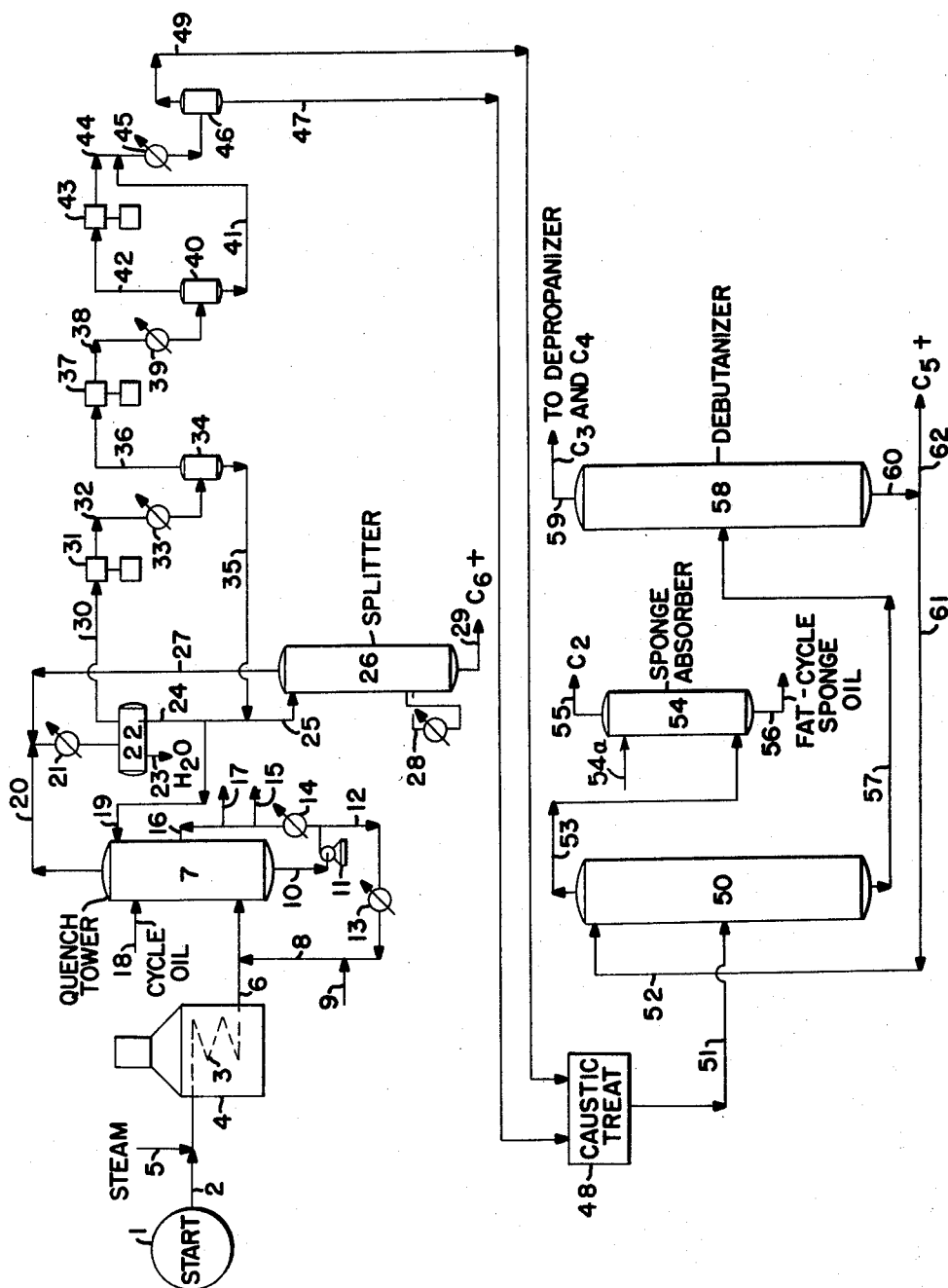


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PROCESSING OF STEAM-CRACKED NAPHTHA LIGHT END PRODUCTS

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PROCESSING OF STEAM-CRACKED NAPHTHA
LIGHT END PRODUCTSRobert H. Johnston, Whippany, and Isaac Pass, Roselle,
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This invention relates to a means and method for processing low-boiling unsaturated hydrocarbon products separated from a quenched steam-cracked naphtha. It is concerned particularly with obtaining a more complete segregation of ethene, propene, butene, butadiene, and pentadiene (C_2 to C_5) concentrates from the more readily condensed higher boiling hydrocarbon products by keeping temperature, pressure, and time of separation steps at low levels to minimize polymerization of the reactive olefinic hydrocarbons in the C_2 to C_5 range.

To obtain quick separation of the C_2 to C_5 hydrocarbons at low temperature and pressure levels, a splitter tower is used on the lowest pressure side of a series of compressors and coolers for removing up through C_5 hydrocarbons from higher boiling hydrocarbons of an initial naphtha range condensate. Since the fractionation is not precise, the overhead vapors from the stripping zone are mainly C_4 to C_6 hydrocarbons with small amounts of higher boiling hydrocarbons.

In steam cracking, the hydrocarbon vapors of a virgin naphtha fraction principally in the C_5 to C_{11} hydrocarbon range are mixed with a sufficiently high proportion of steam to form a cracking mixture containing 60 to 90 mole percent steam which is heated in a cracking coil under a total pressure of generally 1 to 3 atmospheres for a cracking period of a fraction of a minute.

The cracked products are transferred from the outlet of the steam-cracking coil to a quench tower by a transfer line. In the transfer line the cracked mixture is commingled with a sufficient amount of relatively cool quench oil to reduce a temperature in the range of 1350° F. to 1500° F. to a temperature in a range of 400° F. to 650° F. as the mixture is passed into a bottom part of the quench tower. In the quench tower, most of the further cooling is obtained by introducing large amounts of high-boiling hydrocarbon liquids into the upper part of the tower or quenching zone so as to flow countercurrently to the gaseous stream which flows rapidly up through and out overhead from the tower. This gaseous stream contains cracked hydrocarbon products boiling below 430° F. mixed with a higher proportion of steam and some hydrogen and methane.

The overhead gaseous stream from the quench tower is passed to a heat exchange cooling condenser to condense out water and mainly hydrocarbons higher boiling than C_5 hydrocarbons. The water is separated in a separation zone and a portion of the condensed hydrocarbons may be used as reflux to the upper part of the quench tower. The remaining part of the condensed hydrocarbons from the overhead separated from water in said separation zone is fed to the fractionation zone of a splitter tower for removal therefrom of desired vaporized butenes, butadienes, pentenes, and pentadienes (C_5 and lighter), which are to be recovered as light end concentrates.

The operation of the splitter tower in conjunction with the remainder of the steam-cracking unit and its light ends recovery system will be described in more detail with reference to the attached drawing.

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In the drawing is shown diagrammatically a flow plan illustrating the arrangement of the splitter tower and the compressors with respect to the steam-cracking coil, the quench tower and its overhead cooling and condensate receiving means.

Referring to the drawing, the naphtha fraction used as cracking feed starts from supply source 1 to flow by line 2 through the cracking coil 3 in furnace 4. The steam is admixed by line 5. The high-temperature steam-cracking products leave the outlet of the cracking coil through transfer line 6 to be passed into a bottom part of quenching zone in tower 7. Quench oil is injected into the transfer line 6 from line 8. At least a substantial portion of the quench oil passing through line 8 is supplied from an external source by line 9, this external source preferably supplying a light gas oil which is refractory to cracking and at least has a low susceptibility to the formation of tarry polymers which would coke up the transfer line 6. The light gas oil may be obtained by relatively low-temperature cracking of gas oil, e.g., low temperature catalytic cracking, or maybe a virgin light gas oil. Preferably, the gas oil should be aromatic in order to be more refractory to cracking. This light gas oil can be added in suitable amounts to a portion of bottoms withdrawn from the quench tower 7 through line 10, pump 11, line 12 and cooler 13. In combining the gas oil with the recycled cooled bottoms, a sufficient amount of the gas oil is admixed to keep the tarry polymer content of the combined mixture at a suitable low level, e.g., below 10%.

Another portion of the heavy fraction bottoms withdrawn from tower 7 through line 10 and pump 11, is passed through a cooler 14 for recycling to an upper part of quench tower 7. The cooler 14 extracts as much heat as practical to bring the temperature of the bottoms passed therethrough down to below 300° F. A portion of the bottoms is purged through line 15 which branches from line 16 in order to prevent build up of tar. Another portion of the cooled and recycled bottoms is withdrawn from line 16 for use as an absorption sponge oil, i.e., to extract some of the higher boiling components of the cracked light ends in making a separation of ethylene. This sponge oil thus used and enriched is returned to the upper part of quench tower 7 through line 18. An additional cooling liquid stream may be obtained by refluxing condensate from the tower overhead through line 19 if desired.

The overhead vapors are taken from quench tower 7 at a temperature in the range of 200 to 300° F. and a pressure in the range of 1 to 3 atmospheres (14.7 to 58.8 p.s.i.a.) through line 20 into cooling condenser 21 whence condensate and gaseous products are passed into the separation tank 22. A bottom water layer settled in tank 22 is withdrawn through line 23. A portion of the hydrocarbon oil condensate withdrawn from an upper liquid oil layer in tank 22 through line 24 may be returned to tower 7 by line 19 as reflux. The remaining oil condensate withdrawn by line 24 is passed by line 25 into the splitter tower 26.

The splitter tower 26 is a fractionating zone column provided with plates or similar liquid-vapor contacting means for obtaining separation of volatile hydrocarbons in the C_5 and lighter range which are taken overhead through line 27. At the bottom of splitter tower 26 is provided a reboiler 28 for supplying heat. Residual oil is withdrawn from tower 26 through line 29. This residual oil contains principally C_6 and higher boiling liquid hydrocarbons and these liquid hydrocarbons may then be subjected to conventional refining treatments, e.g., clay treatment, or other selective polymerization treatments.

A separate condensing and receiving means can be used, but with the single condenser 21 and single tank 22 there is not only an economy in apparatus but a more

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efficient separation. Condensate from the overhead vapors of tower 7 and condensate from the overhead vapors of the splitter tower 26 are combined in tank 22.

From receiving tank 22 the uncondensed hydrocarbon vapors are drawn through line 30 to the suction side of a first stage compressor 31 and the thus compressed vapors are passed by line 32 through cooling condenser 33 into a first separation drum 34. In drum 34 some condensate of C_5 and higher hydrocarbons is collected as a bottom liquid phase to be withdrawn by line 35 so as to join with the liquid being passed by line 25 into the splitter tower 26. Uncondensed vapors are drawn from the upper part of drum 34 through line 36 by the second compressor 37 which compresses the vapors and sends them through line 38 and cooler 39 into a second separating drum 40. In drum 40 the liquid condensate collected at the bottom contains mainly liquid C_3 and C_4 hydrocarbons. These liquid hydrocarbons are withdrawn by line 41. Vapors are drawn from the upper part of drum 40 through line 42 by the third compressor 43 which compresses the vapors and sends them through line 44 and cooling condenser 45 into a third separating drum 46. To aid in the cooling, liquid withdrawn from drum 40 through line 41 is admixed with the compressed vapors in line 44. In drum 46 another liquid from vapor separation may be made so that liquid and vapor can be treated separately. Liquid from drum 46 is passed by line 47 to a desulfurizing treatment unit 48. Vapor is withdrawn from drum 46 by line 49 to a similar desulfurizing treating unit 48. This last stage of vapor from liquid separation is carried out for the sake of flexibility in treating the vapor and the liquid separately, if so desired, before the naphtha hydrocarbons in the streams are passed finally into a first absorber 50 as by line 51.

The first absorber 50 receives the lean light naphtha in a lower part and a liquid oil as solvent from line 52 in the upper part of the column so that this latter oil can be passed downwardly countercurrent to gaseous C_1 and C_2 hydrocarbons for absorbing out higher boiling components. The unabsorbed gases leave overhead from absorber 50 and are passed through line 53 to the second absorber 54, called a sponge oil absorber. This absorber receives at its upper part through line 54a a lean absorption oil, e.g. a heavy oil or the bottoms fraction taken from the quench tower 7 through line 17. In the sponge oil absorber this heavy oil functions to remove hydrocarbons containing more than two carbon atoms per molecule from the gas rich in ethylene which leaves overhead from the absorber 54 through line 55. The sponge oil enriched by absorbed C_3 and higher hydrocarbons is withdrawn from the bottom of absorber tower 54 through line 56 to be returned to the quench tower 7 through line 18, as previously mentioned. In this sponge oil extraction of higher hydrocarbons from the ethylene-rich gases, some of the higher olefinic and diolefinic hydrocarbons become extracted but are then recovered since they are returned with the sponge oil to the quench tower 7.

The light naphtha fraction rich in absorbed C_3 and C_4 hydrocarbon components is withdrawn from the bottom of the first absorber tower 50 through line 57 to be passed to subsequent fractionating columns, e.g., the debutanizer 58. In debutanizer 58 the propylene-rich fraction is taken overhead through line 59 for transfer to a depropanizer. The debutanized naphtha containing mainly C_5 hydrocarbons stripped of the propylene is withdrawn from the debutanizer 58 through line 60. This lean C_5 rich hydrocarbon oil boiling mainly in the range of 80° F. to 200° F. can be divided to send a portion through line 61 back to line 52 to enter the upper part of the first absorber. The remaining divided portion of the lean naphtha oil can be sent through line 62 to another unit for treatment or separation of compounds as desired.

The arrangement of apparatus and steps described is particularly useful for obtaining quick and sharp sep-

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aration of a C_2 fraction rich in ethylene, and also C_3 and C_4 fractions rich in propylene and butadiene with minimum exposure to high temperatures so as to prevent excessive polymerization with its attendant difficulties and lowering of yield.

The compressors used in stages with intercoolers build up the pressure without extensive increase in temperature. A low boiling naphtha is used as solvent in the absorber 50. This solvent containing mainly C_5 hydrocarbons is made to flow down through the first stage absorber at a rate of about 0.7 to 1.0 mole per mole of hydrocarbon fed from line 51 and under conditions such that the C_2 rich overhead is at a temperature of 60° to 75° F. and temperatures are no higher than about 320° F. down to the bottom of absorber tower 50. In the second absorber 54 temperatures of 50 to 120° F. and pressures essentially the same as absorber 50 are used.

Examples of preferred conditions and advantages with regard to the operation of the splitter tower are given as follows.

The splitter tower 26 is preferably operated as a self-refluxing type rather than as a pump back refluxing type fractionating column. In the self-refluxing tower, which is shown in the drawing, a partial condensation of the overhead vapors is carried out, the resulting condensate becomes admixed with fresh feed to the tower, and the feed to the tower is supplied to a top plate of the tower. Here the pressure is close to 2 atmospheres and the temperature is close to 180° F. At the bottom of the splitter tower the temperature is below 320° F. and the pressure is a little above 2 atmospheres. The splitter tower bottoms contain C_6 and higher boiling hydrocarbons and may be made substantially free of C_5 and lighter material.

An important function of the splitter tower 26 is to separate as much as possible of the C_6 and higher hydrocarbons from the gaseous stream which is passed to the compression stages and then to the absorber-deethanizer in order to avoid excessive temperatures in the absorber and in the debutanizer. When the bottoms temperatures in the absorber and debutanizer exceed 320° F. in bringing the bottoms to the bubble point, excessive polymerization takes place in these towers. With an increase of hydrocarbons higher boiling than C_5 hydrocarbons, the bubble point at the bottom of these towers tends to increase above 320° F. Furthermore, by satisfactory removal of the C_6 and higher hydrocarbons in the bottoms of the splitter tower, the circulation of the lean absorbent oil used in the absorber is decreased in total flow quantity. At the same time this lean oil becomes more concentrated in C_5 components.

Since the splitter tower operates at a low pressure, it is able to fractionate without excessive temperatures, and similarly at a bubble point no higher than 320° F. in the bottoms. The arrangement of the separator tower so that its vapors go to the first compressor permits the operation of the splitter tower at the desired low pressures below 5 atmospheres, and preferably about 3 atmospheres or less.

The uncondensed vapors from the splitter tower and from the quenching zone overhead, separation zone are suitable for compression. Several compression stages are used in order to avoid exceeding a temperature of 250° F. in bringing the vapors up to a pressure of 200 p.s.i.g. or between 13 and 16 atmospheres, which pressure is needed in the subsequent absorber-deethanizer tower 50.

The invention described is claimed as follows:

1. In a process for recovering C_2 to C_5 hydrocarbon fractions rich in alkenes and dienes from a gaseous stream including steam, C_2 to C_5 hydrocarbons and higher boiling naphtha hydrocarbons separated overhead from higher boiling steam-cracked naphtha products in a quenching zone, the improvement which comprises passing said gaseous stream to condensing and separation zones; condensing water with C_4 and higher boiling hydrocarbons from said gaseous stream, separating condensed hydrocarbons from the water and from uncondensed gaseous

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hydrocarbons in the separation zone, passing these uncondensed gaseous hydrocarbons to a vapor compression zone, passing thus separated condensed hydrocarbons into a fractionation zone, and passing at least a substantial part of the vapors rich in C_5 and lighter hydrocarbons from said fractionation zone to join the gaseous stream from the quenching zone prior to condensation thereof, to obtain cooling of said gaseous stream and an increased amount of condensed hydrocarbons in said separation zone.

2. The process of claim 1 wherein said condensed hydrocarbons separated from water in said separation zone being passed into a top part of said fractionation zone for quick stripping of light components.

3. The process of claim 1 wherein said condensed liquid hydrocarbons separated from water in said separation zone being passed to a plate near the top of said fractionation zone so as to obtain quick stripping of light components, said fractionation zone being of the type in which no part of the overhead vapors from the zone are externally condensed, separated from vapors and recycled as a reflux stream to the top of the distillation zone.

4. The process of claim 1 in which the entire overhead vapor stream from the fractionation zone is passed back to join the gaseous stream from the quenching zone.

5. In the process of claim 1, gaseous hydrocarbons drawn from said separation zone into the compression

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zone are compressed and cooled to obtain an additional condensate of hydrocarbons higher boiling than C_5 hydrocarbons, and said condensate is passed into said fractionating zone.

6. In the process of claim 1, said gaseous stream withdrawn from said separation zone to the vapor compression zone is compressed and then cooled to form a compressed gaseous stream richer in ethene, after which said ethene-rich gaseous stream is contacted with a condensate from the steam-cracked naphtha hydrocarbons rich in C_5 dienes and other hydrocarbons boiling principally in the range of 80° to 200° F. to absorb C_3 and higher boiling hydrocarbons from the ethene-rich gaseous stream, subsequently said ethene-rich gaseous stream is contacted with a cooled portion of the higher boiling steam-cracked naphtha product withdrawn as a liquid residual product from said quenching zone to extract from the ethene-rich vapor stream higher boiling components.

7. The process as in claim 6, wherein said cooled portion of the higher boiling steam-cracked naphtha products containing components extracted from said ethene-rich vapor stream is returned to an upper part of said quenching zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,745,889	Johnston et al. -----	May 15, 1956
2,855,433	Cobb -----	Oct. 7, 1958