May 23, 1950 J. A. PATTERSON 2,509,044

SEPARATION OF LOW MOLECULAR WEIGHT HYDROCARBONS FROM PETROLEUM MIXTURES

Filed July 3, 1947 2 Sheets-Sheet 1

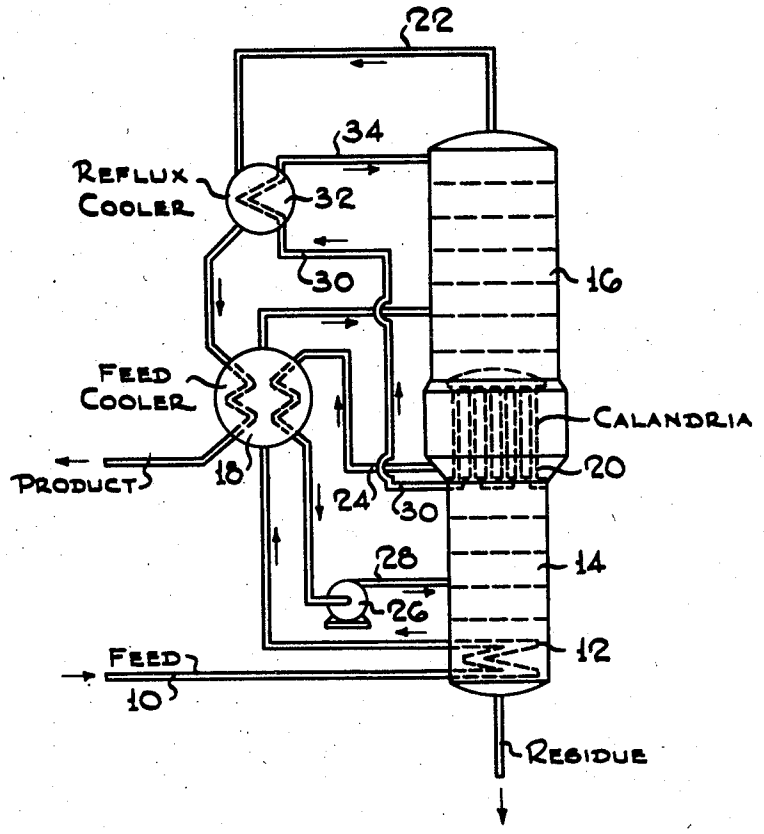


FIG.-1

John A. Patterson Inventor

By J. C. Small Attorney

May 23, 1950 J. A. PATTERSON 2,509,044

SEPARATION OF LOW MOLECULAR WEIGHT HYDROCARBONS FROM PETROLEUM MIXTURES

Filed July 3, 1947 2 Sheets-Sheet 2

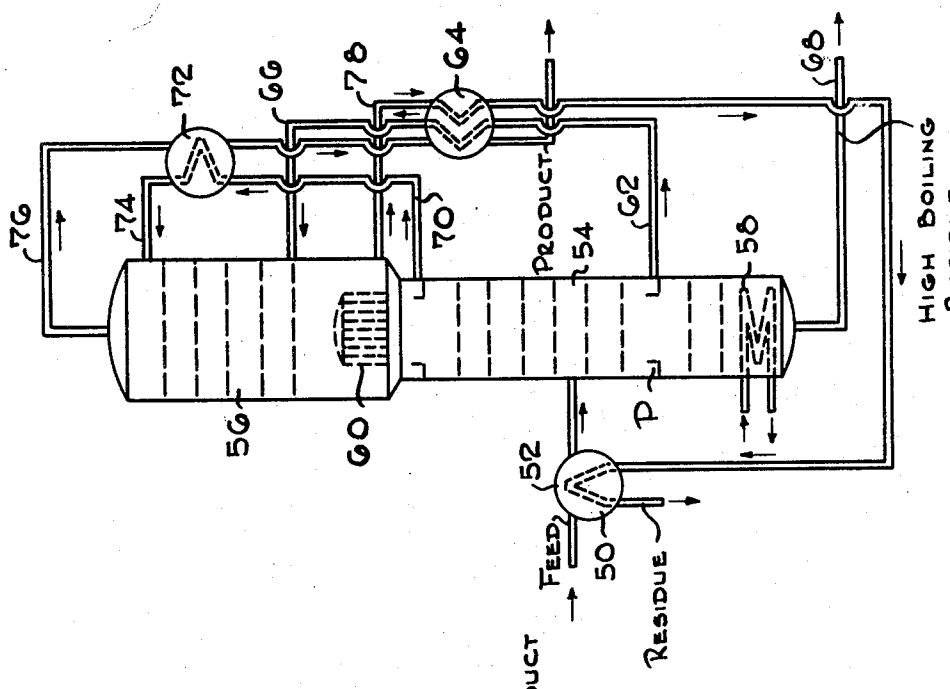


FIG. 2

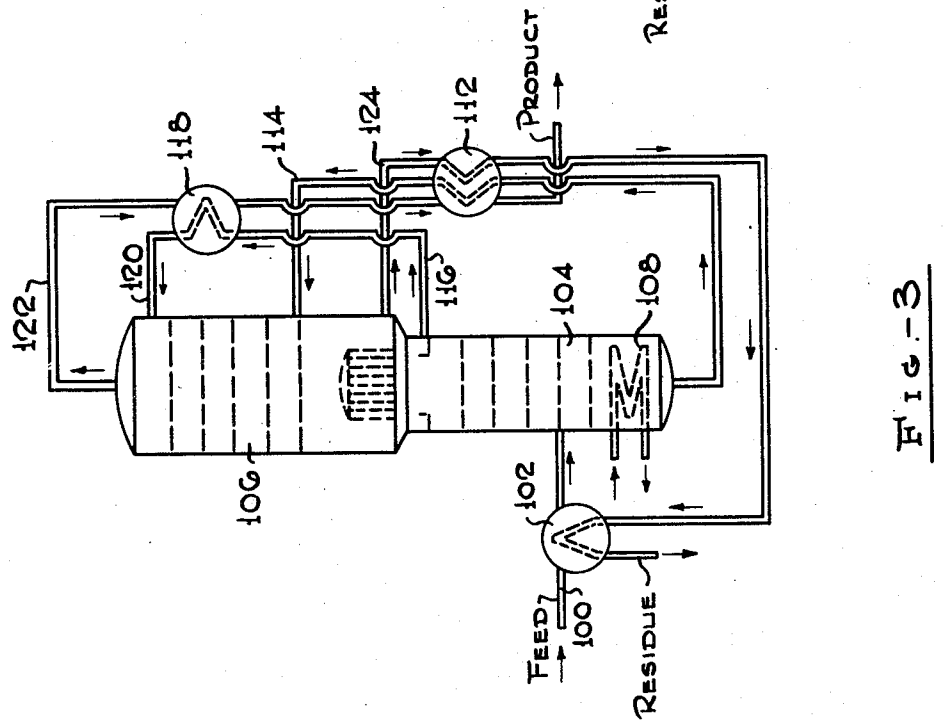


FIG. 3

John A. Patterson Inventor

By J. C. Small Attorney

Patented May 23, 1950

2,509,044

UNITED STATES PATENT OFFICE

2,509,044

SEPARATION OF LOW MOLECULAR WEIGHT HYDROCARBONS FROM PETROLEUM MIXTURES

John A. Patterson, Beverly, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

Application July 3, 1947, Serial No. 758,844

3 Claims. (Cl. 62—175.5)

1

This invention relates to the concentration and separation of low molecular weight hydrocarbons from complex mixtures and in particular to the separation and purification of ethylene by processing involving a modified distillation double tower.

Variation of pressure has been employed in the prior art as a distillation aid in the fractionation of mixtures. Air fractionation is a particular development in this field, depending also on a unique heat exchanger system to reduce the cost of refrigeration. The double tower used in air fractionation involves not only the division of the distillation zone into two pressure sections, but also the separation of the sections by a common heat exchanger unit. The base of the lower pressure section of the zone functions as a reboiler in that section for the bottoms supplied from the high pressure section and as a top condenser for the more volatile constituents of the feed supply furnished to the higher pressure section. To render the unit compact and to minimize refrigeration losses, the lower pressure section is commonly super-imposed upon the higher pressure but the two sections may be arranged as otherwise suitable provided there is a common heat exchanger or condenser-reboiler system.

The common heat exchanger in the double tower functions in a dual capacity, namely, to furnish the heat for fractionation in the lower pressure zone and also to supply the reflux for the high pressure zone. The effectiveness of the heat exchange unit is made possible by reason of the "inversion" of the temperature caused by the pressure chosen for the two sections of the distillation column. In air fractionation, the difference in pressure between the two fractionating dones causes the normal temperature differential of the boiling points of oxygen and nitrogen to be reversed so that the high pressure nitrogen condenses at a higher temperature than that required to boil the low pressure oxygen. This inversion of temperature is only advantageously effected, however, with mixtures of narrow boiling range, such as air and is not generally applicable to more complex mixtures such as the low molecular weight hydrocarbon mixtures available in oil fields and petroleum refineries because of the wide range of the critical constants of the component compounds.

The present invention is concerned with modifications in the normal processing employing the double tower. The modifications are necessary in order that mixtures of wide boiling range be accommodated and suitably fractionated. In the

2

conventional double tower, the presence of the higher boiling hydrocarbons in the feed results in a relatively high bottoms temperature in the low pressure section. The pressure in the higher pressure section of the double tower is determined by the boiling point of the overhead liquid withdrawn from that section which is supplied as reflux to the lower pressure section. Thus, the presence of the high boiling compounds in the feed, and thus in turn in the low pressure section, requires a corresponding increase in temperature and consequently in pressure in the high pressure section. Such high pressure makes operation of the unit inefficient and expensive due to compression requirements and to the fact that separation of constituents is more difficult at higher pressures. Above a definite limiting concentration of high boiling constituents, processing in the conventional double tower arrangement becomes unworkable since the critical temperatures of the hydrocarbons at the top of the high pressure section are exceeded.

Processing according to the present invention permits the separation of the high boiling constituents from such mixtures of wide boiling range, without foregoing the advantages of processing in the double tower. Thus, in one method of processing according to the invention, the feed stock is supplied to the low pressure section of the double tower system and the residue is passed to the higher pressure section. In the high pressure distillation section a light fraction is separated as a condensate in the upper portion from a heavy residual fraction removed from the base of the section. This modification of processing necessitates the use of a pump to transfer the bottoms from the low pressure section to the high pressure section where this residue stream acts as feed to the high pressure section. As in the conventional double tower, maximum advantage is taken of the heat exchange between the streams within the system for efficient operation. By such processing the need for a high temperature in the bottom reboiler portion of the lower pressure section on account of high boiling material in the feed supply is obviated.

Another method of processing according to the invention involves supplying the feed stock to the high pressure section as in normal double tower processing and dividing the high boiling materials thus obtained in the high pressure section into two streams, namely, a distillation residue and a side stream. The side stream is supplied as the feed to the low pressure distillation section while the residual fraction is removed from the

system at the bottom. In this manner the desired lower boiling hydrocarbons such as ethylene and propylene are separated from the heavier C_3 and C_4 hydrocarbons of cracked propane stock by reason of the separation of these lower boiling compounds in the side stream from the much higher boiling compounds removed in the distillation residue from the high pressure section.

Thus, the applicant's invention involves processing in which a high temperature in the reboiler at the base of the low pressure section is not necessarily required in spite of the presence in the feed to the system of high boiling constituents. The applicant's processing essentially involves maintaining a boiling mixture of volatility intermediate between those of the condensate in the high pressure zone and the high boiling constituents separated as distillation residue from the bottom of the high pressure section. This is achieved by obviating the need for isolating the high boiling constituents in the low pressure section in the two principal embodiments of the invention. This is accomplished by (1) in separately removing from the feed in the high pressure section the highest boiling constituents and (2) in making the initial separation of the lightest constituents in the low pressure zone and supplying to the high pressure section the thus reduced feed for closer separation of the hight boiling constituents.

In order that the invention may be more fully understood, the following descriptions of processing together with the attached drawings, Figures 1, 2 and 3, are presented. In Figure 1 diagram is presented in which processing is carried out by supplying the feed stock to the low pressure section of a double tower. In Figures 2 and 3, two flow diagrams are presented as a comparison of processing by supplying the feed stock to the high pressure section and obtaining the two high boiling fractions therefrom (Figure 2) with normal type processing in the double tower (Figure 3). In these drawings, the lower pressure section is shown as being super-imposed upon the higher pressure section but the two sections may be otherwise relatively located provided connection occurs in a common heat transfer or condenser-reboiler unit.

In Figure 1, a hydrocarbon mixture is supplied through line **10**. In this specific illustration, the feed stock has the following composition:

	per cent
Ethylene	42.9
Ethane	17.9
Propylene	26.6
Propane	11.0
C_4+	1.6

For purposes of illustration, this material is processed according to the present particular embodiment.

The feed supply, under a pressure of about 10 pounds per square inch, is passed through the reboiler section **12** in the higher pressure section **14** before passing into the lower pressure section **16** of the double distillation tower as shown. Usually the feed supply, before entering the low pressure section, also passes through a heat exchanger **18**. In the high pressure section **14** an average pressure of about 100 pounds per square inch gauge is maintained, while in the upper low pressure section an average pressure of about 10 pounds per square inch gauge is maintained. Also, in the high pressure section the number of plates is 20, and in the lower pressure section the number of plates is 30. The feed stock enters the low pressure section at a point below about the middle of the tower at a temperature of about −100° F. In order to start the processing, some high boiling materials as obtained from a previous operation as distillation from the low pressure section are pumped into the higher pressure section and distillation carried out in order to supply the heat necessary for carrying out the distillation in the low pressure section. With the feed stock of composition as described under about 10 pounds per square inch pressure, fractionation is obtained by maintaining a temperature of about −90° F. in the low pressure reboiler section **20** and an overhead vapor exit line **22** temperature of about −135° F.

The distillation residue from the loy pressure section is removed through line **24**, passed through heat exchanger **18** and thence through pump **26** and into the high pressure section through line **28**. The pump **26** increases the pressure upon the material supplied to the high pressure section through line 28 to about 100 pounds per square inch. With a reboiler **12** temperature maintained at about −25° F. and an upper condensing effect in the reboiler **20**, a vapor temperature in the upper portion of the distillation zone **14** is maintained at about −50° F. Under such conditions of processing, the distillation residue has a composition as follows:

	Per cent
Ethylene	3.9
Ethane	25.0
Propylene	48.2
Propane	20.0
C_4+	2.9

A portion of the condensate from section **14** is removed through line **30** and passed through cooler **32** and thence as reflux through line **34** to the low pressure section **16**. In passing through line **30** and the cooler **32**, the pressure is reduced to about 10 pounds per square inch.

Through line **22**, the overhead vapors from the distillation zone **16** are first passed through the coolers **32** and **18**, respectively. The product obtained is of the following composition:

	Per cent
Ethylene	90.0
Ethane	9.9
Propylene	0.1

Another manner of processing according to the invention is shown in the flow diagram, Figure 2, and comparison made with the conventional double tower processing shown in Figure 3. In the processings shown in Figures 2 and 3, illustrations are presented with regard to the treatment of a feed stock of the following compositions:

	Per cent
Methane	0.4
Ethylene	38.4
Ethane	16.0
Propylene	27.5
Propane	12.0
C_4+	5.7

The feed is supplied through line **50**, through cooler **52** and into about the middle of the high pressure section **54** of the double tower, the low pressure section being indicated by the numeral **56**. The temperature of the feed supplied to the tower is about −10° F. The pressure in the distillation zone **54** is maintained at about 100 pounds per square inch, while in the lower pres-

sure section the pressure is maintained at about 10 pounds per square inch. With the feed supply as given, the temperature of 20° F. is maintained in the lower portion of the distillation zone 54 by means of the heat exchanger 58. An upper vapor temperature of about −55° F. is maintained as a result of the condensing effect due to the condenser-reboiler 60 of the dividing portion of the double tower. In the high pressure section 54, about 25 plates are maintained; and in the low pressure section 56, about 20 plates. From a lower plate P, at a temperature of −5° F., a side stream is removed through line 62, passed through heat exchanger 64, and thence through line 66 into the lower half of the low pressure distillation zone 56. From the bottom of the high pressure zone, distillation residue is removed through line 68 and passed to other equipment for further processing. The composition of this residue is as follows:

	Per cent
Ethane	0.5
Propylene	53.6
Propane	29.3
C_4+	16.6

From the upper portion of the high pressure distillation zone 54, condensate is removed through line 70 and passed through cooler 72 and thence through line 74 into the upper portion of the low pressure distillation zone 56 as reflux.

With the condenser-reboiler 60 maintaining a condensing temperature of −55° F. in the high pressure section, the reboiler effect in the low pressure section gives a temperature of −65° F. With such a temperature, the overhead vapor exit temperature is −130° F. Under such conditions of processing, the overhead vapors are removed through line 76 and passed through heat exchangers 72 and 64. The composition of the product is:

	Per cent
Methane	0.9
Ethylene	85.1
Ethane	13.8
Propylene	0.2

The distillation residue is removed from the low pressure section through line 78 and thence through coolers 64 and 52. The composition of this product is as follows:

	Per cent
Ethylene	5.2
Ethane	27.3
Propylene	44.8
Propane	16.4
C_4+	6.3

In contrast to such processing, with the same feed stock supplied through line 100 of Figure 3 and through cooler 102 at a temperature of about −10° F., the feed is supplied to the tower in the lower half of the high pressure section 104, the lower pressure section of the tower being indicated by the reference numeral 106. For advantageous separation of the constituents, it has been found that a pressure of 150 pounds per square inch is required in the high pressure section 104 and a bottoms temperature of 0° F. is maintained by the reboiler 108. Under such conditions of temperature and pressure, the condensing vapors in the upper portion have a temperature of −60° F. The distillation residue is removed from the distillation zone 104 through line 110, passes through heat exchanger 112 and thence through line 114 to the lower part of the distillation zone 106. From the upper portion of

the distillation zone 104, the liquid condensate is removed through line 116, through heat exchanger 118, and through line 120 as reflux into the upper portion of the distillation zone 106. With a condensing effect in the high pressure section of −60° F., the reboiling effect in the low pressure section provides a temperature of −70° F. Under such conditions, an overhead vapor exit temperature of −130° F. is maintained. The overhead vapors are passed through line 122 and thence through heat exchangers 118 and 112. This product has the following composition:

	Per cent
Methane	0.9
Ethylene	85.1
Ethane	13.8
Propylene	0.2

From the lower portion of the distillation zone 106, the bottoms are removed through line 124, passed through heat exchangers 112 and 102. The composition of this product is as follows:

	Per cent
Ethylene	3.3
Ethane	17.7
Propylene	48.0
Propane	21.0
C_4+	10.0

It is also evident that in the conventional type processing considerable portion of ethylene is removed in the final residue in low concentration, while in the final residue from the processing according to the invention no ethylene content occurs. Also, in the residue from the low pressure section of the processing according to the invention a higher content of ethylene is obtained than in the residue from the processing involving the use of the conventional double tower. Advantages also with the processing according to the invention are that a lower pressure is maintained in the higher pressure section and that less of a cooling effect is necessary to maintain the bottoms temperature in the higher pressure section of the tower involved in the processing according to the invention.

What is claimed is:

1. In a fractionation process for separating ethane and ethylene in a predominantly C_2 to C_4 hydrocarbon fraction in a unitary distillation zone containing a high pressure section separated from a low pressure section by a common heat transfer zone and wherein the said predominantly C_2 to C_4 fraction is initially fed into the high pressure section, the improvement which comprises the steps of withdrawing from a lower portion of the high pressure section a heavy residual fraction containing predominantly C_3 and C_4 hydrocarbons; withdrawing from the high pressure section an intermediate side stream fraction containing predominantly C_2 hydrocarbons with a minor proportion of C_3 hydrocarbons and sending this fraction as feed to the low pressure section; withdrawing a light liquid fraction condensed on the pressure side of the said common heat transfer zone and comprising predominantly ethylene and containing some ethane from an upper portion of the high pressure section as reflux to the low pressure section; withdrawing a C_2 and higher hydrocarbon distillation residue stream from a lower portion of the low pressure section, the C_2 component of said distillation residue being predominantly ethane; and taking overhead a predominantly ethylene product stream from the low pressure section.

2. A process as in claim 1 in which the intermediate side stream fraction from the high pressure section is heat exchanged with the streams withdrawn from the low pressure section.

3. A process as in claim 2 in which a pressure of about 100 p. s. i. g. is maintained in the high pressure section of the distillation zone and a pressure of about 10 p. s. i. g. is maintained in the low pressure section.

JOHN A. PATTERSON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,963,809	Schuftan	June 19, 1934