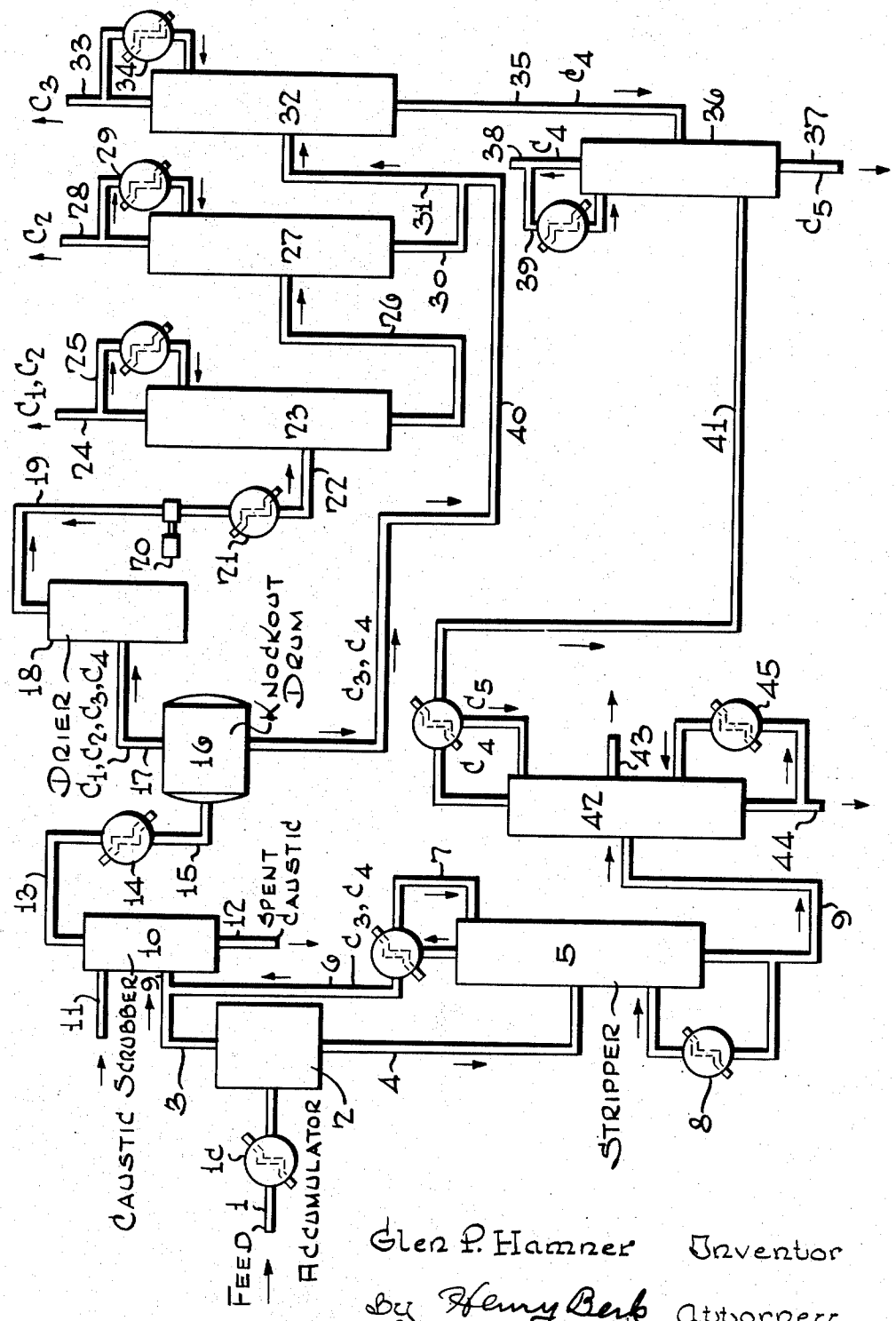
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PROCESS FOR RECOVERING SEPARATED OLEFINS AND DIOLEFINS

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PROCESS FOR RECOVERING SEPARATED OLEFINS AND DIOLEFINS

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The present invention relates to the separation of C_2 to C_5 olefins and diolefins from a complex hydrocarbon stream containing these components.

A large variety of reactive olefinic hydrocarbons are formed when hydrocarbons boiling in the naphtha through gas oil range are subjected to high temperature vapor phase cracking, preferably in the presence of steam. The valuable C_2–C_5 olefinic cracked products include ethylene, propylene, butylenes, butadiene, isoprene, cyclopentadiene, and piperylene.

Cracking processes for obtaining the olefinic cracked products are known and there are processes for segregating some of these products hitherto developed mainly for separating the C_1 to C_4 olefins, as shown in U. S. Patent 2,348,659 of B. I. Smith et al.

The newer developments with which the present invention is concerned have to do with the additional recovery of the C_5 and C_6 diolefins which have a tendency to undergo more or less dimerization, codimerization, and polymerization at moderately elevated temperatures, such as met in recovery systems.

It has been found that certain steps deviating from the normal procedure of recovering only C_1 to C_4 olefins have to be taken for efficient separation of more of the C_5 diolefins. One of these steps deals with selection of a portion of a water-wet feed stream for a dehydrating treatment which is important in the recovery of the low molecular weight hydrocarbons, e. g. ethylene and propylene. In conjunction with a high recovery of the ethylene and propylene components, steps are provided for separating a maximum amount of these components from the higher boiling materials with the smallest loss of the diolefins by polymerization.

Preferred steps will be described with reference to the flow diagram in the drawing.

A vapor-phase cracked hydrocarbon stream containing largely olefins and diolefins in the C_2 to C_5 range from line **1** is cooled in cooler 1C and received in the feed accumulator **2**. In the accumulator **2** the conditions are maintained for separating substantially all C_1 and C_2 hydrocarbons in the gaseous phase, but under these conditions an appreciable amount of C_3 and C_4 hydrocarbons are withdrawn in the gaseous stream by line **3**. Suitable temperatures and pressures in the separating zone or accumulator **2** are: 25° to 30° C. and 170 p. s. i. g.

The residual liquid continuously withdrawn from the accumulator **2** by line **4** essentially contains substantial amounts of C_3 and C_4 hydrocarbons with the higher hydrocarbons. This residual stream is passed by line **4** into a mildly heated stripping zone **5** wherein conditions are maintained for stripping out substantially all C_3 hydrocarbons. The C_3 hydrocarbons with an appreciable amount of C_4 hydrocarbons unavoidably stripped therewith are passed from the upper part of the stripping zone **5** through line **6** and can be joined with the initial gaseous stream removed by line **3** from the accumulator **2**. Liquid condensate from line **6** is returned as reflux to zone **5** through line **7**. A pressure of about 170 to 180 p. s. i. g. is maintained in the stripping zone **5** with a temperature of 60° to 70° C. at the top and temperatures of 130° to 150° C. at the bottom for effecting substantially complete removal of C_3 hydrocarbons. A reboiling means **8** may be provided at the bottom of the stripping column **5**. Thus, satisfactory removal of the lower hydrocarbons including the C_3 hydrocarbons is effected in zone **5** without excessive temperature effects on the remaining higher boiling reactive diolefins.

The residual C_4 and higher hydrocarbons are withdrawn from the bottom of zone **5** by line **9** to be processed as will be further described.

The gas and vapor streams in line **3** and **6** are advantageously combined to be processed in a dehydration unit. As these vapor streams generally contain substantial amounts of sulfur as well as water, it is found desirable to subject these streams to a chemical treatment, e. g., scrubbing with aqueous caustic solution. For this purpose the combined streams from lines **3** and **6** are passed into the caustic scrubber **10**. The caustic treating solution is supplied to the top of the scrubber **10** by line **11** and the spent caustic solution, containing the removed sulfur impurities, is withdrawn from the scrubber by line **12**. In the scrubber, temperatures of about 35° to 50° C. may be maintained and a pressure of about 180 to 215 p. s. i. g. in order to keep the hydrocarbons in the vapor phase. The desulfurized hydrocarbon vapors withdrawn from the top of the scrubber **10** by line **13** are passed through a cooler **14** to lower their temperature to about 10 to 20° C. Such cooling can be economically carried out by heat exchange with water and ammonia refrigeration. The cool vapors are passed from the cooler through line **15** into a knock-out drum **16** maintained at 10°–15° C. and 150–160 p. s. i. g.

The knock-out drum **16** serves an important function of separating condensate formed in the cooler **14** from remaining gaseous hydrocarbons. With the cooler **14** and knock-out drum **16** or similar means, the hydrocarbons remaining in the gas phase can be kept practically free of C_5 and higher hydrocarbons. It has been found desirable to subject the C_1 and C_2 hydrocarbons with the smallest amount of C_4 and C_5 hydrocarbons present to dehydration required in recovering ethylene. The gaseous stream containing the ethylene with C_3 hydrocarbons, a small amount of C_4 hydrocarbons and a slight amount of C_5 hydrocarbons, is withdrawn from drum **16** by line **17** to be passed to the dehydrator **18**.

A practical dehydration uses a material such as alumina or similar desiccating agent for adsorbing or absorbing water from the gas. The moisture-free gas is passed by line **19** into a compressor **20** and cooling means **21** for partial liquefaction, then is fed from line **22** into the fractionating tower **23**.

Fractionating tower **23** is operated under pressures of about 550 to 570 p. s. i. g. with a top temperature of about 0 to −25° C. and a bottoms temperature of about 50° to 70° C. to vaporize and expel methane with some ethylene. The thus dilute ethylene is withdrawn overhead through line **24**. Refluxing means **25** is provided at the top. The bottoms liquid of mainly ethylene and propylene is withdrawn by line **26** to the next tower **27**.

Tower **27** is operated to distill a concentrated ethylene fraction. It is operated under pressures of about 410 to 460 p. s. i. g. with a top temperature of about 0 to −5° C. and a bottom temperature of about 80° to 120° C. The concentrated ethylene distillate is withdrawn overhead through line **28**. Refluxing means **29** is provided at the top. Bottoms product of concentrated propylene is withdrawn from the bottom by line **30**.

It is to be noted that in separating the lowest boiling hydrocarbons, e. g. methane, ethane, and ethylene, temperatures below the freezing point of water are required in the upper part of the separating columns, with gives the reason for having the hydrocarbons substantially free of water. Liquefied proplyene may be used as a refrigerant for cooling the upper parts of the columns.

The propylene concentrate withdrawn as bottoms from tower **27** is passed by line **31** into the propylene separator tower **32**.

Tower **32** is operated under a pressure of about 280 to 300 p. s. i. g. with a top temperature of about 40° to 55° C. which can be maintained with water cooling. The bottoms temperature in column **32** is about 110° C. to 125° C. The propylene distillate is taken overhead through line **33**. Refluxing means **34** is provided at the top. The bottoms or residual product of column **32** contains principally C_4 hydrocarbons, butenes and butadiene, and some low-boiling C_5 olefins and diolefins. This bottoms product is passed by line **35** into tower **36** oper-

ated under conditions for separating C_4 hydrocarbons as the overhead product.

Column **36** is operated under a pressure of 80 to 90 p. s. i. g. with a top temperature of about 55° to 60° C. and a bottom temperature of about 110° to 115° C. Under these conditions the bottoms are left substantially free of C_4 hydrocarbons and will comprise mainly C_5 olefins and diolefins, which is a desired composition for further processing to separate cyclopentadiene, isoprene, and piperylene. The cyclopentadiene may be recovered by soaking the C_5 concentrate at temperatures of the order of 80° to 115° C. (180° to 240° F.) which is suitable for selective dimerization of the cyclopentadiene in periods ranging from about 4 to 20 hours. Column **36** is provided with overhead take-off line **38** and refluxing means **39**.

The present invention is concerned with recovering a satisfactory C_5 concentrate mixture of olefins and diolefins but not with the further processing of this concentrate since such processing has been described in the art.

Included in the C_5 concentrate bottoms from tower **36** will be the heavy ends of the condensate fraction withdrawn from the knock-out drum **16** by line **40**. This condensate from the knock-out drum is purposely made to bypass the dehydrator and the highly refrigerated columns **23** and **27**. This condensate from the knock-out drum will contain some C_3 and C_5 hydrocarbons, but mainly C_4 components. A large number of benefits are obtained by sending this material directly to the propylene recovery tower **32**. Another stream which may contain appreciable amounts of C_4 and C_5 hydrocabons is the overhead vapor stream removed by line **41** from the top or upper part of column **42**. Column **42** receives the bottoms from the stripping tower **5**. Column **42** may be operated to maintain relatively moderate temperatures in the upper part, e. g. 38° to 70° C. for removing C_4 and C_5 components under a pressure of 100 p. s. i. g. The bottom temperature of column **42** is about 150° to 160° C. Another side stream containing higher C_5 components mixed with C_6 components may be withdrawn from column **42** by line **43**. A bottoms fraction of C_6+ components is withdrawn by line **44**. Some of the bottoms is recycled through reboiler **45**.

The C_4 and C_5 hydrocarbons removed overhead from column **42** may be passed into column **36** for separating the C_4 component and collecting the additional C_5 components in the bottoms thereof.

EXAMPLE

The following example illustrates typical conditions and results of the process:

Gas streams containing C_1 to C_6+ olefins and diolefins were produced by heating petroleum distillate oils boiling in the range of 100° to 480° C. in vapor phase mixed with 60 to 80 mole per cent steam to temperatures of 680° to 700° C. under pressures of 13 to 20 p. s. i. g. Cracking products leaving the cracking zone were quenched to about 230° C. and fractionated to separate the gas streams. The gas streams were compressed from about 4 p. s. i. g. to 580 p. s. i. g. and cooled to about 40° C. to obtain the charge to the accumulator **2**. This accumulator acted as a gas-liquid separating zone under conditions that substantially all the ethylene remained in the gas phase.

Analytical studies showed that when the ethylene-containing water-wet gas being passed through the caustic scrubber and then into the dehydrator contained considerable quantities of C_4–C_5 hydrocarbons including diolefins, such feeds carried excessive amounts of moisture into the dehydrator, thus shortening the life of the desiccant. The diolefins in the C_4 and C_5 range form polymers, which coat the surface area of the desiccant. This reduces the efficiency and capacity of the drier section. The problem arose whether it was feasible to condense out part of the C_4 hydrocarbons and higher hydrocarbon components from the ethylene-bearing gas stream and to divert this condensate away from the ethylene separation tower without upsetting the recovery of ethylene.

The partial condensate from the gas stream containing part of the C_4 with the C_5 and higher components was bypassed from knock-out drum **16** around the drier and ethylene removal sections and sent directly

to the propylene seperation column **32** as explained with reference to the drawing. It was determined that this reduction of the material sent through the dehydrator section to the ethylene separation zone gave a better dehydration operation and improved ethylene fraction. In addition, an improved recovery of C_5 diolefins was obtained.

Table

STREAM ANALYSIS

Stream Component, Wt. Percent	2nd Stage Condensate (Line 4)	Condensate Prior to Dehydrators (Line 40)	Feed to Dehydrators (Line 17)
H_2		0.1	0.5
C_1	0.9	1.5	14.9
C_2H_4	0.4	0.6	25.8
C_2H_6	8.4	16.8	11.3
C_3H_6	0.8	1.6	27.0
C_3H_8	7.4	11.1	2.7
C_4H_8	18.4	27.7	4.1
C_4H_8	0.7	1.0	10.7
C_4H_{10}	2.3	3.2	0.4
Cyclopentadiene	4.8	6.5	0.9
Isoprene	4.5	6.1	
Piperylene	17.1	23.7	1.7
C_5H_{10}	0.3	0.1	trace
C_5H_{12}	34.0	trace	trace
C_6			
	100.0	100.0	100.0

The elimination of some of the intermediate treatment on the C_4 and C_5 diolefins accounts for increased recovery of these diolefins, because by exposing the reactive C_4 and C_5 diolefins to temperatures above 80° C. and the vapor phase contact with a desiccant, particularly under elevated temperatures and pressures, these substances tended to undergo undesired interpolymerization. By the interpolymerization these diolefins become converted to substances which are high boiling and not useful for recovery of the desired C_4 diolefins or the C_5 diolefins and their dimers.

What is claimed is:

1. In a process of separating C_2 to C_5 olefins and diolefins from a water-wet gaseous mixture thereof, the improvement which comprises cooling said gaseous mixture to condense therefrom C_5 components with part of the C_3 and C_4 components as an initial partial condensate to leave a remaining gas stream containing C_2 with uncondensed C_3 and C_4 components, cooling said remaining gas stream to further condense out a substantial amount of the C_3 and C_4 components as an intermediate partial condensate, then drying the remaining gas stream containing C_2 to C_4 components relatively enriched in C_2 components to remove water vapor therefrom, fractionating from the resulting dry C_2 to C_4 components an ethylene distillate to leave a liquid residue containing C_3 and C_4 components, passing said liquid residue into a propylene distillation zone, directly passing said intermediate partial condensate of C_3 and C_4 components into said propylene distillation zone, distilling overhead C_3 components in said propylene distillation zone and withdrawing C_4 components as a bottoms product from said propylene distillation zone.

2. In a process of separating olefins and diolefins from a water-wet gaseous mixture containing C_1 through C_5 and higher olefinic hydrocarbons, the improvement which comprises condensing from said mixture part of the C_4 hydrocarbons with the C_5 and higher hydrocarbons, desulfurizing the remaining gaseous mixture containing C_1 to C_4 hydrocarbons in a desulfurizing zone, cooling the desulfurized gaseous mixture to condense therefrom a condensate containing part of the C_3 hydrocarbons with most of the C_4 hydrocarbons, contacting the remaining desulfurized gaseous hydrocarbon mixture through a dehydrating zone, separating methane and ethylene fractions from the dried and desulfurized hydrocarbon mixture, then forming a combined stream of the residual C_3 and C_4 hydrocarbons which passed through the dehydrating zone with the condensate containing the C_3 hydrocarbons and C_4 hydrocarbons removed from the desulfurized gaseous mixture prior to the drying thereof, and separating the C_3 and C_4 hydrocarbons from said combined stream.

3. In a process of separating olefins and diolefins from a water-wet gaseous mixture of C_1 through C_5 hydrocarbons, the steps which comprise condensing from said mixture the C_5 components with part of the C_3 and C_4 components, further condensing C_3 and C_4 components

from the water-wet gaseous mixture to leave the remaining gaseous mixture substantially free of C_5 components and with a decreased content of C_4 diolefins, drying the gaseous mixture which is free of C_5 components and of decreased C_4 diolefin content, separating C_3 and C_4 components as liquids from the thus dried gaseous mixture, combining the C_3 and C_4 components separated as liquids with the C_3 and C_4 components condensed as liquid from the water-wet gaseous mixture, and separating the C_3 components from said combined liquids by fractional distillation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,324,955	Rupp et al.	July 20, 1943
2,368,497	Shipley et al.	Jan. 30, 1945
2,514,294	Rupp	July 4, 1950