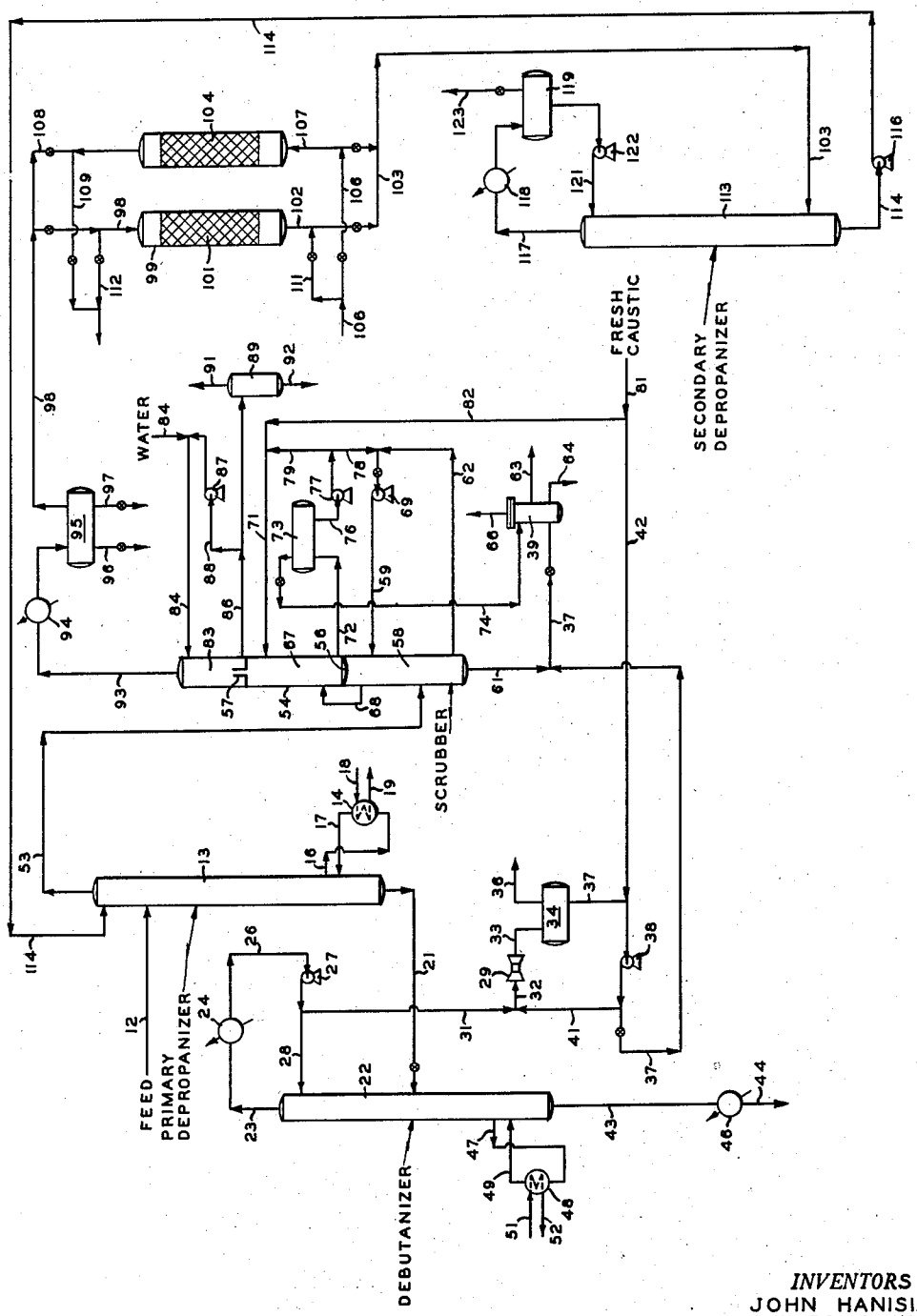
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PROCESS FOR THE SEPARATE RECOVERY OF C_3 AND C_4 HYDROCARBONS

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PROCESS FOR THE SEPARATE RECOVERY OF C_3 AND C_4 HYDROCARBONS

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This invention relates to an improved process for the separation of hydrocarbons. It also relates to an improved process for the removal of sulfur compounds from hydrocarbon fractions.

This invention is useful, generally, in situations where it is desired to recover separately C_3 and C_4 hydrocarbons from mixtures containing the same and sulfur compounds. It is also useful where hydrocarbon fractions containing C_4 and heavier as well as C_3 and lighter hydrocarbons and sulfur compounds are to be fractionated into fractions containing only C_4 and heavier hydrocarbons and fractions containing only C_3 and lighter hydrocarbons. Our invention provides an improved method for accomplishing this fractionation between C_3 and C_4 hydrocarbons and, at the same time, obtaining some or all of the resulting hydrocarbon fractions substantially free of sulfur or sulfur compounds.

It is frequently desired to separate mixtures of hydrocarbons into two or more fractions and, in the same process, remove sulfur compounds from some or all of the hydrocarbon fractions. In the production of ethylene by the pyrolytic conversion of hydrocarbons, for instance, a product is usually obtained containing ethylene and other lighter and heavier hydrocarbons. This ethylene-containing product frequently also contains impurities in the form of sulfur compounds, such as hydrogen sulfide or mercaptans, which should be removed prior to the recovery of ethylene from the product. Previously, the sulfur compounds have customarily been removed by scrubbing the entire product with an aqueous solution of a suitable sulfur removing agent, such as NaOH, drying the product and then processing the product for the separation of the various hydrocarbon fractions. One disadvantage of this method is that it is necessary to subject the entire product to the sulfur removal and drying steps. Another disadvantage of this method is that the heavier and more unsaturated hydrocarbons are more readily absorbed in the desiccants commonly used for drying than are the lighter and more saturated hydrocarbons. This results in a reduction of drying efficiency and shortening of the useful life of the desiccant as well as causing undue polymerization.

It is an object of our invention to provide an improved process for the fractionation of hydrocarbon fractions and the removal of sulfur compounds therefrom.

It is another object of our invention to provide an improved process for the production of ethylene in which an ethylene-containing product is fractionated into a fraction containing C_3 and lighter hydrocarbons, including ethylene, and a fraction containing C_4 and heavier hydrocarbons and the fraction containing C_3 and lighter hydrocarbons is obtained substantially free of sulfur compounds.

It is another object of our invention to provide an improved method for recovering a fraction containing ethylene and C_3 hydrocarbons from a hydrocarbon conversion product containing the same, C_4 and heavier hydrocarbons and sulfur compounds.

A further object of our invention is to provide an improved process for the production of ethylene.

According to one aspect of our invention, a hydrocarbon fraction comprising C_3 hydrocarbons is separated from a mixture containing the same, C_4 hydrocarbons and a sulfur compound by first fractionating said mixture in a first distillation zone. An overhead fraction comprising C_3 and C_4 hydrocarbons and sulfur compound is then withdrawn from the first distillation zone, treated for the removal of sulfur compound and passed to a second distillation zone. In the second distillation zone, a bottoms fraction comprising C_3 and C_4 hydrocarbons and an overhead fraction comprising C_3 hydrocarbons are separated. All or part of the bottoms fraction from the second distillation zone is passed to the first distillation zone where it serves as reflux. Overhead fraction from the second distillation zone is withdrawn from the process. A bottoms fraction comprising C_4 hydrocarbons is withdrawn from the first distillation zone.

According to another aspect of our invention, the feed fraction comprising C_3 and C_4 hydrocarbons may also include ethylene and/or other lighter or heavier hydrocarbons. Under such circumstances, the ethylene and other light hydrocarbons, if any are present, would pass from the first distillation zone in the overhead fraction and would be withdrawn with the overhead from the second distillation zone. Any hydrocarbons heavier than C_4 would be withdrawn with the bottoms fraction from the first distillation zone. Some C_4 hydrocarbons will usually be carried from the first distillation zone with the overhead from the first distillation zone. Carry-over of heavier than C_4 hydrocarbons will be negligible.

Our invention is particularly well suited for use in connection with the production of ethylene, as by the pyrolytic conversion of naphtha or other hydrocarbons. Such a process yields a product which usually contains, in addition to ethylene, C_3 and C_4 hydrocarbons, as well as other lighter and heavier hydrocarbons and such product is usually contaminated with sulfur compounds such as hydrogen sulfide or mercaptans. Sulfur or sulfur compounds are frequently present in such a product in concentrations of about 0.1 to about 1.0 mol percent. Our invention may be practiced in connection with the recovery of ethylene from such a product and the use of our invention minimizes or eliminates certain of the difficulties previously encountered in such processes.

When our invention is used in connection with the recovery of ethylene, the entire product from the pyrolysis step is not treated for removal of sulfur compounds inasmuch as almost all of the components heavier than C_4 hydrocarbons have been removed prior to the sulfur removal step. The fraction containing C_4 and heavier hydrocarbons, if any are present, may of course, be further treated for the removal or separation of desired components. This fraction may, for instance, be fractionated to produce a predominantly butane fraction and a debutanized gasoline fraction with the butane fraction being treated for sulfur removal if desired. Since the debutanized gasoline fraction does not contain appreciable quantities of sulfur compounds, there is no necessity for treating this fraction for sulfur removal in most instances.

Removal of sulfur compounds from the overhead fraction of the first distillation zone may be accomplished by any suitable means such as contacting with ethanolamines, tripotassium phosphate or bauxite. In situations where the sulfur content is sufficiently low, sulfur removal is normally accomplished by contacting the overhead fraction with a caustic wash such as sodium hydroxide or potassium hydroxide. This contacting is usually accomplished in a scrubbing tower and the caustic is usually employed in an aqueous solution containing about 5 to about 15, weight

percent caustic, although other solutions may be used. The caustic wash is usually followed by a water wash in order to insure removal of all caustic from the hydrocarbon stream. The overhead fraction from the first distillation zone which is treated for the removal of sulfur components frequently should be dried prior to further processing in the second distillation zone in order to prevent icing in the second distillation zone at the operating conditions normally used. To accomplish this, it is usually necessary to dry this fraction sufficiently so that its dew point is below the temperature at which the overhead fraction is withdrawn from the second distillation zone.

The removal of heavier than C_4 hydrocarbons from the first distillation zone prior to the sulfur removal step means that such product need not be treated for sulfur removal and then dried. This results in a corresponding reduction in equipment size and operating costs for the sulfur removal and drying stages of the process. In addition, the removal of the heavier hydrocarbons prior to the drying step increases the efficiency and useful life of the desiccants normally used for drying since such heavier hydrocarbons are very readily absorbed by the desiccants. Also, the early removal of heavier than C_4 hydrocarbons minimizes the formation of polymers of these hydrocarbons in both the sulfur removal and drying steps.

Any suitable means may be used to dry the overhead fraction from the first distillation zone following the caustic and water washes. For example, the wet fraction may be dried by contacting it with a desiccant such as, calcium chloride, silica gel or alumina. When the desiccant has absorbed sufficient water so that its efficiency is effected, it can usually be regenerated by passing hot, dry gas through it to remove the absorbed water or the water can be removed by other suitable means. Regeneration can be accomplished without interfering with continuous processes if two or more beds of desiccant are provided so that one can be on stream while one or more are being regenerated. Alternatively, the deiccant itself can be passed in a continuous cycle of absorption and regeneration, as by the use of a moving bed system.

The separating and treating steps of our invention can be practiced under any suitable operating conditions but pressures of about 50 to about 500 p.s.i.g., more usually about 100 to about 200 p.s.i.g., are preferred. The temperature at which the overhead fraction is withdrawn from the first distillation zone is preferably at least as low as the temperature at which it enters the second distillation zone so that condensation of liquid hydrocarbons may be avoided when the fraction is recooled to the temperature at which it enters the second distillation zone following the caustic wash but should be sufficiently high so that formation of hydrate is avoided. At the preferred operating pressures, the temperature of the overhead fraction withdrawn from the first distillation zone will usually be between about 35 and about 100° F. preferably about 50 to about 70° F. but conditions outside these ranges may be used without departing from the scope of our invention.

The temperature of the fraction comprising C_3 and lighter hydrocarbons which is recovered by the use of our invention is preferably about −35 to about +10° F. if preferred pressures are used but other temperatures may be maintained without departing from the scope of our invention. Final separation of this fraction at these temperatures assures the inclusion of a minimum of C_4 hydrocarbons. Usually the amount of C_4 hydrocarbons in the C_3 and lighter hydrocarbon fraction removed from the process is less than about 0.5 mol percent, more preferably less than about 0.1 mol percent.

The bottom fraction from the first distillation zone which contains the C_4 and heavier hydrocarbons is preferably withdrawn at a temperature of about 150 to about 300° F. under the preferred pressure conditions, in order to limit the amount of C_3 hydrocarbons withdrawn with this fraction. Other temperatures may be used, however, without departing from the scope of our invention. The amount of C_3 hydrocarbons withdrawn with this fraction under the above conditions of temperature and pressure is usually less than about 5 mol percent and is usually less than about 2 mol percent under the preferred conditions.

EXAMPLE

For a better understanding of our invention, reference should be had to the accompanying drawing which is a diagrammatic illustration in elevation of a suitable arrangement of apparatus for carrying out a preferred embodiment of our invention showing specific working conditions.

In the drawing 72,192 lb./hr. of hydrocarbon feed enters through a conduit **12** at a temperature of 106° F. and a pressure of 168 p.s.i.g. This hydrocarbon feed is the product of a process for pyrolytic conversion of naphtha to produce ethylene and has the composition shown in Table I below:

Table I

FEED COMPOSITION

	Mol percent
H_2	11.7
C_1	24.7
C_2	35.5
C_3	11.7
C_4	5.4
C_5	0.5
C_6+heavier	10.5
	100.0

The hydrocarbon feed, which is at such a temperature and pressure that it is mixed liquid and vapor, passes through conduit **12** to a primary depropanizer **13**. The top of primary depropanizer **13** is maintained at a temperature of 58° F. and a pressure of 166 p.s.i.g., while the bottom is maintained at a temperature of 255° F. and a pressure of 168 p.s.i.g. Bottoms of primary depropanizer **13** are heated by a conventional reboiler **14** which heats a bottom fraction withdrawn through a conduit **16** and returned through a conduit **17**. Reboiler **14** is supplied with heat by steam which enters through a conduit **18** and leaves through a conduit **19**. A bottoms fraction comprising C_4 and heavier hydrocarbons and containing only about 1.0 percent C_3 hydrocarbons and having the composition shown in Table II is withdrawn from primary depropanizer **13** at the rate of 29,898 lb./hr. through a conduit **21** and passed to a debutanizer **22**.

Table II

COMPOSITION OF BOTTOMS FROM PRIMARY DEPROPANIZER 13

	Mol percent
C_3	1.0
C_4	32.8
C_5	2.8
C_6+heavier	63.4
	100.0

The top of debutanizer **22** is operated at a temperature of 101° F. and a pressure of 41 p.s.i.g. while the bottom is maintained at a temperature of 315° F. and a pressure of 45 p.s.i.g. An overhead fraction having the composition shown in Table III is withdrawn from debutanizer **22** through a conduit **23** at the rate of 21,584 lb./hr. and condensed by a reflux condenser **24**.

Table III

COMPOSITION OF OVERHEAD FROM DEBUTANIZER 22

Component:	Mol percent
C_3	3.0
C_4	95.0
C_5	2.0
	100.0

15,020 lb./hr. of the condensate is returned to debutanizer 22 as reflux via a conduit 26, a pump 27 and a conduit 28. The remainder of the condensate is passed from reflux condenser 24 to a mixer 29 via conduit 26, pump 27, conduit 28, a conduit 31 and a conduit 32. In mixer 29 the condensate is mixed with caustic solution obtained as explained below. The caustic solution serves to remove any sulfur compounds, such as hydrogen sulfide or mercaptans, from the condensate. From mixer 29, the mixture of condensate and caustic passes through a conduit 33 to a settling drum 34 which is maintained at a temperature of 100° F. and a pressure of 95 p.s.i.g. From settling drum 34, the hydrocarbon condensate is withdrawn as butane product through a conduit 36 at the rate of 6,564 lb./hr. while the caustic solution is withdrawn through conduit 37 to a pump 38. From pump 38 a portion of the spent caustic continues through conduit 37 to a spent caustic separator 39 to be disposed of as explained below. The remainder of the spent caustic from pump 38 passes through conduits 37, 41 and 32 to mixer 29. Fresh make-up caustic solution is added to conduit 37 through a conduit 42.

A bottom fraction comprising debutanized gasoline is withdrawn from debutanizer 22 through conduit 43 at the rate of 23,334 lb./hr. and recovered as debutanized gasoline product through a conduit 44 after being cooled to a temperature of 100° F. in a cooler 46. A bottom fraction is withdrawn from debutanizer 22 through a conduit 47, heated in a reboiler 48 and returned to debutanizer 22 through a conduit 49. Heat for reboiler 48 is obtained from steam which enters through a conduit 51 and leaves through a conduit 52.

An overhead fraction having the composition shown in Table IV is withdrawn from primary depropanizer 13 through a conduit 53 at the rate of 70,608 lb./hr. and passed to a scrubber 54.

Table IV

COMPOSITION OF OVERHEAD FROM PRIMARY DEPROPANIZER

	Mol percent
H_2	9.6
C_1	22.8
C_2	35.1
C_3	19.0
C_4	13.3
H_2S	0.2
	100.0

In scrubber 54 the overhead from the primary depropanizer is subjected to a caustic wash for the removal of sulfur compounds. Scrubber 54 is divided by a partition 56 and a collecting tray 57 into two caustic wash stages and one water wash stage. The overhead from the primary depropanizer enters the first caustic wash stage 58 of scrubber 54 through conduit 53. Caustic solution is introduced into the first caustic wash stage through a conduit 59 at the rate of 29,200 lb./hr. Spent caustic is withdrawn from the first caustic wash stage through conduits 61 and 62. The caustic withdrawn through conduit 61 passes to spent caustic separator 39 through conduit 37. In spent caustic separator 39 the caustic is separated from any polymer material, such as di-olefin polymers, which may be present and such polymer material is withdrawn through a conduit 63. Spent caustic is withdrawn from spent caustic separator 39 through a conduit 64, while any hydrocarbon vapors present in the spent caustic separator are vented through a conduit 66.

Hydrocarbon vapors from the first caustic wash stage 58 are passed to the second caustic wash stage 67 of scrubber 54 through a conduit 68. Spent caustic in conduit 62 is recycled to first caustic wash stage 58 via conduit 59 and a pump 69.

Caustic solution is introduced into the second caustic wash stage 67 through a conduit 71. Caustic is withdrawn from the second caustic wash stage 67 through a conduit 72 and passes to a caustic circulating drum 73. From the drum 73, part of the caustic solution is passed to spent caustic separator 39 through a conduit 74, while the remainder passes from drum 73 via a conduit 76 and a pump 77 at the rate of 29,200 lb./hr. Caustic circulating drum 73 serves as a reservoir to maintain an inventory of caustic solution within the system. From conduit 76 a portion of the caustic is passed to the first caustic wash stage 58 via conduits 78 and 59 and pump 69. The remainder of the caustic solution from conduit 76 is returned to the second caustic stage 67 through conduits 79 and 71. Fresh caustic is introduced into the system through a conduit 81 at the rate of 1800 lb./hr. A portion of the fresh caustic introduced through conduit 81 passes to conduit 37 through conduit 42 as previously explained. The remainder of the fresh caustic passes to conduit 71 through a conduit 82. The fresh caustic solution used in this case is an aqueous solution of sodium hydroxide containing 10 weight percent sodium hydroxide.

From the second caustic wash stage 67 of scrubber 54, the hydrocarbon vapors pass through collecting tray 57 to a water wash stage 83. Water is introduced to the water wash stage through a conduit 84 and is used to scrub entrained caustic from the hydrocarbon vapors. Water contaminated with caustic is collected in collecting tray 57 and withdrawn through a conduit 86. 29,200 lb./hr. of the water and caustic from conduit 86 is recycled to the water wash stage by a pump 87 through conduits 88 and 84 while the remainder continues through conduit 86 to a separator drum 89. Make-up water enters through conduit 84 at the rate of 12,500 lb./hr. at a temperature of 90° F. Vapors are vented from drum 89 through conduit 91 and water and caustic are removed through conduit 92.

70,454 lb./hr. of hydrocarbon vapors are removed from scrubber 54 through a conduit 93 at a temperature of 90° F. and a pressure of 161 p.s.i.g., cooled in a cooler 94 and passed through conduit 93 to a separator drum 95. Separator drum 95 is maintained at a temperature of 58° F. and a pressure of 160 p.s.i.g. Condensed water is removed from separator drum 95 through a conduit 96 and any condensed hydrocarbons are removed from drum 95 through a conduit 97. Hydrocarbon vapors are withdrawn from drum 95 through a conduit 98 and passed to a drier 99 containing a bed of desiccant 101 which removes moisture from the hydrocarbon stream. From drier 99, the dried hydrocarbons pass through a conduit 102 to a conduit 103.

The desiccant used in drier 99 in this particular instance is alumina but any suitable desiccant may, of course, be used. Since the desiccant material is limited as to the quantity of water it can remove from the hydrocarbon stream, a second drier 104 is provided so that while one drier is being used to remove water from the hydrocarbon stream, the other drier may be regenerated by passing hot gases through it to remove moisture therefrom. Drier 104 is similar in all respects to drier 99. While the hydrocarbon stream is passing through drier 99, drier 104, which has previously been used to remove water from the hydrocarbon stream, is being regenerated by hot flue gas which enters through conduits 106 and 107 at a temperature of 650° F. In drier 104, the hot flue gas absorbs the water from the desiccant thereby drying the desiccant and leaving it ready to absorb more water from the hydrocarbon stream. Moist flue gas passes from dryer 104 through conduits 108 and 109 at a temperature of 150–650° F. depending on part of regeneration cycle. The moist flue gas from conduit 109 may then be cooled to condense absorbed moisture and the dried gas may be reheated for further use in removing water from the desiccant material in the

driers. When it becomes necessary to regenerate drier **99**, the hydrocarbon stream from conduit **98** is passed through conduit **108** to drier **104** while the hot flue gas is admitted to drier **99** through conduits **106**, **111** and **102**. During this portion of the cycle, the dried hydrocarbon stream passes from drier **104** through conduit **107** to conduit **103**, while the moist flue gas passes from drier **99** through conduits **98** and **112** to conduit **109**.

The dried hydrocarbon vapor in conduit **103** passes to a secondary depropanizer **113**. The top of secondary depropanizer **113** operates at a temperature of 7° F. and a pressure of 153 p.s.i.g. while the bottom operates at a temperature of 50° F. and a pressure of 155 p.s.i.g. A bottom fraction having the composition shown in Table V is withdrawn from secondary depropanizer **113** through a conduit **114** at the rate of 28,400 lb./hr. and is passed to the upper portion of primary depropanizer **13** by means of a pump **116** and conduit **114**.

Table V

COMPOSITION OF BOTTOM FRACTION FROM SECONDARY DEPROPANIZER 113

	Mol percent
H_2	0.1
C_1	2.1
C_2	12.7
C_3	31.5
C_4	53.6
	100.0

In this way, the bottom fraction from the secondary depropanizer is used as reflux to the primary depropanizer. An overhead fraction is withdrawn from secondary depropanizer **113** through a conduit **117** at the rate of 71,582 lb./hr. The overhead fraction from secondary depropanizer **113** is cooled and partially condensed in cooler **118** and continues through conduit **117** to separation drum **119** which is maintained at a temperature of −25° F. and a pressure of 150 p.s.i.g. 29,528 lb./hr. of liquid from separation drum **119** is withdrawn through a conduit **121** and returned as reflux to the upper portion of secondary depropanizer **113** by a pump **122**. Vapors from separation drum **119** are withdrawn through a conduit **123** at the rate of 42,054 lb./hr. and are further processed for the recovery of ethylene therefrom. Vapors withdrawn through conduit **123** have the composition shown in Table VI and contain only 0.01 mol percent C_4 hydrocarbons.

Table VI

COMPOSITION OF HYDROCARBONS VAPORS WITHDRAWN THROUGH CONDUIT 123

	Mol percent
H	12.8
C_1	29.6
C_2	42.5
C_3	15.0
C_4	0.01
	99.91

It can be seen that the use of our invention in this process results in an extremely efficient recovery of C_3 and lighter hydrocarbons for further processing for the recovery of ethylene therefrom while at the same time much of the loss due to C_3 and lighter hydrocarbons being withdrawn with the heavier product fractions is eliminated. Also, the formation of undesired polymers has been greatly reduced by removing a substantial amount of heavier than C_4 hydrocarbons prior to the caustic wash step. In addition, the prior removal of the heavier than C_4 product has eliminated the necessity of subjecting such product to the caustic wash and drying treatments.

Our invention is not, of course, limited to the preferred embodiment and specific example given above. Other aspects of our invention which are mentioned above or which will become apparent from the above disclosure, are equally within the scope of our invention.

We claim:

1. The process for the separation of a hydrocarbon fraction comprising C_3 hydrocarbons from a mixture containing the same, C_4 hydrocarbons and a sulfur compound which comprises fractionating said mixture in a first distillation zone, withdrawing an overhead fraction comprising C_3 and C_4 hydrocarbons and sulfur compound from the first distillation zone, treating said overhead fraction for the removal of sulfur compound, passing said thus-treated overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising C_3 hydrocarbons and a bottoms fraction comprising C_3 and C_4 hydrocarbons, passing bottoms fraction from the second distillation zone as reflux to the upper portion of said first distillation zone and withdrawing overhead fraction from the second distillation zone.

2. The process of claim 1 in which the sulfur compound is H_2S.

3. The process for the separation of a hydrocarbon fraction comprising C_3 and lighter hydrocarbons from a mixture containing the same, C_4 hydrocarbons and H_2S which comprises fractionating said mixture in a first distillation zone, withdrawing an overhead fraction comprising C_3 and C_4 hydrocarbons and H_2S from said first distillation zone, contacting said overhead fraction with caustic for the removal of H_2S therefrom, passing said thus-treated overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising C_3 and lighter hydrocarbons and a bottoms fraction comprising C_3 and C_4 hydrocarbons, passing bottoms fraction from said second distillation zone as reflux to the upper portion of said first distillation zone, withdrawing a bottom fraction containing C_4 hydrocarbons from said first distillation zone and withdrawing said overhead fraction comprising C_3 and lighter hydrocarbons from said second distillation zone.

4. In a process for the production of ethylene in which a hydrocarbon product is obtained containing ethylene, C_3 hydrocarbons, C_4 and heavier hydrocarbons and a sulfur compound, the improvement which comprises fractionating said product in a first distillation zone, withdrawing an overhead fraction comprising C_3 and C_4 hydrocarbons and sulfur compound from said first distillation zone, scrubbing said overhead fraction with caustic for the removal of sulfur compound therefrom, passing said thus-treated overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising C_3 and lighter hydrocarbons and a bottoms fraction comprising C_3 and C_4 hydrocarbons, passing bottoms fraction from said second distillation zone as a reflux to the upper portion of said first distillation zone, withdrawing a bottom fraction containing C_4 and heavier hydrocarbons from said first distillation zone and withdrawing overhead fraction from said second distillation zone.

5. The process of claim 4 in which the sulfur compound is H_2S and the caustic is NaOH.

6. In a process for the production of ethylene by the pyrolysis of naphtha in which a hydrocarbon product is obtained containing ethylene, C_3 hydrocarbons, C_4 and heavier hydrocarbons and H_2S, the improvement which comprises fractionating said product in a first distillation zone, withdrawing an overhead fraction comprising C_3 and C_4 hydrocarbons and H_2S from said first distillation zone, scrubbing said overhead fraction with aqueous NaOH for removal of H_2S therefrom, drying said overhead fraction, passing said thus-treated overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising C_3 and lighter hydrocarbons and a bottoms fraction comprising C_3 and C_4 hydrocarbons, passing bottoms frac-

tion from said second distillation zone as reflux to the upper portion of said first distillation zone, withdrawing a bottom fraction containing C_4 and heavier hydrocarbons from said first distillation zone and withdrawing overhead fraction from said second distillation zone.

7. In a process for the production of ethylene by the pyrolysis of naphtha in which a hydrocarbon product is obtained containing ethylene, C_3 hydrocarbons, C_4 and heavier hydrocarbons and H_2S, the improvement which comprises fractionating said product in a first distillation zone, withdrawing an overhead fraction comprising C_3 and C_4 hydrocarbons and H_2S from said first distillation zone, scrubbing said overhead fraction with aqueous NaOH for removal of H_2S therefrom, drying said overhead fraction by contact with a desiccant, passing said thus-treated overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising C_3 and lighter hydrocarbons and a bottoms fraction comprising C_3 and C_4 hydrocarbons, passing bottoms fraction from said second distillation zone as reflux to the upper portion of said first distillation zone, withdrawing a bottom fraction containing C_4 and heavier hydrocarbons from said first distillation zone and withdrawing overhead fraction from said second distillation zone.

8. In a process for the production of ethylene by the pyrolysis of naphtha in which a hydrocarbon product is obtained containing ethylene, C_3 hydrocarbons, C_4 and heavier hydrocarbons and H_2S, the improvement which comprises fractionating said product in a first distillation zone, withdrawing an overhead fraction comprising C_3 and C_4 hydrocarbons and H_2S from said first distillation zone, scrubbing said overhead fraction with aqueous NaOH for removal of H_2S therefrom, drying said overhead fraction by contacting the same with a desiccant comprising alumina, passing said thus-treated overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising C_3 and lighter hydrocarbons and a bottoms fraction comprising C_3 and C_4 hydrocarbons, passing bottoms fraction from said second distillation zone as reflux to the upper portion of said first distillation zone, withdrawing a bottom fraction containing C_4 and heavier hydrocarbons from said first distillation zone and withdrawing overhead fraction from said second distillation zone.

9. In a process for the production of ethylene by the pyrolysis of naphtha in which a hydrocarbon product containing ethylene, C_3 hydrocarbons, C_4 and heavier hydrocarbons and H_2S is obtained, the method for recovering ethylene substantially free of sulfur which comprises passing said product to a first distillation zone, withdrawing from first said distillation zone a bottoms fraction comprising C_4 and heavier hydrocarbons at a temperature between about 150 and about 300° F. and a pressure between 100 and about 200 p.s.i.g., withdrawing from said first distillation zone an overhead fraction comprising ethylene, C_3 and C_4 hydrocarbons and H_2S at a pressure between about 100 and about 200 p.s.i.g. and a temperature between about 50 and about 70° F. scrubbing said overhead fraction with an aqueous solution of sodium hydroxide to remove substantially all of the H_2S therefrom, thereafter drying said overhead fraction by contacting the same with a desiccant comprising alumina to remove any water contained therein, passing said treated and dried overhead fraction to a second distillation zone, in said second distillation zone separating an overhead fraction comprising ethylene and C_3 hydrocarbons at a temperature between about −35 and about 10° F. and a pressure between about 100 and about 200 p.s.i.g. and a bottoms fraction comprising C_3 and C_4 hydrocarbons at a temperature of about 20 to about 70° F. and a pressure of about 100 to about 200 p.s.i.g., passing bottoms fraction from said second distillation zone as reflux to the upper portion of said first distillation zone, withdrawing overhead fraction from said second distillation zone and recovering ethylene therefrom.

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