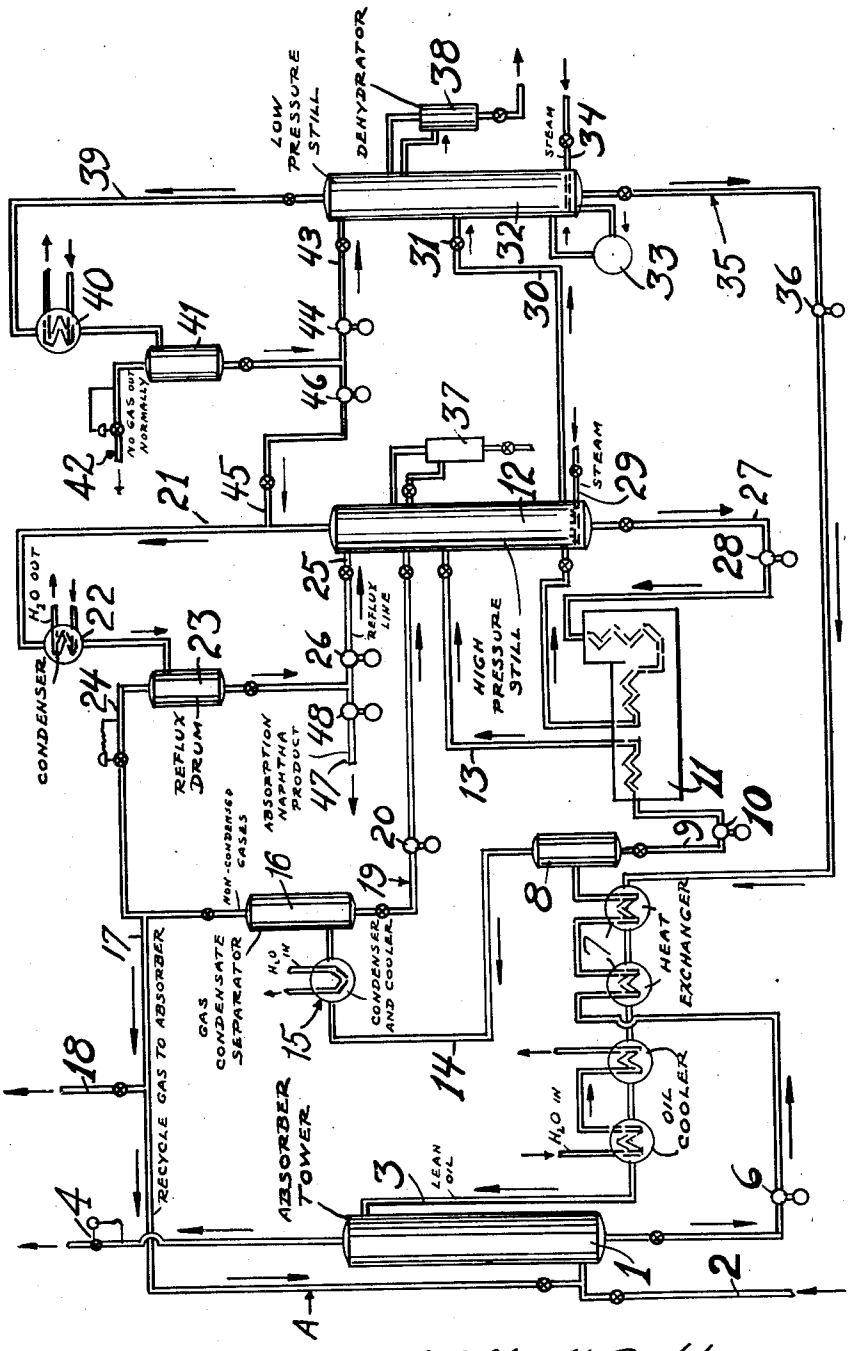
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REFINING PROCESS

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REFINING PROCESS

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The present invention relates to the refining of mineral oils. The invention is particularly concerned with an improved process for recovering valuable petroleum hydrocarbons which may be incorporated in motor fuels and utilized as feed stocks for alkylation and polymerization processes from feed gases containing the same. The invention especially relates to an improved method of processing rich absorption oil containing absorbed hydrocarbons which comprises processing the same in a series of heating, separating and cooling zones prior to completely removing the absorbed hydrocarbons from the absorption oil by means of distillation equipment.

It is known in the art to process gases derived from distilling, reforming, cracking and related petroleum oil refining operations by various methods for the recovery of hydrocarbon constituents which may be incorporated in motor fuels. A usual process is to countercurrently treat the gases containing the recoverable hydrocarbon constituents with an absorption oil under temperature and pressure conditions adapted to remove the recoverable hydrocarbons therefrom. In these absorption operations the common procedure is to withdraw the rich absorption oil containing the dissolved hydrocarbon constituents from the bottom of the absorption tower and then to substantially completely remove the dissolved hydrocarbon constituents from the 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. The absorption tower operating conditions in general are regulated to recover the desired amount of the lowest boiling desirable hydrocarbon constituent 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 constituent or key component usually recovered from hydrocarbon gases for incorporation in motor fuels was a hydrocarbon constituent containing four carbon atoms in the molecule. Thus, absorption towers were generally operated under conditions to recover from the feed gases the desired amounts of hydrocarbon constituents containing four carbon atoms in the molecule with a minimum absorption of lower boiling undesirable hydrocarbons containing three or less carbon atoms in the molecule. Thus, the usual practice was to operate absorption towers in a manner to remove 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. 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 along with the butanes, butylenes, and higher boiling hydrocarbons and the entire fraction passed through a condenser and 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. In operations of this character, particularly when the conditions were regulated on the absorber to recover a substantial proportion of or to secure substantially complete recovery of the key component or butane, an appreciable amount of lower boiling hydrocarbons were also absorbed which had to be removed from the absorption oil and segregated from the desirable hydrocarbons in the distillation equipment. Thus, the capacity of the distillation equipment with respect to the yield of desirable hydrocarbons was materially reduced.

We have now discovered a process by which an absorption operation may be conducted in a manner to secure substantially complete recovery of or the desired recovery of the lowest boiling hydrocarbon and higher boiling hydrocarbon constituents and by which the overall capacity of the absorption operation may be substantially increased. In accordance with our process, the rich absorption oil containing the dissolved hydrocarbons removed from the absorption tower is heated and passed to an initial separation zone in which separation occurs between gases and liquid. The liquid is withdrawn from the initial separation zone, further heated and passed to the distillation equipment which preferably comprises a high pressure and a low pressure still. The vapors from the initial separation zone are withdrawn, cooled, and introduced into a secondary separation zone in which a further separation of vapors and condensate occurs. The vapors are withdrawn from the secondary separation zone and preferably recycled with the feed gas to the absorption tower. The condensate of the secondary separation zone is withdrawn and passed to the distillation equipment. The distillation equipment is operated to remove and recover the absorbed hydrocarbons from the absorption oil and to produce a lean oil substantially free of dissolved hydrocarbons suitable for recycling to the absorption tower.

The process of 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 downflowing lean 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 boiling hydrocarbons 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 for various alkylation, polymerization and similar processes is withdrawn from absorption tower 1 by means of line 5. The absorption operation is conducted under conditions adapted to secure 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 rich absorption oil withdrawn from tower 1 is pumped by means of pump 6 through suitable heat exchanging means 7 in which the temperature of the oil is raised the desired degree and 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 a high pressure still 12 of the distillation equipment 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.

The rich absorption oil substantially completely free of hydrocarbon constituents containing 2 or less carbon atoms in the molecule which is removed from initial separation zone 8 and introduced into high pressure still 12 and is handled in a manner adapted to completely recover the absorbed butanes, butylenes and higher boiling hydrocarbons from the absorption oil. 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 high pressure still 12 by means of line 21, condensed in condenser 22 and passed to reflux accumulator 23. Although when operating in accordance with the present process substantially complete condensation of the overhead is secured, any uncondensed gases may be removed from reflux accumulator 23 by means of line 24 and recycled to the absorption tower with gases removed from the top of secondary separation zone 16. Reflux is recycled to high pressure still 12 from reflux accumulator 23 by means of line 25 and pump 26. The desired temperature is maintained in high pressure still 12 by recycling bottoms through heating means 11 by means of line 27 and pump 28. Open steam may be introduced into high pressure still 12 by means of line 29. The amount of this steam may be adjusted to control the amount of recycle 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 12 by means of line 30, passed through a pressure release valve 31 and introduced into low pressure still 32. The temperature and pressure maintained on low pressure still 32 may vary widely. The desired temperature is maintained in low pressure still 32 by means of reboiler 33. Open steam may be introduced into low pressure still 32 by means of line 34. The operating conditions of low pressure still 32 are adjusted so that absorption oil substantially free of dissolved hydrocarbons is removed by means of line 35 and pump 36. This oil is recycled to the absorption tower and handled as described. Condensed water is removed from the stills by means of dehydrators 37 and 38, respectively. Hydrocarbon vapors are removed overhead from low pressure still 32 by means of line 39, condensed in condenser 40 and passed to low pressure reflux accumulator 41. Although, in general, substantially complete condensation is secured, any uncondensed gases may be removed overhead from reflux accumulator 41 by means of line 42 and disposed of in any desirable manner. Reflux is introduced into low pressure still 32 from reflux accumulator 41 by means of line 43 and pump 44. The remaining condensed overhead from low pressure still 32 not utilized as reflux is recycled to reflux accumulator 23 by means of line 45 and pump 46. The recovered liquid hydrocarbon product is removed from the distillation system by means of line 47, from the bottom of reflux accumulator 23, and passed to storage by means of pump 48. The recovered product may be further processed or utilized as an intermediate feed stock or may be blended directly into motor fuels

The process of the present invention may be widely varied. The process essentially comprises an arrangement of heating, cooling, separation and distillation stages by which it is possible to more advantageously and economically remove the absorbed hydrocarbon constituents from an absorption oil and to segregate a recovered hydrocarbon fraction substantially free of undesirable hydrocarbon constituents. Although the process may be adapted to the treatment of rich absorption oils derived from substantially all types of absorption operations, the process is particularly suitable for the treatment of absorption oils derived from absorption processes, the operating conditions of which are adjusted to absorb hydrocarbon constituents containing 4 carbon atoms in the molecule as the key component, especially when the absorption operations are conducted to secure substantial or relatively complete recovery of hydrocarbons having 4 carbon atoms in the molecule. In general, these conditions are preferably secured by maintaining a pressure on the absorption zone from 50 to 125 lbs. per square inch, and an oil rate in the range from 30 to 100 gals. of absorption oil per 1,000 cu. ft. of gas.

In general, the temperature of the rich absorption oil withdrawn from the absorption system and containing the dissolved hydrocarbons should not exceed about 120° F. to 130° F., and preferably should be below about 110° F. The rich absorption oil is passed through a heating zone which may comprise suitable heat exchanging or equivalent means by which the temperature of the oil is raised to above about 250° F., preferably to a temperature in the range from about 300° F. to 350° F. The heated rich absorption oil is passed to an initial separation zone, in which a separation is made between the vapors and the liquid. It is preferred that the initial separation be made under flash conditions at pressures in the range from about 60 lbs. to 125 lbs. per square inch, which pressures are in general regulated so that gases may be recycled into the absorption zone without recompression of the same being necessary. Conditions are generally regulated to produce a liquid product free of hydrocarbons which are noncondensable at atmospheric temperatures and at pressures in the range from about 80 lbs. to 120 lbs. per square inch, which conditions prevail in the high pressure still condenser. The liquid product is withdrawn from the initial separation zone, passed through a further heating zone in which the temperature is raised to a temperature above about 300° F., preferably to a temperature in the range from about 320° F. to 360° F. The vapors from the initial separation zone are passed through a cooling zone adapted to produce substantial condensation of the same. In general, it is desirable to cool the vapors from the initial separation zone to a temperature below about 100° F., preferably to a temperature in the range from 70° F. to 85° F. When processing a rich absorption oil derived from a process in which substantially complete removal of butane from the feed gas is effected, it is preferred to adapt conditions to remove as a vaporous product from the initial separation zone from about 40% to 60% of the hydrocarbons dissolved in the rich absorption oil and to condense in the subsequent cooling zone from about 40% to 60% of the vapors which are then separated from the remaining vapors in the secondary separation zone. The cooled vapors in the secondary separation zone are separated and preferably recycled to the absorption zone with the feed gases. The condensate from the secondary separation zone along with the heated condensate from the primary separation zone is introduced into the distillation equipment. It is preferred that the condensate from the secondary separation zone be introduced into the distillation equipment at a point above the point of introduction of the heated liquid from the initial separation zone. The distillation equipment preferably comprises a high and low pressure still arrangement, in which the pressure on the high pressure still is in the range from about 80 lbs. to 120 lbs. per square inch, and the pressure on the low pressure still is in the range from about 3 lbs. to 10 lbs. per square inch. A desirable bottoms temperature on the high pressure still is in the range from about 350° F. to 450° F., while the preferred temperature on the low pressure still is in the range from about 320° F. to 380° F.

In order to further illustrate the invention, the following example is given which should not be construed as limiting the same in any manner whatsoever:

Example I

Feed gases of the following composition derived from petroleum distilling, cracking and reforming operations were passed into an absorption tower as described.

	Mols Per cent
C_1*	35.5
C_2	21.9
C_3	25.0
C_4	13.4
C_5	3.2
C_{6+}	1.0
	100.0

*Denotes number of carbon atoms in hydrocarbon molecule.

These gases were countercurrently contacted with an absorption oil which had a gravity of 43° A. P. I., a mid-boiling point of about 425° F., a boiling range from about 350° F. to 475° F. and an air equilibrium vapor pressure of about 5 mms. at 100° F. The oil rate was approximately 29 gals. per 1,000 cu. ft. of gas, and the pressure maintained on the absorption tower was about 70 lbs. per square inch.

The rich absorption oil was withdrawn from the absorption tower at a temperature of about 110° F., passed through a heating zone in which the temperature of the rich absorption oil was raised to about 340° F. The heated rich absorption oil was then passed into an initial separation zone in which uncondensed vapors were separated. The liquid was removed from the initial separation zone, passed through a secondary heating zone and then introduced into a high pressure still of a distillation unit. The gases were removed from the initial separation zone, were cooled to a temperature of about 80° F., and introduced into a secondary separation zone. Uncondensed gases were removed from the secondary separation zone and recycled without compression to the absorption tower. The liquid condensate was removed from the secondary separation zone and introduced into said high pressure still of the distillation unit at a point above the introduction of the liquid removed from said initial separation zone.

The pressure maintained on the high pressure still of the distillation equipment was about 80 lbs. per square inch and the bottoms temperature was about 400° F. The pressure maintained on the low pressure still was about 5 lbs. per square inch and the bottoms temperature was about 360° F.

The results of this operation are summarized in the following material balance, excluding the absorption oil, based upon 100 mols of feed gas to the absorption zone:

	Analysis of feed gases to absorption tower	Hydrocarbons absorbed in absorption oil	Mols of absorbed hydrocarbons removed from initial separation zone	
			Liquid	Vapors
	Mols	*Mols*		
C_1	35.5	0.75	0.15	0.60
C_2	21.9	2.10	0.46	1.64
C_3	25.0	8.00	3.47	4.53
C_4	13.4	7.00	4.26	2.74
C_5	3.2	3.34	2.50	0.84
C_{6+}	1.0	1.01	0.88	0.13
	100.0	22.20	11.72	10.48

	Mols absorbed hydrocarbons removed from secondary separation zone		Absorbed hydrocarbons removed overhead from high pressure still	Absorbed hydrocarbons removed overhead from low pressure still
	Condensate	Vapors		
			Mols	*Mols*
C_1	0.03	0.57	0.18	
C_2	0.33	1.31	0.79	
C_3	1.97	2.54	5.46	
C_4	1.88	0.86	5.45	0.69
C_5	0.73	0.11		3.23
C_{6+}	0.12	0.01		1.00
	5.06	5.40	11.88	4.92

When operating as described above it was possible to process 28.4 unit volumes of feed gas per day.

Example II

In a similar operation conducted under conditions described with respect to Example I utilizing the same feed gas and operating under conditions to produce products substantially identical in character with the exception that the rich absorption oil was passed directly to the high pressure still of the distillation equipment, it was found possible to process only 21.4 unit volumes of feed gas per day.

What we claim as new and wish to protect by Letters Patent is:

1. Process for the removal of absorbed hydrocarbon from absorption oil containing the same, comprising passing the absorption oil through a heating zone, introducing the heated oil into an initial separation zone under flash conditions to secure a separation between vapors and liquid, withdrawing the liquid from the initial separation zone and further heating the same, introducing said liquid at an intermediate point of a distillation tower, withdrawing the vapors from the initial separation zone, treating the same in a cooling zone and passing the same to a secondary separation zone, effecting a separation between vapors and condensate in said secondary separation zone, introducing the condensate from said secondary separation zone into said distillation tower at a point intermediate the point at which said liquid is introduced and the top of the tower, removing absorbed hydrocarbons overhead from said distillation tower, substantially fully condensing said overhead, withdrawing a portion of said condensate as a recovered product, and returning a portion of the same to the top of said distillation tower as reflux.

2. Process in accordance with claim 1 in which said absorption oil is heated to a temperature of in the range above about 250° F. prior to introducing the same into the initial separation zone and in which the vapor is removed from said initial separation zone and cooled to a temperature below about 100° F. prior to introducing the same into said secondary separation zone.

3. Process for the removal and recovery of hydrocarbon constituents which may be included in motor fuels from hydrocarbon gases containing the same comprising countercurrently contacting the feed gases containing the hydrocarbon constituents which may be included in motor fuels with an absorption oil under temperature and pressure conditions whereby said hydrocarbon constituents are absorbed in said absorption oil, withdrawing the absorption oil containing the absorbed hydrocarbons from the absorption zone, passing the absorption oil through a heating zone, introducing the heated oil into an initial separation zone under flash conditions to effect a separation between vapors and liquid, withdrawing the liquid from the initial separation zone and further heating the same, introducing the heated liquid into an intermediate point of a distillation tower, withdrawing vapors from the initial separation zone, treating the same in a cooling zone and passing the same to a secondary separation zone, effecting a separation from between vapors and condensate in said secondary zone, introducing the condensate from said secondary separation zone into said distillation tower at a point between the top of said tower and the point at which said heated liquid is introduced, removing overhead from said distillation tower the absorbed hydrocarbons, substantially fully condensing said overhead, withdrawing a portion of the condensate as a final product, and introducing the remainder thereof to the top of said distillation tower as reflux.

4. Process in accordance with claim 3 in which said hydrocarbon constituents may be incorporated in motor fuels containing 4 or more carbon atoms in the molecule.

5. Process according to claim 3 in which the rich absorption oil is removed from the bottom of absorption zone at a temperature below about 120° F. and in which said absorption oil is heated to a temperature above about 250° F. prior to introducing the same into said initial separation zone and in which the vapors removed from said initial separation zone are cooled to a temperature below about 100° F. prior to passing the same to said secondary separation zone.

6. Process according to claim 3 in which said distillation tower is a high pressure still operated at a pressure of from 80 to 120 lbs. per square inch, and is utilized in conjunction with a low pressure still operated at a pressure of about 3 to 10 lbs. per square inch and under conditions whereby the overheads from the respective stills are substantially fully condensed at temperatures in the range below about 100° F.

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