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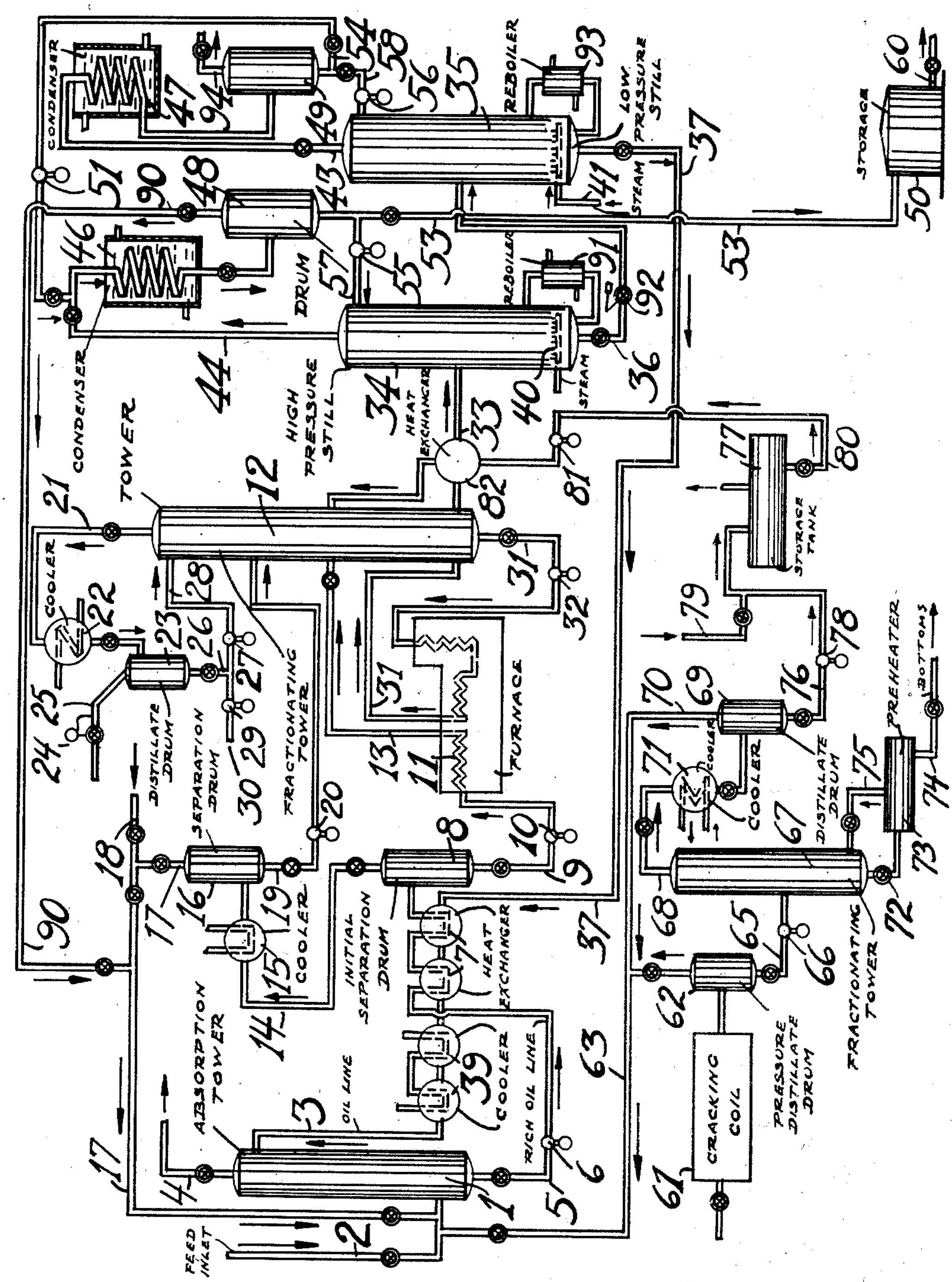

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REFINING OF MINERAL OILS

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2 Claims. (Cl. 196—8)

The present invention relates to the refining of mineral oils. The invention is more particularly concerned with an improved process for recovering and segregating valuable petroleum hydrocarbons contained in gases into desirable fractions which are especially suited as feed stocks for subsequent operations. The invention is particularly concerned with the production of a hydrocarbon fraction comprising a high concentration of hydrocarbons containing three carbon atoms in the molecule and with the production of a hydrocarbon fraction comprising a high concentration of hydrocarbons containing four carbon atoms in the molecule from gaseous feed hydrocarbon fractions containing the same.

It is known in the art to process crude petroleum oils for the production of various refined hydrocarbon fractions boiling in the motor fuel, kerosene, diesel oil, and lubricating oil boiling range, as well as other related products. These oils are refined by numerous well known methods which essentially comprise various distilling, cracking, reforming, and rerunning operations. It is also known to process the gases evolved from the respective operations in a manner to substantially fully recover valuable hydrocarbons which may be incorporated in motor fuels. These processes essentially comprise absorption operations in which the feed gases containing the desirable recoverable hydrocarbons countercurrently contact absorption oils under various temperature and pressure conditions which, to a large extent, depend upon the character of the absorption oil, the oil feed rate, and upon the composition of the feed gases. In these absorption processes, the common procedure is to withdraw the rich absorption oil containing dissolved therein the desirable recoverable hydrocarbons from the bottom of the absorption tower and to substantially completely remove the dissolved hydrocarbons from the absorption oil by distillation means which may comprise one or more distillation towers operated in series or parallel under identical or different temperature and pressure conditions. Overall operating conditions, in general, are regulated to recover the maximum amount of the lowest boiling desirable hydrocarbon termed the "key component" with a minimum recovery of hydrocarbon constituents boiling in the range below the boiling range of the key component. Heretofore the lowest boiling hydrocarbon or key component recovered for incorporation in motor fuels was a hydrocarbon containing four carbon atoms in the molecule. Thus, absorption towers were generally operated under conditions to remove from the feed gases the maximum amount of hydrocarbons containing four carbon atoms in the molecule with the minimum absorption of lower boiling hydrocarbons containing three or less carbon atoms in the molecule. Thus, the usual practice was to operate absorption plants in a manner to recover approximately 60% to 80% of the hydrocarbons containing four carbon atoms in the molecule and substantially the entire amount of higher boiling hydrocarbons from the feed gases in the absorption oil. However, under these conditions some lower boiling hydrocarbons such as propane and propylene and to a lesser extent some ethane and methane were also dissolved in the absorption oil. These latter gases were removed overhead in the still with the butanes, butylenes, and higher boiling hydrocarbons and the entire fraction passed through a condenser and then into a distillate drum. Fixed or recycled gases comprising essentially propane and lower boiling gases were removed from the distillate drum and passed to the burning line or recycled to the equipment. Although the recycle gas from the distillate drum could be compressed in a manner to condense the propane, this was not practical and thus these processes were not adapted for the efficient recovery of a liquid fraction having a high concentration of hydrocarbons boiling in the range of propane and propylene. Furthermore, the process could not be adapted for the production of hydrocarbon fractions having a high concentration of butanes and butylenes. This is a distinct disadvantage since it is essential for the success of various alkylation and polymerization processes that the feed stock be relatively pure or have a relatively high concentration of the desired constituent or constituents. Thus, the practice has been to subsequently fractionate the recovered hydrocarbon fraction after separation of the same from the absorption oil.

We have now discovered a process by which hydrocarbon fractions containing a high concentration of hydrocarbons boiling in the propane and propylene boiling range and containing a high concentration of hydrocarbons boiling in the butane and butylene boiling range may be readily and efficiently segregrated from hydrocarbon gas mixtures containing the same. Our process essentially comprises handling the rich absorption oil removed from the absorption tower in a novel manner adapted to substantially completely remove and segregate hydrocarbon fractions boiling in these ranges.

Our invention may be readily understood by reference to the attached drawing illustrating modifications of the same. For purposes of illustration it is assumed that the feed gases comprise hydrocarbons produced in various refining operations. These gases comprise hydrocarbons containing from one to six and higher carbon atoms in the molecule. The feed gases are introduced into absorption tower 1 by means of feed line 2. The gases flow upwardly through absorption tower 1 and countercurrently contact down-flowing absorption oil which is introduced into tower 1 by means of line 3. Treated gases substantially free of hydrocarbons boiling in the boiling range of butanes, butylenes, and higher are withdrawn from absorption tower 1 by means of line 4 and handled in any manner desirable, usually by passing to a burning line. The rich absorption oil containing dissolved therein the desired recoverable hydrocarbons which may be included in motor fuels and utilized as feed stocks is withdrawn from absorption tower 1 by means of line 5. The absorption operation is conducted under conditions adapted to secure a substantially complete recovery of hydrocarbons containing four carbon atoms in the molecule. Thus, the absorption oil likewise will contain appreciable quantities of hydrocarbons boiling in the propane and propylene boiling range. The feed oil is pumped by means of pump 6 through suitable heat exchanging means 7 in which the temperature is raised the desired degree and then introduced into initial separation or flash drum 8. The liquid product is removed from tank 8 by means of line 9 and pumped by means of pump 10 through heating means 11 and introduced into high pressure fractionating tower 12 by means of line 13. The flashed gases are withdrawn from initial separation drum 8 by means of line 14, passed through condenser or cooler 15 and introduced into secondary separation drum 16. Uncondensed gases are withdrawn from secondary separation drum 16 by means of line 17 and preferably recycled with the feed gases to absorption tower 1. These gases, however, if desired, may be discarded or passed to the burning line by means of line 18. The condensate is withdrawn from drum 16 by means of line 19 and pumped by means of pump 20 into fractionating tower 12 at a point above the point of introduction of the absorption oil feed which is introduced by means of line 13. Temperature and pressure conditions are maintained on tower 12 adapted to remove overhead by means of line 21 substantially all hydrocarbon constituents boiling in the range below the boiling range of butanes and butylenes. These fractions are cooled and condensed in condenser 22 in which substantially complete condensation of the entire overhead fraction occurs and then passed to distillate drum 23. The pressure on the system and on the distillate drum is maintained and controlled by means of back pressure regulating valve 24 maintained on line 25. The condensed distillate is withdrawn from distillate drum 23 by means of line 26. A portion of the condensate is returned to tower 12 as reflux by means of pump 27 and line 28, while the remaining condensate is withdrawn by means of pump 29 and line 30 and handled in any manner desirable. This fraction is extremely suitable as feed material for alkylation or polymerization processes. The desired temperature is maintained on tower 12 by recirculating heavy ends through furnace 11 which are withdrawn from tower 12 by means of line 31 and pump 32. The rich absorption oil substantially completely free of hydrocarbon constituents containing three or less carbon atoms in the molecule is withdrawn from tower 12 by means of line 33 and handled in a manner adapted to recover the absorbed butanes and higher boiling hydrocarbons from the absorption oil. This is preferably accomplished by passing the hydrocarbon rich absorption oil to a high pressure still 34 of a distillation unit by means of line 33. The high pressure still is operated at temperatures and pressures under which it is possible to permit the recycling of any gas from the reflux accumulator back to the absorber without any recompressing being necessary. Gases are removed overhead from still 34 by means of line 44, condensed in condenser 46 and passed to reflux accumulator 48. Any uncondensed gases may be removed from reflux accumulator 48 by means of line 90 and recycled to the absorption tower with gases removed from the top of secondary separation zone 16. Reflux is recycled to high pressure still 34 from reflux accumulator 48 by means of line 57 and pump 55. The desired temperature is maintained on high pressure still 34 by means of reboiler 91. Open steam may be introduced into high pressure still 34 by means of line 40. The amount of this steam may be adjusted to control the amount of recycled gas released from the still or to regulate the pressure on the still when no gas is released therefrom. Bottoms are withdrawn from high pressure still 34 by means of line 36, passed through a pressure release valve 92 and introduced into low pressure still 35. The temperature and pressure maintained on low pressure still 35 may vary widely. The desired temperature is maintained in low pressure still 35 by means of reboiler 93. Open steam is introduced into still 35 by means of line 41. The operating conditions of low pressure still 35 are adjusted so that absorption oil substantially free of dissolved hydrocarbons is removed by means of line 37. This oil is recycled to the absorption tower as described. Hydrocarbon vapors are removed overhead from low pressure still 35 by means of line 45, condensed in condenser 47 and passed to low pressure reflux accumulator 49. Although, in general, substantially complete condensation is secured, any uncondensed gases may be removed overhead from reflux accumulator 49 by means of line 94 and disposed of in any desirable manner. Reflux is introduced into low pressure still 35 from reflux accumulator 49 by means of line 58 and pump 56. The remaining condensed overhead from low pressure still 35 not utilized as reflux is recycled to reflux accumulator 48 by means of line 54 and pump 51. The recovered liquid hydrocarbon product is removed from the distillation system by means of line 53, from the bottom of reflux accumulator 48, and passed to storage 50. The recovered product may then be further processed or utilized as an intermediate feed stock or may be blended directly into motor fuels by means of line 60. Under certain conditions, a preferred modification of our invention comprises processing the gases evolved in the refining of oils, particularly of the gases evolved in the cracking of oils. Gas oil, which for the purposes of illustration is assumed to be the oil from which the feed gases to absorption tower 1 are evolved, is introduced into cracking coil 61 by means of feed line 60. The cracked distillate is withdrawn, cooled, and then introduced into pressure distillate drum 62. Uncondensed gases are withdrawn as high line gases from distillate drum 62 by means of line 63 and passed to absorption tower 1 and processed as described. The condensed pressure distillate is withdrawn from distillate drum 62 by means of line 65 and pump 66 and introduced into a fractionating tower 67. Bottoms are withdrawn from tower 67 by means of line 72 and passed to re-heater 73. A final bottoms product is withdrawn by means of line 74, while a recycled product is returned to tower 67 by means of line 75. Hydrocarbon constituents boiling in the range below butanes and butylenes are removed by means of line 68. These gases are cooled in cooler 71 and passed to distillate drum 69 from which uncondensed gases are removed overhead by means of line 70 and introduced into absorption tower 1. The condensed distillate is withdrawn by means of line 76 and passed into storage tank 77 by means of pump 78. Additional light stock secured from other sources may be introduced by means of line 79. The distillate is removed from drum 77 by means of line 80, pump 81, passed through heat exchanger 82, and then introduced into fractionating tower 12 and handled in the manner described.

The process of the present invention may be widely varied. The invention essentially comprises processing a rich absorption oil containing the desirable recovered hydrocarbons in a high pressure fractionating tower prior to passing the same to the stills. Operating conditions on the high pressure fractionating tower are adapted to remove overhead a fraction containing substantially all hydrocarbons having three or less carbon atoms in the molecule and to substantially completely condense said overhead fraction at tower pressures by cooling the same to atmospheric temperatures. This fraction comprising essentially hydrocarbons containing three or four carbon atoms in the molecule comprises a very desirable feed oil for subsequent alkylation and polymerization and related processes. The temperatures and pressures maintained on the high pressure fractionating tower will vary considerably, depending particularly upon the character and composition of the rich feed absorption oil. In general, the pressures maintained on the high pressure fractionating tower are in the range of from 150 pounds to 250 pounds per square inch and temperatures are in the range from about 100° F. to 500° F. For example, when the rich absorption oil is derived from an absorption operation, the conditions of which are adapted to secure from 80% to 100% butane recovery and the absorption oil is handled in the manner described, the pressure on the high pressure fractionating tower is in the range from about 170 pounds to 190 pounds per square inch. The temperature on the bottom of the high pressure fractionating tower under these conditions is maintained at about 450° F., while the vapor line temperature is maintained at about 150° F. Substantially complete condensation of the overhead fraction is secured by cooling said fraction with water to a temperature of about 100° F. When employing these conditions, the temperature of the absorption oil withdrawn from the bottom of the absorber is maintained in the range from about 120° F. to 130° F., preferably in the range below about 110° F. The absorption oil is then heated to a temperature in the range from about 250° F. to 350° F., preferably to a temperature in the range from about 280° F. to 300° F. prior to introducing the same into the initial separation zone. The uncondensed gases withdrawn from said initial separation zone are cooled to a temperature of from 80° F. to 120° F. at a pressure of from 100 pounds to 120 pounds per square inch.

The rich absorption oil withdrawn from the bottom of the high pressure fractionating tower is then processed by conventional means which comprises passing the same to distillation equipment adapted to completely remove and recover the dissolved hydrocarbons from the rich absorption oil. The distillation equipment, in accordance with the present process, preferably comprises a high pressure still operated at a pressure in the range from 60 pounds to 100 pounds and a low pressure still in series therewith operated at a pressure of from 3 pounds to 10 pounds per square inch.

A very desirable modification of the high pressure fractionating tower of the present invention comprises its adaptation to the processing of hydrocarbons derived from feed oils from which the gases processed in the absorption operation are previously derived. When operating in accordance with this adaptation of the process, gases containing desirable recoverable hydrocarbons are separated from the cracked distillate and passed to the absorption operation in which they are contacted with absorption oil as described. The cracked distillate free of these gases is then passed to a distillation unit operated under conditions to substantially free said distillate of hydrocarbons containing three or less carbon atoms in the molecule, which fraction is removed overhead, condensed and passed to a separation zone. The uncondensed gases having a high concentration of hydrocarbons containing three carbon atoms and less in the molecule are removed overhead from said zone, combined with the gases initially removed from said distillate, and processed in the absorption oil with the same. The condensed fraction having a high concentration of hydrocarbons containing four carbon atoms in the molecule is withdrawn from said separation zone and introduced into said high pressure fractionating tower and processed in the manner described.

The process of the present invention is not to be limited by any theory or mode of operation, but only in and by the following claims in which it is desired to claim all novelty in so far as the prior art will permit.

We claim:

1. Process for the recovery and segregation of hydrocarbons containing three carbon atoms in the molecule and fractions containing four carbon atoms in the molecule derived in the cracking of petroleum oils comprising passing the cracked distillate to a separation zone, removing uncondensed gases in said separation zone and contacting the same in an absorption zone with absorption oil under conditions to substantially completely remove from said gases hydrocarbons containing four carbon atoms in the molecule, removing said distillate from said separation zone and distilling the same in a manner to substantially completely remove overhead hydrocarbons containing three carbon atoms in the molecule, cooling said overhead and passing the same to a separation zone, removing uncondensed gases and processing the same in said absorption zone, removing condensate and passing the same to a

high pressure fractionating tower, withdrawing rich absorption oil from said absorption zone, passing the same to said high pressure fractionating tower operated under conditions adapted to substantially completely remove hydrocarbons containing three carbon atoms from said absorption oil, removing said hydrocarbon fractions containing three carbon atoms in the molecule overhead from said high pressure fractionating tower and substantially completely condensing the same at the pressure maintained in said high pressure fractionating tower by cooling to atmospheric temperature, withdrawing said absorption oil free of hydrocarbons containing three carbon atoms in the molecule from said high pressure fractionating tower and processing the same in subsequent distillation equipment adapted to remove and recover the dissolved hydrocarbons from said absorption oil, recycling said absorption oil to said absorption tower.

2. Process in accordance with claim 1 in which said high pressure fractionating tower is operated at a pressure from 150 pounds to 250 pounds per square inch and said distillation equipment comprises a high pressure still operated at a pressure from about 60 pounds to 100 pounds per square inch and a low pressure still operated at a pressure of from about 3 pounds to 10 pounds per square inch.

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