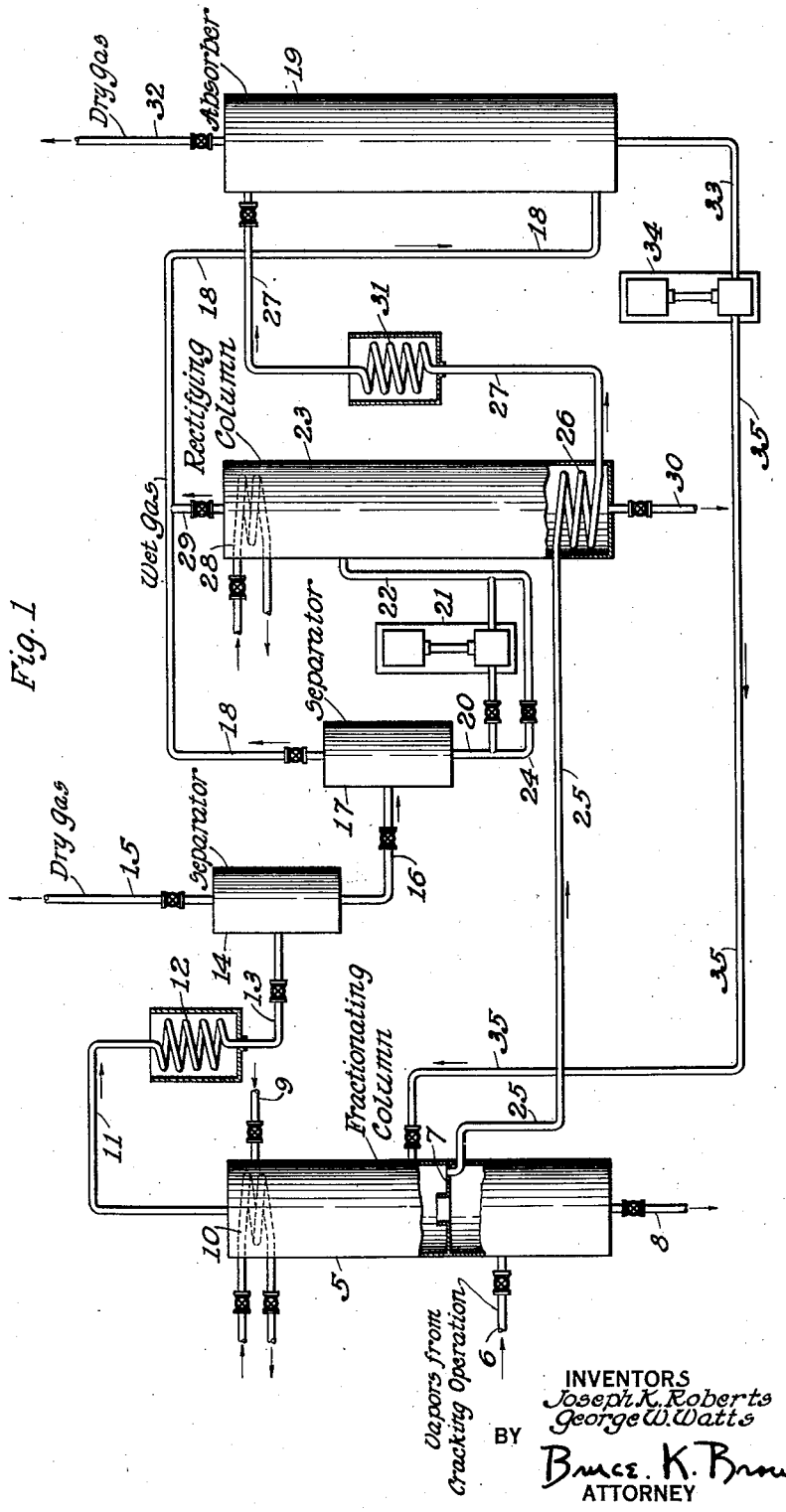


Fig. 1

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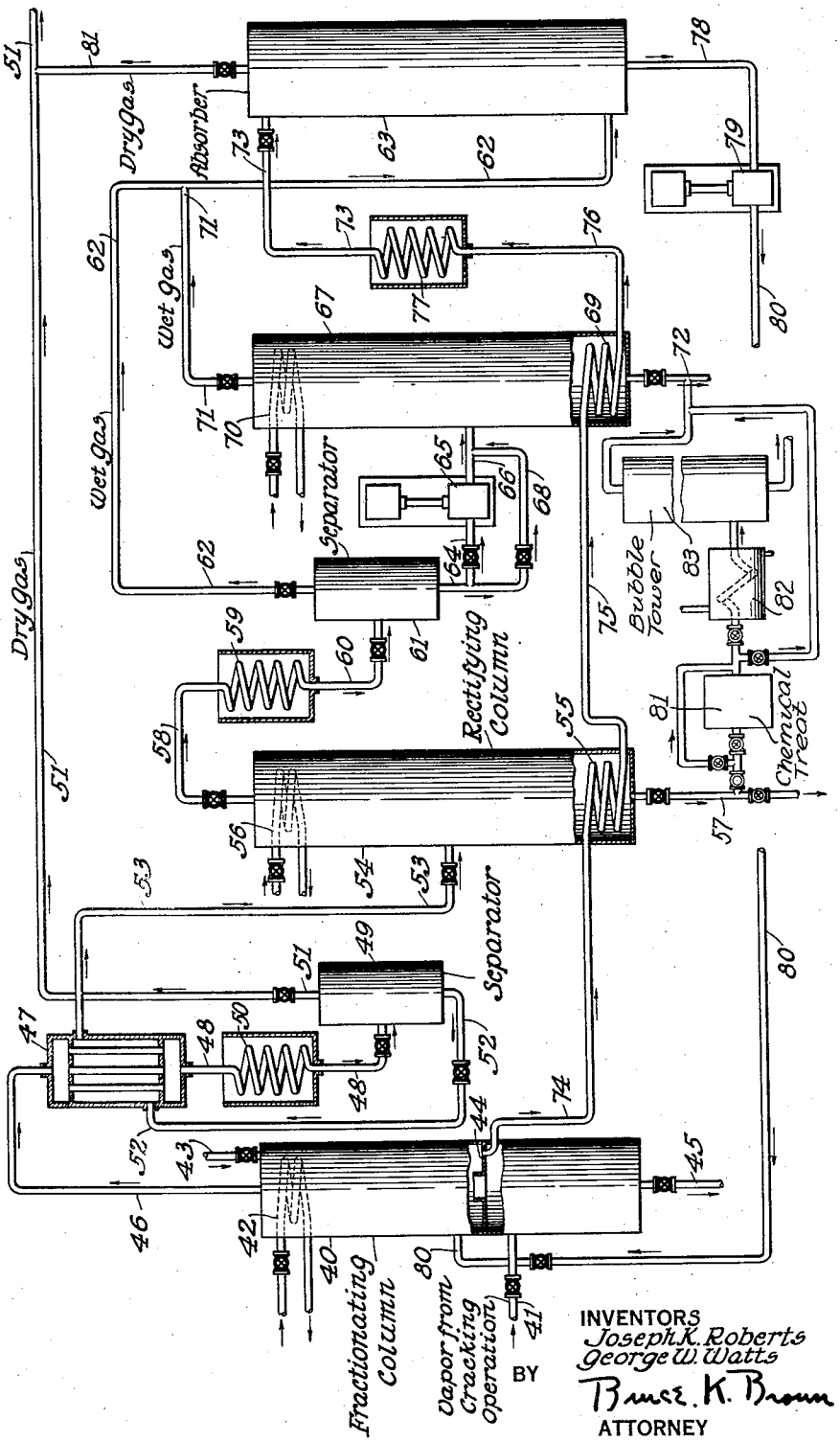
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Fig. 2



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STABILIZATION OF LOW BOILING HYDROCARBON OILS AND PARTICULARLY CRACKED HYDROCARBON VAPORS

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4 Claims. (Cl. 196—11)

This invention relates to the stabilization of light or low-boiling hydrocarbon oils and, particularly, to the stabilization of low-boiling oils derived from the cracking of higher boiling hydrocarbon oils under substantial superatmospheric pressure. The invention will be fully understood by reference to the following description in conjunction with the accompanying drawings, in which:

Fig. 1 is an elevational view, somewhat diagrammatic in character, of an apparatus suitable for carrying out the process of the invention; and

Fig. 2 is a similar type of view of a different form of apparatus suitable for carrying out a modification of the process.

Referring to the drawings, and to Fig. 1 in particular, the numeral 5 indicates a fractionating column which receives low-boiling hydrocarbon oil products in vapor form through a line 6 leading from a cracking process wherein higher boiling hydrocarbon oils are subjected to cracking. The vapors supplied to column 5 may comprise all vapor products given off by the oil undergoing cracking and may, under such conditions, contain a substantial portion of constituents of higher boiling point than those desired in the final distillate product. The column 5 is provided with a plurality of spaced fractionating elements (not shown) of a suitable type, for example, bubble-cap plates, screen plates, or doughnut and disk plates. The column 5 is provided, at an intermediate point above the line 6, with a trap-out plate 7 upon which may be collected reflux condensate from the portion of the column thereabove.

The heated vapors discharged into column 5 are maintained under a relatively high pressure, say 200–300 lbs. gauge, more or less, and are subjected to fractionation to remove therefrom, as condensate, the higher boiling constituents undesired in the final distillate product, a lower boiling portion of such condensate being collected on the trap-out plate 7 and the remainder and higher boiling constituents of such condensate being withdrawn from the lower end of the column through a valved line 8, and comprising suitable charging stock for a cracking operation. Thus, for example, when treating gasoline-containing vapors, a heavy naphtha or kerosene may be collected upon trap-out plate 7, and a gas oil, or similar stock may be collected in the lower end of column 5, the uncondensed vapors passing out of line 11 comprising gasoline and certain undesired excessively volatile fractions. If desired, the condensate may be passed through line 8 to the cracking process from which the vapor products supplied by line 6 were derived. The necessary cooling for fractionation may be effected by the introduction of a relatively cool fluid, such as oil, into the upper portion of the column through a valved line 9 and/or a cool fluid may be passed through a coil 10 mounted in the upper portion to effect condensation of a portion of the vapors, which condensate functions as a reflux cooling medium.

The fractionated vapors, substantially free of heavy undesired constituents, are withdrawn from the top of column 5 through line 11 and are passed to a condenser 12 wherein substantially all of the desired constituents thereof are condensed. When treating a gasoline stock, substantially all butane and higher boiling constituents are condensed in condenser 12. The condensed desired constituents and the dry gases and uncondensed vapors of excessively volatile constituents undesired in the final product are passed from condenser 12 through a line 13 into a separating drum 14 maintained under a substantially high pressure, for example, a pressure approximately the same as that maintained in column 5, wherein the condensate separates from the undesired gases and vapors, the latter being passed from the system through a valved line 15 and consisting substantially entirely of excessively volatile constituents undesired in the final distillate product, i. e. dry gases. With a gasoline stock, such uncondensed constituents may comprise all fractions having a boiling point below that of butane. The condensate is withdrawn from chamber 14 and is passed by a valved line 16 into a chamber 17 maintained under a substantially reduced superatmospheric pressure, say 40–100 lbs., more or less, thereby effecting flashing or vaporization of a substantial portion of the remaining undesired excessively volatile constituents, together with a portion of the lower boiling of the constituents desired in the final distillate product. When treating a gasoline stock, the flashed gases and vapors at this point may comprise methane, ethane, propane, butane, and possibly some higher boiling fractions. The wet mixture of gases and vapors (consisting of desired and undesired excessively volatile constituents) is passed through a valved line 18 to the lower portion of a suitable absorption tower 19, the operation of which will be hereinafter more fully described.

The condensate in chamber 17, from which a substantial portion of undesired excessively volatile constituents has been removed, is withdrawn through a line 20 and passed to the inlet of a pump 21 by which it is forced under increased super-

atmospheric pressure through a line 22 and into a stabilizing column 23. If desired, the condensate may be passed to the column 23 at substantially the same pressure as, or at a lower pressure than that in the chamber 17, by by-passing it around the pump 21 by means of a valved by-pass line 24 interconnecting the lines 20 and 22. The column 23 is maintained under a superatmospheric pressure, preferably in excess of 75 lbs., and is provided internally with a plurality of spaced elements (not shown) for effecting intimate contact of vapors and liquids therein, for example, fractionating elements of a type similar to those employed in column 5 may be employed therein.

The oil discharged into column 23 from chamber 17 is subjected to rectification therein to remove therefrom substantially all of the excessively volatile constituents undesired in the final distillate product. The oil entering column 23 flows downwardly and comes into intimate contact with upwardly flowing warm vapors, whereby it is heated and at least partially vaporized. The unvaporized oil, including reflux condensate, collects in the bottom of the column 23 and is subjected to heating to effect reboiling thereof and insure removal of excessively volatile constituents. The heat for this operation is supplied by means of hot reflux condensate withdrawn from the fractionating column 5, and preferably comprises that condensate collected upon the trap-out plate 7. The condensate on plate 7 may be passed from column 5 through a line 25 and through a coil 26 mounted in the lower end portion of column 23. The condensate, after flowing through coil 26, passes through a line 27 from which it is discharged into the upper portion of the absorption tower 19. The vapors produced by the reboiling of the liquid oil ascend the column 23 and intimately contact downflowing cooler liquid oil, whereby they are fractionated. The necessary cooling for fractionation in column 23 may be effected by the passage of a cool fluid through a coil 28 mounted in the upper portion to effect condensation of a portion of the vapors, which condensate functions as a reflux cooling medium.

The gases and vapors are withdrawn from the top of column 23 through a line 29 leading to the line 18 wherein they become admixed with the gases and vapors flowing to the absorption tower 19 from the chamber 17. The gases and vapors so withdrawn from the top of column 23 comprise substantially all of the remaining excessively volatile constituents remaining in the oil and comprise, as well, certain of the lower boiling of the constituents desired in the final distillate product. For example, with a gasoline stock, these wet gases or vapors may comprise methane, ethane, propane, butane, and some higher boiling constituents. The unvaporized portion, from which substantially all of the undesired excessively volatile constituents have been removed, is withdrawn from the bottom of column 23, and from the system, through a valved line 30. This product is substantially entirely stabilized and may or may not be subjected to suitable refining or sweetening operations, as desired.

The mixed gases and vapors comprising excessively volatile fractions undesired in the final product and the lower boiling of the fractions desired in the final product pass from chamber 17 and column 23 through line 18 and into the lower portion of absorption tower 19 and flow upwardly therethrough, coming into intimate contact with the descending condensate from the fractionating column 5, passed through line 27 into the upper portion of the tower 19. The tower 19 may suitably be of the type ordinarily employed in absorption processes for recovering light hydrocarbon oils from gases, for example, refinery or casing head gas. It is preferred to cool the condensate before discharging it into the tower 19. This cooling may be accomplished by means of a cooling coil 31 interposed in the line 27. The relatively cool downflowing condensate intimately contacts the upflowing wet gases and vapors and absorbs substantially all of the constituents thereof desired in the final distillate product. The unabsorbed gases, which consist substantially entirely of excessively volatile constituents undesired in the final distillate product, are withdrawn from the top of tower 19, and discharged from the system through a line 32. In an operation with a gasoline stock substantially all of the butane and higher boiling constituents will be absorbed in the liquid absorbent, together with some of the lower boiling constituents. The remaining unabsorbed excessively volatile constituents (propane and lower boiling constituents) are separately withdrawn from the tower 19. The enriched liquid condensate, containing the absorbed desired constituents, is withdrawn from the bottom of tower 19 and passed through a line 33 to a pump 34 by which it is forced through a line 35 into the column 5 at an intermediate point thereof. The enriched condensate is preferably introduced into the column 5 at a point substantially above the trap-out plate 7. The enriched condensate undergoes fractionation in the column 5, the absorbed constituents, or fractions, being vaporized and thus recycled through the system with the vapors flowing through line 11.

In a specific operation, the following gauge pressures may be maintained in the system when treating a gasoline containing stock: A pressure of about 200 lbs. may be maintained in the column 5 and the chamber 14; and pressures of about 75 lbs. may be maintained in the chamber 17, the column 23 and the tower 19; however it is to be understood that these pressures may vary considerably, it being preferred to always maintain a pressure of at least 75 lbs. gauge in the column 23. The temperature conditions of course will vary, depending upon the type of product desired and the pressure conditions. With the above mentioned pressures the tops of columns 5 and 23 may be maintained at about 430° F. and 120° F., respectively, and the bottoms of columns 5 and 23 may be maintained at about 675° F. and 250° F., respectively. The temperature of the column 5 at the trap-out plate 7 may be about 650° F. The oil in chamber 14 may be at about 85° F. and at about 80° F. in the chamber 17. The cycle absorber oil may be cooled to about 100° F. before it is introduced into the tower 19. It will be understood that the gases and vapors passed to tower 19 may be cooled before they enter the tower 19, as desired.

In the modification shown in Fig. 2, the stock is separated into lighter and heavier portions which are stabilized in separate stabilizing operations. The vapors from a cracking operation enter a fractionating column 40 through a line 41 and are subjected to fractionation under a relatively high pressure, say 200 to 300 lbs., in a manner similar to that already described relative to column 5, the column 40 being of a structure similar to that of the column 5, and being provided with suitable cooling means such as the

coil 42 and/or a line 43 through which a cool liquid, such as oil, may be introduced, an intermediate trap-out plate 44, and a valved line 45 for withdrawal of condensate from the lower end thereof. The fractionated vapors are passed from column 40 through a line 46 to a heat exchanger 47 wherein they are cooled, the cooled oil vapors and condensate being passed from the heat exchanger 47 through a valved line 48 to a separating chamber 49 wherein uncondensed dry gases or vapors separate from the condensate. The separating chamber is preferably maintained under a high superatmospheric pressure, preferably at a pressure approximating that maintained in the column 40. If desired, additional cooling of the oil may be effected by means of a cooling coil 50 interposed in line 48. It is preferred to condense substantially all of the desired constituents of the vapors at this point, together with some excessively volatile, undesired constituents, leaving in gaseous or vapor form only excessively volatile constituents undesired in the final distillate product. For example, with a gasoline stock, these uncondensed constituents mainly comprise those dry gases having a boiling point below that of butane. The separated undesired dry gases and/or vapors are withdrawn from the chamber 49, and are discharged from the system, through a valved line 51. The separated condensate is withdrawn through a valved line 52 and is passed to the heat exchanger 47 where it is heated by the already described hot vapors flowing therethrough from column 40. The heated condensate is withdrawn through line 53 and passed to a stabilizing column 54. The column 54 may be of a structure similar to that of the column 23 already described, being provided at its lower end with a heating coil 55 through which a hot fluid may be passed, for reboiling liquid in the column, and with a coil 56 at its upper end through which a suitable cooling fluid may be passed, for effecting condensation of a portion of the vapors for reflux cooling purposes. The column 54 may be maintained under any desired pressure, say from 35 to 100 lbs., more or less.

The oil discharged into the column 54 is heated therein by the hot condensate flowing through coil 55, a substantial portion of the oil being vaporized. The heavier portion of the oil is condensed and collected in the lower end thereof, and comprises a stable heavy fraction or portion of the original stock, and is removed from the column 54, and from the system, through a valved line 57. The uncondensed vapors in column 54 comprise the remaining portion or fraction of the original stock and consist of the lighter constituents desired in the final product together with remaining excessively volatile constituents undesired in the final product. These vapors are withdrawn from the top of column 54 through a valved line 58 and are passed to a condenser coil 59 wherein most of the normally liquid or desired constituents are condensed, the condensate and uncondensed gases and vapors being passed through a line 60 to a separator 61 wherein the condensate separates from the vapors and/or gases. The pressure in the separator 61 may be reduced, but it is preferred to maintain it substantially the same as that maintained in the column 54. The gases and/or vapors at this point consist of excessively volatile constituents undesired in the final product together with a portion of the lighter constituents desired in the final product. With a gasoline stock, the vapors in separator 61 comprise chiefly constituents boiling below the boiling point of butane, together with some butane and higher boiling hydrocarbons, while the condensate therein will comprise mainly butane and higher boiling constituents together with some undesired excessively volatile constituents. The mixture of wet gases and vapors is passed from separator 61 through a line 62 to the lower portion of an absorption column 63, while the condensate is passed through a line 64 to a pump 65 by which it is forced through a line 66 into a stabilizing column 67. The column 67 is preferably operated under a pressure of at least 70 lbs. gauge. A valved by-pass line 68 interconnects the lines 64 and 66 for the passage of the condensate around the pump 65 and into the column 67 at a pressure equal to or less than that in the separator 61.

The stabilizer column 67 may be similar in structure to the columns 23 and 54, being provided with a heating coil 69 in its lower end for effecting reboiling of liquid therein, and with a cooling coil 70 in its upper end for effecting condensation of a portion of the vapors to effect the desired cooling within the column. The light liquid portion of the original distillate stock is stabilized in column 67, and is substantially entirely freed of any remaining excessively volatile constituents undesired in the final distillate product, together with a portion of the lighter desired constituents thereof. The uncondensed vapors and gases which comprise undesired constituents and certain lighter desired constituents are withdrawn from the top of column 67 by a valved line 71 and are passed to the wet gas line 62 and into the absorption tower 63. When treating gasoline in the system, these gases consist mainly of butane and lower boiling constituents. The stabilized liquid is withdrawn from the bottom of column 67, and from the system, through a valved line 72. This liquid portion comprises the lighter portion of the original distillate stock and may be blended with the stable heavier portion withdrawn from column 54 to produce the desired stable distillate product. If desired, the heavier stock from column 54 may be subjected to chemical treatment as shown diagrammatically at 81 and/or redistillation as shown diagrammatically by heater 82 and fractionating column 83 before it is blended with the lighter portion from column 67. When treating a gasoline stock, the light liquid portion from column 67 does not ordinarily require chemical treatment and/or redistillation. If desired, this light cut may be sweetened before blending it with the heavier cut from column 54.

The wet gases and/or vapors withdrawn from separator 61 and column 67 enter the lower end of tower 63 and flow upwardly therethrough and come into intimate contact with a downflowing liquid which absorbs desired constituents thereof. This liquid is introduced into the upper portion of column 63 through a line 73 and may comprise condensate from the fractionating column 40 collected upon trap-out plate 44 and passed therefrom through lines 74, coil 55, line 75, coil 69, line 76, and cooling coil 77, to line 73 and into the tower 63. The condensate is cooled in its passage through coils 55 and 69 as it imparts heat to the liquid in the columns 54 and 67, thereby effecting the desired reboiling of the liquid in columns 54 and 67. Any desired additional cooling of the condensate may be effected before it is passed to tower 63 by means of the coil 77. The enriched absorbent liquid, containing absorbed desired constituents, is removed from the lower end of tower 63 through line 78 and is passed to

a pump 79 by which it is forced through a line 80 and into the fractionating column 40, preferably at a point above the trap-out plate 44. When treating a gasoline stock the constituents absorbed in tower 63 mainly comprise butane and higher boiling fractions, although some lower boiling constituents are also absorbed. The enriched absorber oil returned to the fractionating column 40 becomes heated therein and the light absorbed constituents thereof are vaporized and pass in such form from the column 40, and into the remainder of the system, through the line 46. The unabsorbed dry gases, substantially free from butane and heavier hydrocarbons, pass from the top of tower 63 through a line 81 connected to the line 51 through which they are passed from the system together with the dry gases separated in chamber 49.

The pressure and temperature conditions may be considerably varied throughout the system. However, when treating a gasoline stock, it is preferred to maintain the fractionating column 40 and the separator 49 under a substantially high pressure, say about 200 to 300 lbs. gauge, in order to avoid, as far as possible, vaporization in separator 49 of light desired constituents. The column 54 may be operated at any suitable superatmospheric pressure, say from 30 to 100 lbs. gauge, more or less. It is preferred to maintain the chamber 61 at the pressure maintained in column 54. It is preferred to maintain the column 67 at a pressure of at least 70 lbs. gauge, or higher. The absorption tower may be maintained under any desired pressure, for example, it may be maintained under approximately that maintained in the chamber 61.

In a specific operation, the column 40 and chamber 49 may be maintained at 200 lbs. gauge, the top of column 40 being maintained at about 430° F. and the bottom at about 675° F. The temperature at trap-out plate 44 may be about 650° F. The temperature of the oil in chamber 49 may be about 85° F. The column 54 and chamber 61 may be maintained at about 70 lbs. gauge, the top of column 54 being about 185° F. and the botom being about 380° F. The oil in chamber 61 may be about 85° F. The column 67 may be maintained at about 75 lbs. gauge, its top being maintained at about 100° F. and its bottom being maintained at about 160° F. The absorber tower 63 may be maintained at about 70 lbs., its top being maintained at about 90° F. and its bottom at about 105° F.

It will be seen that a high degree of thermal efficiency is realized in that heat derived from the cracking operation is employed in the entire stabilizing operation. A substantial capacity is provided by effecting a relatively rough separation of undesired constituents together with some desired constituents in the rectifying operation, the desired constituents being recovered in the absorption operation in the condensate trapped out of the fractionating column of the cracking system, the absorbed desired constituents being returned to the fractionating column and recycled through the system, whereby they are eventually recovered in the stabilized finished product.

It will be understood that the aforedescribed operations may be carried out without employing the separators 14 and 17 in Fig. 1, and 49 and 61 in Fig. 2, the wet gases being separated in the stabilizing or rectifying columns alone.

We claim:

1. The method of stabilizing and refining hot hydrocarbon oil vapors derived from the cracking of higher boiling oils and consisting largely of constituents boiling in the gasoline range but containing other constituents which are not desired in the final product because of excessive volatility or because of insufficient volatility, which comprises passing such vapors into a primary fractionating zone maintained under conditions adapted to condense only those undesired constituents which are of insufficient volatility, removing the vapors from said primary fractionating zone, cooling said vapors to condense hydrocarbons substantially all of the gasoline boiling range and separating these condensed hydrocarbons without reduction of pressure from uncondensed dry normally gaseous hydrocarbons which are discarded, passing the said condensed hydrocarbons into a secondary fractionating zone maintained under a pressure lower than that of the primary fractionating zone and rectifying the hydrocarbons in the said secondary fractionating zone to produce a condensed stabilized heavy gasoline boiling entirely within the gasoline range and an uncondensed overhead fraction, passing the uncondensed overhead fraction into a tertiary fractionating zone to produce a condensed stabilized light gasoline boiling entirely within the gasoline range and an uncondensed wet gas fraction comprising butane and lower boiling hydrocarbons, withdrawing the said condensed stabilized heavy gasoline from the secondary fractionating zone, chemically treating said heavy gasoline and thereafter blending it with the condensed stabilized light gasoline withdrawn from the tertiary fractionating zone to produce a finished stabilized gasoline, passing the said wet gas fraction into an absorption zone, withdrawing and cooling part of the condensate from the primary fractionating zone and passing such withdrawn part to the absorption zone wherein butane and other desired higher boiling hydrocarbons are absorbed from the wet gas being passed therethrough, withdrawing and discarding the unabsorbed propane and lower boiling hydrocarbons as a dry gas, withdrawing the enriched condensate from the absorption zone and returning it to the primary fractionating zone wherein the absorbed butane and higher boiling hydrocarbons are released therefrom.

2. The method of stabilizing and refining hot hydrocarbon oil vapors derived from the cracking of higher boiling oils and consisting largely of constituents boiling in the gasoline range but containing other constituents which are not desired in the final product because of excessive volatility or because of insufficient volatility, which comprises passing such vapors into a primary fractionating zone maintained under conditions adapted to condense only those undesired constituents which are of insufficient volatility, removing the vapors from said primary fractionating zone, cooling said vapors to condense substantially all hydrocarbons of the gasoline boiling range and separating these condensed hydrocarbons without reduction of pressure from uncondensed dry normally gaseous hydrocarbons which are discarded, passing the said condensed hydrocarbons into a secondary fractionating zone maintained under a pressure lower than that of the primary fractionating zone and rectifying the hydrocarbons in the said secondary fractionating zone to produce a condensed stabilized heavy gasoline boiling entirely within the gasoline range and an uncondensed overhead fraction, cooling the uncondensed overhead fraction

to produce an unstable light gasoline liquid and a wet gas, separating the wet gas from the liquid and transferring it to an absorption zone, transferring the unstable light gasoline liquid to a tertiary fractionating zone maintained at a higher pressure than the pressure of said secondary fractionating zone, rectifying the hydrocarbons in said tertiary fractionating zone to produce a condensed stabilized light gasoline boiling entirely within the gasoline range and an uncondensed overhead vapor fraction, passing said vapor fraction to said absorption zone, withdrawing and cooling part of the condensate from the primary fractionating zone and passing such withdrawn part to the said absorption zone wherein butane and other desired higher boiling hydrocarbons are absorbed from the wet gas being passed thereto, withdrawing and discarding the unabsorbed propane and lower boiling hydrocarbons as a dry gas, withdrawing the enriched condensate from the absorption zone and returning it to the primary fractionating zone wherein the absorbed butane and higher boiling hydrocarbons are released therefrom and withdrawing and combining stabilized heavy gasoline and light gasoline from said secondary and tertiary fractionating zones to produce a stabilized finished gasoline.

3. The method of stabilizing hot hydrocarbon oil vapors derived from the cracking of higher boiling oils and consisting largely of constituents boiling in the gasoline range but containing other constituents which are not desired in the final product because of excessive volatility or because of insufficient volatility, which comprises passing such vapors into a primary fractionating column maintained under a pressure of about 200 pounds per square inch and under temperature conditions adapted to condense only those undesired constituents which are of insufficient volatility, removing the vapors from said primary fractionating column, cooling said vapors, condensing substantially all hydrocarbons of the gasoline boiling range and separating these condensed hydrocarbons without reduction of pressure from the uncondensed dry normally gaseous hydrocarbons which are discarded, passing the said condensed hydrocarbons into a secondary fractionating column maintained under a pressure between about 35 and 100 pounds per square inch and rectifying the hydrocarbons in said secondary fractionating column to produce a condensed stabilized high boiling gasoline, boiling entirely within the gasoline range and an uncondensed overhead fraction, passing the uncondensed overhead fraction into a tertiary fractionating column maintained under a pressure of about 70 pounds per square inch to produce a condensed stabilized low boiling gasoline boiling entirely within the gasoline range and an uncondensed wet gas fraction comprising mainly pentane, butane, and lower boiling hydrocarbons, withdrawing the said condensed stabilized high boiling gasoline from the secondary fractionating column, chemically treating said withdrawn high boiling portion and thereafter blending it with the condensed stabilized low boiling gasoline withdrawn from the tertiary fractionating column to produce a finished stabilized gasoline, passing the said wet gas fraction into an absorption tower, withdrawing and cooling part of the condensate heavier than gasoline from the primary fractionating column and passing such withdrawn part to the absorption tower wherein butane and other desired higher boiling hydrocarbons are absorbed from the wet gas being passed therethrough, withdrawing and discarding the unabsorbed propane and lower boiling hydrocarbons as a dry gas, and withdrawing the enriched condensate from the absorption tower and returning said enriched condensate to the primary fractionating column wherein the enriched condensate is rectified and the absorbed butane and higher boiling hydrocarbons are released therefrom.

4. A method such as that defined in claim 3 in which the condensate fraction withdrawn from the primary fractionating column is passed in indirect heat exchange relation through the bottom of the secondary fractionating column, then through the bottom of the tertiary fractionating column to effect reboiling of the condensate in each of said columns and at the same time to cool the said withdrawn condensate fraction prior to passing it to the absorption tower.

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