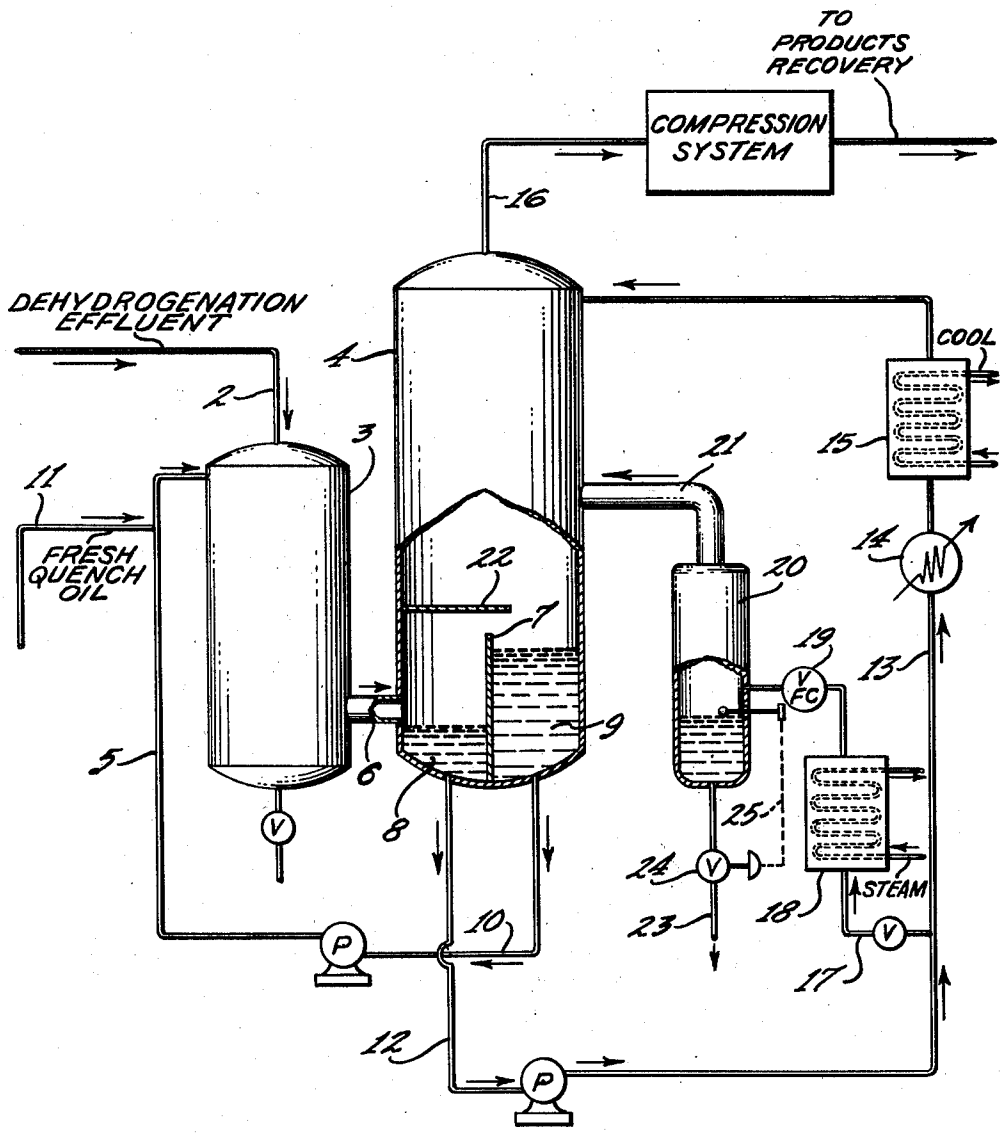
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QUENCH OIL SYSTEM

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QUENCH OIL SYSTEM

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The present invention relates to the recovery of products from an aliphatic dehydrogenation system and is particularly concerned with the conservation of the quench oil employed in cooling of the effluent discharged from such dehydrogenation systems.

The novel features of the invention may be applied in the handling of the vapor effluent from dehydrogenation of hydrocarbons having 3 to 5 carbon atoms as illustrated by the typical commercial systems designed for the production of butylene and/or butadiene by catalytic dehydrogenation of normal butane or butane-butylene mixtures. While the invention will be particularly described with reference to such "buta" systems, it will be understood that the essential features also find use in the recovery of products from dehydrogenation of pentane as in the production of isoprene, or the production of propylene from propane.

In a typical dehydrogenation system designed for the production of butylene and/or butadiene, the vapor charge of C_4 hydrocarbons, which comprise normal butane, normal butylene, or mixtures of these, is passed over catalyst of the chromia-alumina type in a fixed bed reactor of a system providing a number of such reactors for alternate hydrocarbon processing and regeneration. The effluent from such reactor is quenched as soon as possible by direct contact with a liquid quench oil and is then further cooled to the lower temperature at which it is sent to compression in a multi-stage compression system equipped with means for cooling between the compression stages. The liquid condensate from the last compression stage and the vapor separating from such liquid are then passed to a conventional absorption-stripping section. The recovered C_4 hydrocarbon mixture, which may contain some C_3 and a small amount of C_5 and higher hydrocarbons, is transferred to a products recovery plant in which butadiene and one or more mixed butane-butylene streams are obtained separately. The butane-butylene streams may be further processed to separate the butane and butylene, or the combined stream may be recycled directly to the dehydrogenation system.

At elevated temperatures diolefins and to a lesser extent mono-olefins, such as butadiene and butylene, are easily polymerized to heavier hydrocarbons with consequent loss of valuable product. By rapid cooling of the dehydrogenation effluent with the quench oil and maintaining subsequent handling at low temperature, this loss is minimized. A small amount of polymer is nevertheless formed, a part of which accumulates in the quench oil, so that it is necessary in practice to withdraw a slipstream of the circulating quench oil and to replace the same with fresh make-up oil to maintain acceptable density and viscosity ranges. The recommended quench oil which is an aromatic hydrocarbon composition boiling in the range of 400–600° F., is relatively expensive, so that the replacement of a comparatively large portion of the circulating quench oil constitutes an important element of cost in the operation of the process.

In accordance with the present invention a large portion of the ordinarily rejected quench oil is recovered for further use in the system, thereby not only reducing the amount of make-up quench oil required, but also making possible a cleaner system with less coke deposition in the quench towers and less fouling of auxiliary equipment. Such conservation of quench oil is effected by distillation of the stream of oil which would ordinarily be rejected so as to selectively remove therefrom only the higher boiling materials, such as materials boiling above about 650° F. Such distillation of the quench oil, moreover, is accomplished with only a minor modification of the equipment heretofore employed in the quench section. Thus, a small portion of the hot quench oil withdrawn from the bottom of the quench tower is subjected to flash vaporization and the obtained vapors returned to an intermediate portion of such tower, the unvaporized portion being collected and discharged as rejected oil.

It has been found that the equilibrium oil obtained by such selective discharge of the higher boiling components has greater thermal stability than the ordinary fresh quench oils which can be provided at desired low cost, in that the equilibrium oil is superior to the fresh make-up oil in its high content of non-olefinic aromatic compounds and in its lower concentration of easily cracked hydrocarbons and readily coking components which latter, in accordance with the invention, are largely removed from the distilled oil in the discharged liquid bottoms. The removal of heavy ends reduces the fouling characteristics of the oil and furthermore, since peroxides which may be formed in the oil would also accumulate in such heavy ends, the build-up of these peroxides in the circulating oil is minimized or avoided. These peroxides tend to promote chain polymerization of olefins, so that by their removal the extent of chain polymerization with consequent fouling of the system is also considerably reduced.

Other important advantages of the novel features of the present invention will be appreciated from the detailed description which follows read in connection with the accompanying drawing showing a flow chart of a portion of the recovery system associated with a dehydrogenation plant, wherein the quench section is depicted schematically partly in elevation.

As will be seen from the drawing, the vapor effluent from the dehydrogenation system is sent by means of a line 2 to the quench section comprising principally a pre-quench tower 3 and a quench tower 4. Where the dehydrogenation system is one which has been designed for the treatment of a C_4 hydrocarbon fraction, the vapor products in line 2 will comprise butadiene, various isomers of butylene, unreacted butane and possibly some isobutane. There may also be small amounts of saturated and unsaturated C_3 and C_5 hydrocarbons in the line. In the pre-quench tower 3, the dehydrogenation effluent is subjected to contact with a spray of cooler quench liquid admitted through line 5 and sprayed over the concurrently passing hydrocarbons from line 2. As a result of partial vaporization of the liquid quench oil, rapid cooling of the reactor effluent is effected with the reduction of the temperature of such effluent to a sufficiently low level to avoid any substantial thermal cracking or polymerization. The thus pre-cooled vapors are further cooled by direct counter-current contact with cool quench oil in the main quench tower 4. Any form of a quench oil which is stable under the operating conditions may be employed. In practice there has been employed with satisfactory results light catalytic fuel oil, such as that boiling over the range of about 350–600° F. and which is highly aromatic, containing less than about 35% by volume of paraffins and naphthenes.

The quench oil and quenched product from the tower 3 are admitted by a connecting conduit 6 into one side

of the bottom of the quench tower 4; such bottom section being divided by a partition 7 to form separate chambers 8 and 9, each of which will contain a pool of liquid. The liquid product from chamber 9 is returned by means of line 10 through a pump connecting with line 5 feeding the spray head (not shown) at the top of pre-quench tower 3. Provision is made for the addition of fresh makeup oil to line 5 by means of a supply line 11, to replace quench oil rejected from the circulating system, as will be hereinafter described.

Liquid product from the chamber 8 is withdrawn by means of line 12 and a principal portion of such withdrawn liquid is returned through line 13 to the top of quench tower 4, passing down through that tower over suitable plates in contact with ascending vapors which are cooled thereby. In line 13 provision is made for cooling the circulating quench oil, such as the exchanger 14, wherein the oil is cooled by indirect exchange with cool hydrocarbon reactor feed and through several banks of coolers provided with cooling water coils diagrammatically indicated at 15. Thus the pre-quenched product gas which enters quench tower 4 through conduit 6 at say about 300° F. is cooled to approximately 100–110° F., at which latter temperature the overhead vapors are discharged through line 16.

A small portion of the hot oil discharged from chamber 8 through line 12 is sent by means of branch line 17 through heater 18 and then through a flow control valve 19, into flash chamber 20 which is in vapor communication through a relatively large conduit 21 with quench tower 4. In usual practice quench tower 4 is maintained at sub-atmospheric pressure, and accordingly, vessel 20 in direct communication with the quench tower will be at approximately the same low pressure, the line pressure in line 17 being reduced at valve 19. At the low absolute pressure maintained down-stream of valve 19, the major part of the oil passed through branch line 17 is flash vaporized at the prevailing low pressure and separated in vessel 20 to provide a vapor overhead which flows through conduit 21 into an intermediate level of quench tower 4, while the higher boiling non-vaporized portion of the oil is collected in the bottom of flash chamber 20. The oil vapor admitted through conduit 21 ascends in the quench tower and as it is condensed drips back as liquid onto an imperforate plate 22 above partition 7, such liquid cascading over the edge of the plate into chamber 9.

By the particular arrangement thus shown and described, more effective utilization of the heat capacity of the reaction product can be achieved with important economies in operation. For instance, the vapors entering the quench system through line 2 may be at approximately 1000° F. and at a pressure of about 3 p.s.i.a. The oil withdrawn from chamber 9 may be at approximately 180° F., while the oil discharged from chamber 8 may be at a considerably higher temperature in the order of 100° F. or so greater than that in chamber 9, say about 280° F. The effluent gases withdrawn overhead from the top of the quench tower 4 by means of line 16 would be in the temperature range of about 100–110° F. and may or may not be initially cooled before entering into the compression system. The oil withdrawn through line 12, at about 280° F. is further cooled by the exchangers in line 13 to approximately 95° F., at which temperature it is re-admitted into the top of tower 4. The side stream of oil which is circulated through line 17 is heated at 18 to approximately 430° F., at which temperature it is discharged into flash chamber 20. Because of the sub-atmospheric pressure (below 3 p.s.i.a.) in this chamber a larger portion of the oil passed through line 17 is flash-vaporized and escapes into the quench tower admixing with the other ascending vapors, while the higher boiling unvaporized portion, largely that having an atmospheric boiling point above 650° F., is collected as liquid in the bottom of chamber 20. The heavy oil collected in chamber 20 is withdrawn continuously or periodically by line 23 and rejected from the circulating quench oil system. In the preferred arrangement shown, line 23 is provided with a valve 24 responsive to a level control device generally indicated at 25.

The proportionation of the relative quantities of oil to be flowed respectively through lines 13 and 17, (each of which communicates with discharge line 12) will depend chiefly upon the quality and properties of the original quench oil and of the circulating equilibrium oil. Employing a fresh quench oil in the 350–600° F. boiling range derived as an aromatic extract from thermal or catalytic cracking of a gas oil, which has an aromtics content of 65–75% by volume, line 13 will circulate about 99.8% or more of the oil withdrawn through line 12, the rest being passed to flash vaporization through line 17. At the prevailing pressure and temperature conditions 50 to 80% of the oil circulated through branch line 17 will be vaporized and returned to quench tower 4, so that the quantity of oil rejected through line 23, to be replaced by fresh quench oil, will constitute only a very small portion of the total oil being circulated in the quench system, in the order of 0.01% to no more than about 0.1% thereof. The amount of oil to be rejected from the system can be adjusted so as to maintain the desired predetermined quality from the standpoint of composition and properties of the retained equilibrium oil.

In the system shown in the figure a vertical partition 7 divides the bottom of the quench tower to provide separate liquid collecting chambers 8 and 9. In a construction of this type the individual circulation rates through lines 10 and 13, respectively, are designed on the basis of the desired heat exchange balances in vessels 3 and 4.

While the partitioning of the bottom of vessel 4 as above described is preferred in most instances, the invention can be practiced in an alternative embodiment without such partitioning. In the absence of the separate partitioned chambers, the oil at the bottom of tower 4 can be at about 230° F., thereby providing oil at somewhat lower temperature for return to the pre-quench tower, which is offset by the higher temperature of the oil circulated through line 12 to the coolers at 14 and 15.

In either embodiment of the invention the gaseous overhead withdrawn from line 16, with or without further cooling, is passed through the compression system 22 wherein the gases are subjected to a multi-stage system of compressors to bring the gas up to about 150–170 pounds per square inch absolute. Between the several compression stages the gases are cooled so as to remain below about 240° F., thereby avoiding production of undesired polymer and loss of diolefin. The compressed vapors are then passed into a conventional system for separation and recovery of desired olefinic and diolefinic products.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The method of recovering olefins and diolefins from the hot vaporous effluent of a dehydrogenation reaction, which comprises the steps of rapidly pre-quenching said effluent by direct contact with a first supply of liquid quench oil within a pre-quench zone, introducing the vaporous and liquid pre-quench effluent into a main quench zone, further cooling the pre-quenched vapors by upward flow through said main quench zone in countercurrent contact with a descending, pre-cooled, second supply of liquid quench oil, withdrawing the cooled vaporous effluent of said main quench zone, accumulating both pre-quench and main quench oil at the bottom of said

main quench zone, recycling a first portion of said accumulated oil from said main quench zone to said pre-quench zone to constitute said first supply of quench oil, withdrawing a second portion of said accumulated oil from said main quench zone, cooling all but a minor part of said second portion and recycling the cooled oil to said main quench zone to constitute said second supply of quench oil, heating said minor part of said second portion, flash vaporizing at least about half by volume of said heated oil so as to provide a relatively high-boiling liquid fraction and a vapor fraction, introducing said vapor fraction into said main quench zone and into contact with said descending quench oil, and discharging said high-boiling liquid fraction from the body of circulating liquid comprising said supplies of quench oil, thereby selectively removing from said body the contaminating components contained in said high-boiling liquid fraction.

2. The method of maintaining the quality and desired physical properties of a circulating body of quench oil employed for rapid quenching of a vaporous dehydrogenation effluent to safe temperatures minimizing polymerization of easily polymerizable components of such effluent, which comprises the steps of continuously circulating the substantial major portion of said quench oil while effecting periodic direct contact with a continuously flowing stream of the vapor effluent, continuously withdrawing a small portion of quench oil from said circulating body of quench oil as a side stream, distilling said side stream portion by flash vaporization to provide an overhead vapor fraction and a bottom higher-boiling liquid fraction, recontacting said vapor fraction, freed of said higher-boiling liquid fraction, with said circulating body of quench oil, withdrawing said higher-boiling liquid fraction and replacing the same by addition to said body of a substantially equal quantity of fresh make-up quench oil of a boiling range lower than that of the withdrawn higher-boiling liquid fraction.

3. In the operation of a quench oil system for rapidly cooling the hot vapor effluent from a dehydrogenation reaction, which effluent contains polymerizable unsaturated compounds, the method which comprises the steps of: initially contacting said effluent with a liquid spray of cooler quench oil composed of an extreme preponderance of recirculated equilibrium oil and a minor portion of fresh makeup oil, thereby pre-quenching said effluent, separating the pre-quenched vapor effluent from said quench oil and accumulating the latter as a liquid reservoir, passing said pre-quenched vapor effluent upwardly through a main quench zone, withdrawing a first portion of oil from said reservoir and admixing the same with fresh make-up oil to provide said cooler quench oil utilized as the aforesaid liquid spray, withdrawing a second portion of oil from said reservoir, dividing said second portion into a major stream and a minor stream, cooling said major stream and passing the same downwardly through said main quench zone in direct countercurrent contact with said pre-quenched vapor effluent; collecting said major stream in said reservoir; distilling said minor stream

to provide a vapor fraction and a higher-boiling liquid fraction of higher boiling range than said fresh make-up oil; discarding said liquid fraction; introducing said vapor fraction at an intermediae level within said main quench zone, thereby condensing said vapor fraction; and returning the latter in liquid state to said reservoir.

4. The method according to claim 3 wherein said liquid reservoir comprises two separated oil pools, the aforesaid first portion of oil being withdrawn from one of said pools and the aforesaid second portion of oil being withdrawn from the other of said pools and being collected, after downward flow through said main quench zone, in the pool other than the one from which said second portion was withdrawn.

5. The method according to claim 3 wherein said distillation of the minor stream of oil is effected by flashing the same at sub-atmospheric pressure.

6. The method according to claim 5 wherein said main quench zone is maintained at sub-atmospheric pressure and said flashing is effected by introducing said minor stream in mixed phase into a flash zone communicating with the main quench zone at an intermediate level thereof, the non-vaporized portion being collected as high boiling liquid residue and discharged from the circulating quench oil system.

7. In a quench system comprising a pre-quench tower and a quench tower connected at the lower portions thereof with a communicating fluid flow passage, means including a first conduit for withdrawing liquid oil from the bottom of said quench tower and passing the same to the top of the pre-quench tower, means including a separate second conduit for withdrawing liquid oil from the bottom of the quench tower and passing the same to the top of said quench tower, a branch conduit connecting with said second conduit and in flow communication therewith, cooling means associated with said second conduit upstream of said connection with the branch conduit for effecting cooling of the liquid passing through said second conduit to the top of the quench tower, heating means associated with the branch conduit at an intermediate length thereof arranged to heat the oil flowing through said branch conduit, flow control means associated with said branch conduit upstream of said heating means to enable discharge of fluids from said branch conduit at predetermined low pressure, vapor-liquid separating means associated with said quench tower and in open vapor communication therewith, said branch conduit discharging into said separating means, whereby the separated vapors pass upwardly into said quench tower, free of separated liquid, and means for withdrawing the separated liquid from said separating means.

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