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DISTILLATION OF LIGHT HYDROCARBONS

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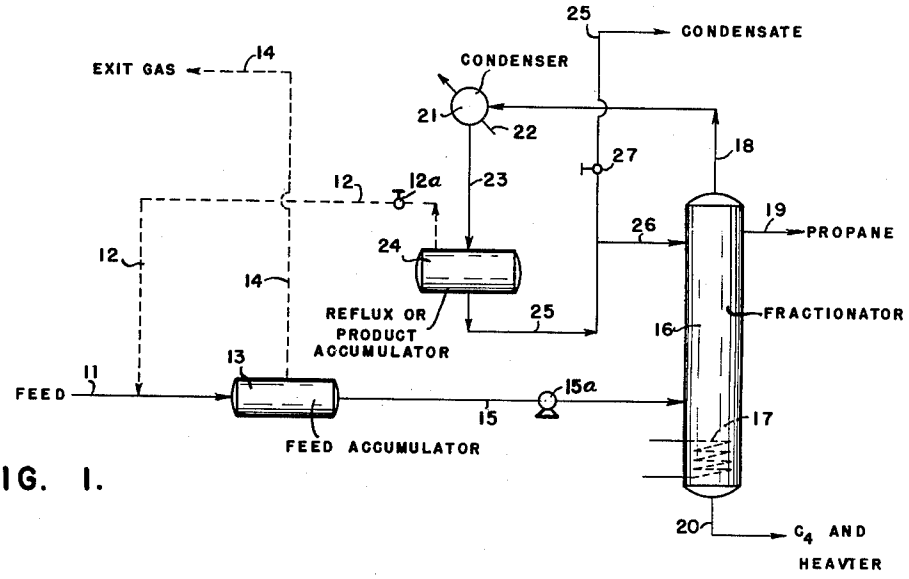


FIG. 1.

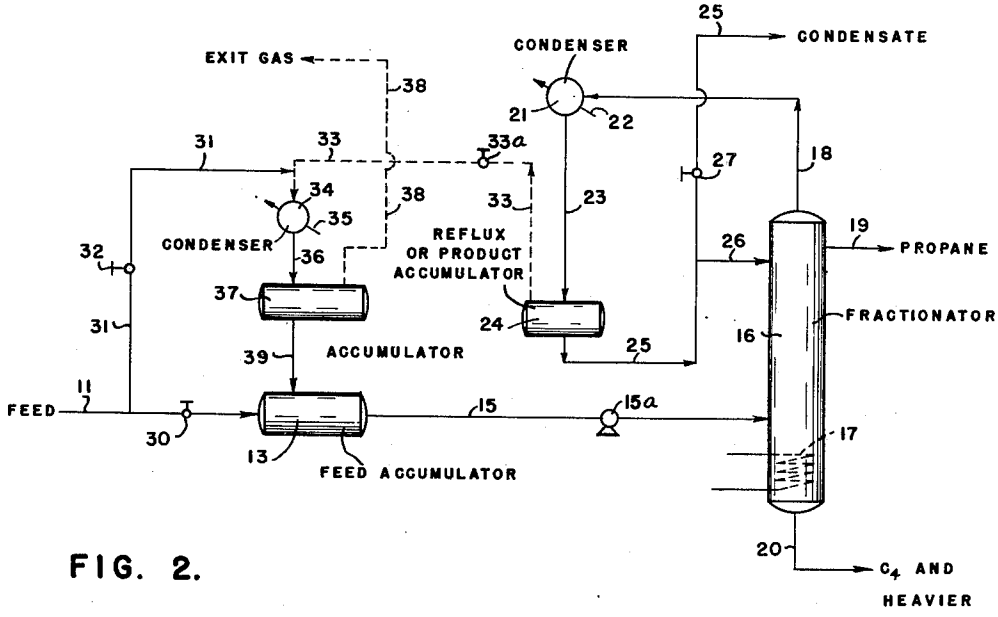


FIG. 2.

INVENTOR.
Roger Wylie,
BY
Thomas B. McBride
AGENT.

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DISTILLATION OF LIGHT HYDROCARBONS

Roger Wylie, Baytown, Tex., assignor, by mesne assignments, to Standard Oil Development Company, Elizabeth, N. J., a corporation of Delaware

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14 Claims. (Cl. 62—175.5)

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The present invention is directed to a method for distilling normally gaseous hydrocarbons. More particularly, the invention is directed to a distillation method for obtaining increased yields of desirable normally gaseous hydrocarbons.

Prior to the present invention it has been common to distill a normally gaseous hydrocarbon fraction containing propane and propylene for use as a liquefied petroleum gas or as feed stock to an alkylation, polymerization or other conversion process. In distilling mixtures containing propane and propylene it is customary to subject the mixture to distillation conditions in a suitable distillation zone under temperature and pressure conditions such that an overhead fraction is obtained containing some propane and lighter hydrocarbons and a side stream fraction is withdrawn consisting essentially of the desirable propane and propylene. Heavier hydrocarbons are withdrawn as a bottom fraction. In operating this process a considerable amount of desirable propane and propylene is discarded in the overhead gas. It is possible to recover some of this propane and propylene by absorption in conventional absorption towers; however, such absorption towers are inefficient when a mixture such as an overhead mixture containing propane and lighter hydrocarbons is being absorbed and only a small amount of the propane and propylene is recovered.

It is, therefore, the main object of the present invention to provide an improved distillation operation in which substantially larger quantities of propane and propylene are recovered than was possible heretofore.

Another object of the present invention is to provide an improved distillation method for recovering normally gaseous hydrocarbons by distilling mixtures containing same.

A still further object of the present invention is to provide a distillation operation in which a mixture containing at least 3 hydrocarbons; a low boiling hydrocarbon, an intermediate boiling hydrocarbon and a higher boiling hydrocarbon are distilled under conditions to recover substantially larger quantities of the intermediate boiling hydrocarbon than was possible heretofore.

The objects of the present invention may be achieved by admixing a mixture of normally

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gaseous hydrocarbons containing heavier hydrocarbons with a gaseous stream distilled from the mixture and then charging the resulting mixture to a distillation zone wherein the hydrocarbons charged in the distillation zone are separated into at least 3 fractions, an overhead fraction from which the gaseous stream is recovered, an intermediate fraction comprising the desirable hydrocarbon which is recovered and a bottom fraction containing heavier hydrocarbons.

The invention may be described briefly as involving the formation of a feed mixture containing, for example, hydrocarbons having 5 and less carbon atoms in the molecule and including those having 3 and less carbon atoms in the molecule. This feed mixture is admixed with a gaseous stream obtained by distillation of the feed mixture and allowed to separate into a gaseous phase and a liquid phase, the gaseous phase being discarded and the liquid phase being charged into the distillation zone where conditions are adjusted to produce an overhead fraction, an intermediate boiling fraction and a higher boiling fraction. The overhead fraction is cooled and condensed and allowed to separate into a gaseous stream which is the stream admixed with the feed and a liquid stream which may be withdrawn as a condensate or preferably is returned at least wholly or in part to provide reflux in the distillation zone.

The present invention has application to recovery of ethane and/or ethylene, propane and/or propylene, or butanes and/or butylenes from low boiling hydrocarbon mixtures containing them. Such fractions may be obtained from crude petroleum or from conversion operations such as thermal and catalytic cracking operations, polymerization processes, alkylation and isomerization operations, as well as many others too numerous to mention. When the feed mixture is obtained from petroleum it will be understood that propylene and butylenes or ethylene will be substantially absent since the olefinic hydrocarbons have normally not been encountered in substantial amounts in natural petroleums.

The invention will be described in more detail by reference to the drawing in which

Fig. 1 is a flow diagram of a preferred mode of my invention; and

Fig. 2 is a flow diagram of a modified mode of practicing the invention.

In the drawing identical numerals will be employed to identify identical parts.

Referring now to the drawing and specifically to Fig. 1, numeral 11 designates a feed line by way of which a low boiling hydrocarbon mixture such as one containing ethane and lighter, propane and propylenes, butane and butylenes, as well as a small amount of hydrocarbons having 5 and more carbon atoms in the molecule is fed into the system from a source not shown. The feed mixture in line 11 has admixed with it a gaseous hydrocarbon stream introduced by line 12 and obtained as will be described further. The gaseous mixture in admixture with the liquid stream introduced by line 11 flows into an accumulator drum 13 which is of sufficient size to allow a residence time for separation of the gaseous material therefrom and to obtain a liquid phase. The gases are withdrawn from accumulator drum 13 by line 14 and may be used as a fuel gas or may be routed to conventional absorption equipment for recovery of valuable components therein or optionally may be charged to a conversion operation. The liquid stream in drum 13 is withdrawn by line 15 and is charged by pump 15*a* into a distillation zone illustrated by fractionation tower 16 which is equipped with a heating means illustrated by coil 17. Fractionator 16 is provided with internal contacting equipment such as bell cap trays or other contacting means well known to the art wherewith intimate contact between liquid and vapors is obtained. Fractionator tower 16 is also of sufficient size to allow separation by adjustment of conditions of temperature and pressure therein of an overhead fraction by way of line 18, a side stream by way of line 19 and a bottoms fraction by way of line 20. The side stream withdrawn by line 19 will consist essentially of propane and propylene, while the bottoms fraction will comprise essentially C_4 and heavier hydrocarbons. The overhead fraction withdrawn by line 18 contains some propane and propylene, but also contains lighter hydrocarbons. This fraction is discharged by line 18 into a condenser 21 through which a cooling medium flows by line 22. In condenser 21 the temperature of stream 18 is reduced to cause substantial liquefaction of the overhead stream 18 on discharge of it from condenser 21 by line 23 into reflux or product accumulator 24. From reflux or product accumulator 24 a gaseous stream is withdrawn by line 12 controlled by valve 12*a* for admixture with the feed mixture in line 11 while the liquefied condensate is withdrawn therefrom by line 25 and returned in large part by branch line 26 to tower 16 to provide reflux therein. If desired, a portion of the condensate may be withdrawn from the system by manipulation of valve 27 for other uses as may be desired. It is preferred, however, to return a greater portion of the condensate to tower 16 for employment as reflux therein.

By the simple expedient of admixing the feed mixture in line 11 with the gaseous stream, it is possible to increase substantially the amount of propane recovered by line 19. The amount of the gaseous stream admixed from line 12 with the feed mixture in line 11 will usually be in the ratio of one volume of gaseous stream to about 4 volumes of the feed mixture. However, this may vary from about 1 volume of the gaseous mixture to about 2 to 8 volumes of feed mixture, depending on the composition of both the gaseous stream and the feed mixture and on the distillation tower operating conditions.

Referring now to Fig. 2, a feed mixture similar to that charged in the description taken in connection with Fig. 1 is introduced into the system by line 11 from a source not shown and is divided into two streams, part of which flows by line 11 controlled by valve 30 into the feed accumulator drum 13, while another portion flows by way of line 31 controlled by valve 32 to be admixed with a gaseous stream flowing through line 33 from a source which will be described later. The mixture of the gaseous stream in line 33 from drum 24 flows into a condenser 34 provided with a line 35 through which a cooling fluid flows whereby the mixture of gas and feed is cooled and condensed. The cooled and condensed mixture is discharged from condenser 34 by line 36 into an accumulator drum 37 from whence there is discharged by line 38 an exit gas which may be employed in a manner similar to that described with respect to the gas withdrawn by line 14 in Fig. 1. The liquid in accumulator drum 37 discharges therefrom by line 39 into accumulator drum 13 from whence it is pumped in admixture with the feed from line 11 into fractionator tower 16 by way of line 15 containing pump 15*a*. In fractionator tower 16 conditions are adjusted as described with respect to Fig. 1 to obtain an overhead fraction by line 18, an intermediate fraction by line 19, and a bottom fraction by line 20. The overhead fraction is cooled and condensed in condenser 21 through which a cooling medium flows by line 22, and the condensed liquid discharged into reflux or product accumulator 24 by line 23. A gaseous stream is withdraw from product accumulator 24 by line 33 controlled by valve 33*a* and is mixed with a portion of the feed from line 31 before it discharges into condenser 34 as heretofore described.

From the description of Fig. 2 it will be seen that this mode of operation is a modification of that of Fig. 1 where the gaseous stream obtained from the product accumulator is admixed with a portion of the feed and the resulting admixture cooled and condensed prior to separation therefrom of a gaseous stream and the discharge of the resulting condensate into the feed accumulator.

As an alternative to the mode of operation described with respect to Fig. 2, condenser 34 may be located in line 31 to cool that portion of the feed stream prior to admixture with the gas stream from line 33 or the condenser 34 may be located in line 11 and the feed mixture cooled instead of only a portion thereof.

In a typical operation in accordance with Fig. 1 in which a propane stream was recovered by line 19 from tower 16, this tower was operated under conditions to provide a vapor temperature of 126° F., a bottoms temperature of 272° F. and a pressure of approximately 342 p. s. i. g. The feed mixture containing propane, propylene, as well as butanes and heavier, and ethane and lighter, was withdrawn from feed accumulator 13 which was operated at a pressure of 156 p. s. i. g. and was charged to tower 16 at the rate of 14,625 barrels per day. A side stream of propane and propylene amounting to 2,160 barrels per day was withdrawn. The bottoms fraction withdrawn consisted of 10,045 barrels per day. The amount of

reflux pumped back to the tower was 18,500 barrels per day, while the gaseous stream admixed with the feed mixture amounted to 3,960,000 cu. ft. per day. The gaseous stream withdrawn through line 14 amounted to 3,940,000 cu. ft. per day.

The charge to tower 16 and the various product streams were analyzed and found to have the composition given in the following table:

	Liquid Vol. Percent			Gas Vol. Percent	
	Charge to tower 16	Side stream from line 19	Bottoms from line 20	Gas from line 12	Gas from line 14
Methane and non-condensables	0.3			2.1	6.8
C_2 hydrocarbons	5.0	3.5		23.1	24.4
H_2S	0.8	0.9		6.8	4.1
C_3 hydrocarbons	25.6	93.5		68.0	39.1
C_4 hydrocarbons	41.7	2.1	60.1		21.8
C_5 hydrocarbons	26.6		39.9		3.8
Total	100.0	100.0	100.0	100.0	100.0

It is seen from these operating data that there is an interchange of butane and pentane for propane in the gas stream which is brought about by contacting the butane free gas with the feed stream which contains large amounts of the heavier hydrocarbons.

To illustrate further the advantages of using the method of the present invention over the conventional method of distilling hydrocarbon mixtures, the following comparison of stream rates is given. In the conventional operation, product gas is discharged from accumulators 13 and 24, while in the method in accordance with the present invention, the gas from accumulator 24 contacts the feed in accumulator 13 and the gas from this accumulator is the only gaseous product. In both operations the feed composition is similar to that given in the above table.

	Conventional Operation	Present Invention Fig. 1
Feed to tower 16, bbls./day	20,000	20,000
Sidestream 19, cu. ft./day:		
Total	3,700,000	4,500,000
C_4+C_5-	3,600,000	4,400,000
Gas from accumulator 24, cu. ft./day:		
Total	3,200,000	
C_3+C_5-	1,800,000	
Gas from accumulator 13, cu. ft./day:		
Total	300,000	3,300,000
C_3+C_5-	100,000	1,100,000
Product Gas, cu. ft./day:		
Total	3,500,000	3,300,000
C_3+C_5-	1,900,000	1,100,000

From the foregoing comparison, it will be apparent that an additional 800,000 cu. ft. per day of propane-propylene mixture may be obtained when practicing my invention over that obtainable in the conventional operation.

The invention is preferably applicable to the recovery of propane and propylene from hydrocarbon mixtures as described. However, it is also applicable to separation of ethane and ethylene mixtures, as well as to recovery of butane and butylenes from gaseous mixtures containing them. However, the invention has most application to the distillation of liquefied petroleum gas to obtain propane and propylene containing fractions.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. In the distillation of a normally gaseous feed mixture of hydrocarbons including normally liquid hydrocarbons comprising at least three hydrocarbons in which the feed mixture is introduced into a distillation zone at a lower point therein and an intermediate boiling hydrocarbon originally present in the feed mixture is separated from lower and higher boiling hydrocarbons including said normally liquid hydrocarbons and in which a normally gaseous fraction is distilled overhead therefrom, the steps of withdrawing a side stream of said intermediate hydrocarbon from said distillation zone at a point substantially above the point of introduction of said feed mixture, admixing at least a portion of said normally gaseous fraction with said feed mixture to form a second mixture consisting of said gaseous fraction and said feed mixture, separating said second mixture into a gaseous phase and a liquid phase, withdrawing said gaseous phase, and distilling said liquid phase to obtain said side stream.

2. A method in accordance with claim 1 in which the intermediate boiling hydrocarbon has two carbon atoms in the molecule.

3. A method in accordance with claim 1 in which the intermediate boiling hydrocarbon has 3 carbon atoms in the molecule.

4. A method in accordance with claim 1 in which the intermediate boiling hydrocarbon has 4 carbon atoms in the molecule.

5. A method for distilling low boiling normally gaseous hydrocarbons which comprises forming a normally gaseous feed mixture including at least 3 hydrocarbons; an intermediate boiling hydrocarbon, a lower boiling hydrocarbon, a higher boiling hydrocarbon, and normally liquid hydrocarbons, admixing said feed mixture with a gaseous stream obtained in a later stage of the process to form a second mixture consisting of said gaseous fraction and said feed mixture, separating said second mixture into a gaseous phase and a first liquid phase, discarding said gaseous phase, introducing said first liquid phase into a distillation zone at a lower point therein, distilling said first liquid phase, withdrawing a side stream of said intermediate boiling hydrocarbon from said distillation zone at a point substantially above the point of introduction of said first liquid phase, and recovering from said distillation zone a bottoms fraction of said higher boiling and liquid hydrocarbons, and an overhead fraction, and cooling said overhead fraction to form said gaseous stream and a second liquid phase.

6. A method in accordance with claim 5 in which the intermediate boiling hydrocarbon has 2 carbon atoms in the molecule.

7. A method in accordance with claim 5 in which the intermediate boiling hydrocarbon has 3 carbon atoms in the molecule.

8. A method in accordance with claim 5 in which the intermediate boiling hydrocarbon has 4 carbon atoms in the molecule.

9. A method in accordance with claim 5 in which the liquid phase is returned as reflux to the distillation zone.

10. A method for distilling low boiling normally gaseous hydrocarbons which comprises forming a normally gaseous feed mixture including at least 3 hydrocarbons, an intermediate boiling hydrocarbon, a lower boiling hydrocarbon, a higher boiling hydrocarbon, and normally

liquid hydrocarbons, admixing at least a portion of said feed mixture with a gaseous stream obtained in a later stage of the process to form a second mixture consisting of said gaseous stream and said feed mixture, separating said second mixture into a gaseous phase and a first liquid phase, discarding said gaseous phase, admixing said first liquid phase with at least a portion of said feed mixture to form a third mixture, introducing said third mixture into a distillation zone at a lower point therein, distilling said third mixture, withdrawing a side stream of said intermediate hydrocarbon from said distillation zone at a point substantially above the point of introduction of said third mixture, and recovering from said distillation zone a bottoms fraction of said higher boiling and liquid hydrocarbons and an overhead fraction, cooling said overhead fraction to form said gaseous stream and a second liquid phase and returning said second liquid phase as reflux to said distillation zone.

11. A method in accordance with claim 10 in which the intermediate boiling hydrocarbon has 2 carbon atoms in the molecule.

12. A method in accordance with claim 10 in which the intermediate boiling hydrocarbon has 3 carbon atoms in the molecule.

13. A method in accordance with claim 10 in which the intermediate boiling hydrocarbon has 4 carbon atoms in the molecule.

14. A method for distilling a normally gaseous mixture comprising ethane and lighter hydrocarbons, propane and propylene and hydrocarbons having 4 and more carbon atoms in the molecule including normally liquid hydrocarbons which comprises admixing said mixture with a gaseous stream obtained in a later stage of the process to form a second mixture consisting of said gaseous stream and said feed mixture, separating said second mixture into a gaseous phase and a first liquid phase, discarding said gaseous phase, introducing said first liquid phase into a distillation zone at a lower point therein, distilling said first liquid phase, withdrawing a side stream consisting essentially of propane and propylene from said distillation zone at a point substantially above the point of introduction of said first liquid phase, and recovering from said distillation zone a bottoms fraction comprising C_4 and heavier hydrocarbons and an overhead fraction comprising propane and lighter hydrocarbons, cooling said overhead fraction to form said gaseous stream and a second liquid phase and returning said second liquid phase as reflux to said distillation zone.

ROGER WYLIE.

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