Jan. 10, 1956 A. ETIENNE 2,729,954

SEPARATION OF GASEOUS MIXTURES

Filed July 8, 1952 2 Sheets-Sheet 1

Fig. 1

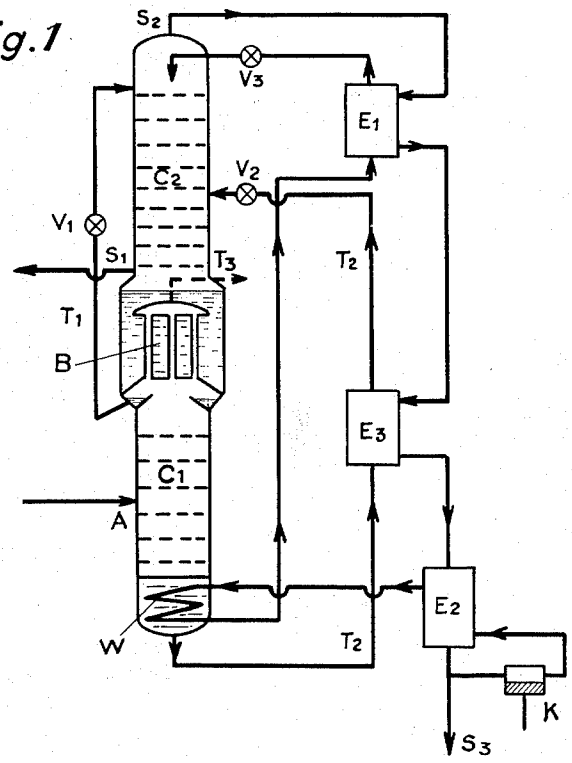
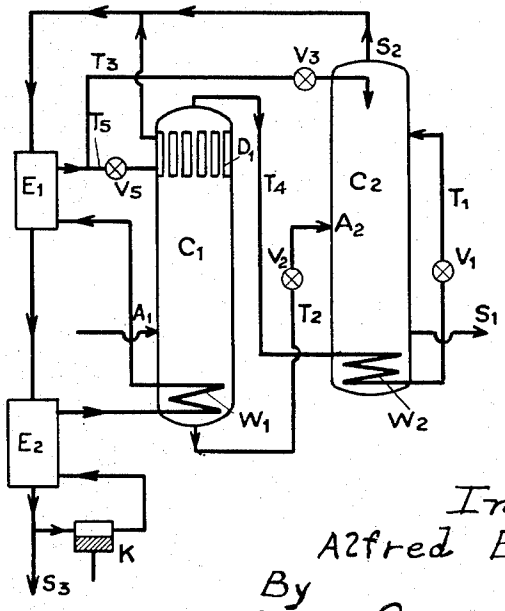


Fig. 2



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Filed July 8, 1952 2 Sheets-Sheet 2

Fig. 3

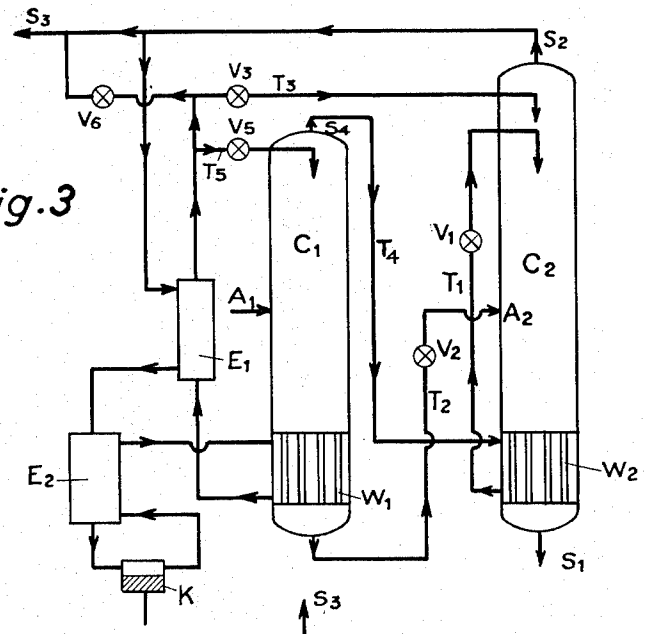
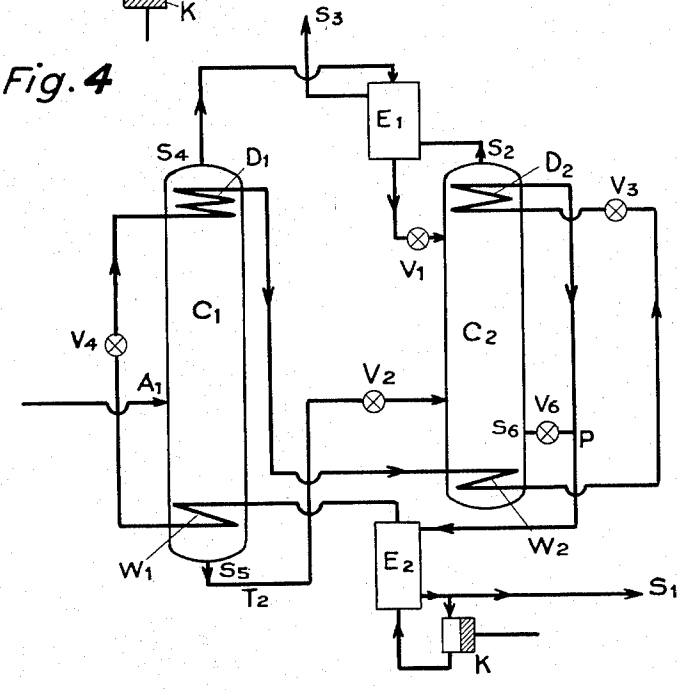


Fig. 4



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SEPARATION OF GASEOUS MIXTURES

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Claims priority, application France August 1, 1951

1 Claim. (Cl. 62—175.5)

This invention relates to improvements in the cold fractionation of gaseous mixtures. More particularly it applies to the cases where this fractionation is performed in a set of two rectification columns operated at different pressures and in heat exchange relation with one another, this set delivering as final products at least two fractions of different volatilities.

It is known that the easiness of the cold fractionation of a gaseous mixture depends, as main factors, on the difference of the volatilities of the components and on their relative proportions in the mixture. Considering for example the case of air, to be separated into industrially pure oxygen and nitrogen, the difference in the boiling points (—183° C. and —196° C.) and the relative amounts (21% and 79%) of oxygen and nitrogen make this separation rather easy by using the conventional double column apparatus. But such is not the case, for instance, for a mixture of carbon monoxide and nitrogen, the boiling points of which are respectively —190° C. and —196° C. or for a mixture of ethane and ethylene holding 80% of the first component and 20% of the second, on account not specially of their respective boiling points (—84° C. and —103° C.) but chiefly of their respective proportions, which make it difficult to have available the relatively large amount of the lower boiling component, i. e. ethylene in the present case, necessary as washing liquid at the top of both columns.

It is a first object of the present invention to make easier than by the known processes the separation of components with close boiling points.

It is a further object to obtain with a good yield and in a state of high purity each of the components of a mixture wherein a comparatively little amount of a given component is diluted in a much larger amount of another component.

Regardless of the composition of the mixture, it is a more specific object to augment in a double rectification column the liquid reflux ratio, as much as it may be desired for any separation.

These objects and other objects which will appear hereinafter are essentially attained by the following features.

In a set of two rectification columns operated at different pressures and in heat exchange relation with one another, a portion of any one of the two fractions resulting from the rectification under the lowest pressure and taken in a gaseous condition is compressed and circulated in a cycle wherein it is at least partly liquified through indirect contact with the highest boiling point liquid fraction resulting from the rectification under the highest pressure, so providing the reboiling at the base of this column, this liquefaction being possibly further carried on by indirect contact with the highest boiling point liquid fraction resulting from the rectification under the lowest pressure, the so obtained liquid being used for the cooling of the upper part of the column operated under the lowest pressure, and possibly of the column operated under the highest pressure.

The above described cycle makes it possible, in the mentioned case where the separation is performed in two rectification columns operated under different pressures, to obtain any amounts of refluxing liquids which may be necessary. The gas amount employed in the cycle, that is to say the gas which is recompressed when issuing from the lower pressure column, varies with the peculiar difficulty of the separation, i. e. with the relative volatility of the components and with their respective amounts in the mixture. The closer are the volatilities and the smaller is the amount of the most volatile component, the greater is the amount of the gas to be employed in the cycle.

Thus this cycle provides, on the one hand the reboiling in the base of the higher pressure column and on the other hand the cooling by either direct or indirect contact at the top of the lower pressure column. But it may provide, too, reboiling in the base of the lower pressure column and cooling at the top of the higher pressure column, as will appear from the hereinafter described examples, illustrated by the accompanying drawings, wherein:

Fig. 1 is a diagrammatic view of one embodiment of the invention, and comprising a double rectification column,

Fig. 2 is a diagrammatic view of a second embodiment, the columns being side by side,

Fig. 3 is a schematic view of yet another embodiment, useful for the separation from a mixture of components having close boiling points, and

Fig. 4 is a schematic view of yet another embodiment of the invention.

In the following description, the two columns will be termed respectively "high pressure column" and "low pressure column" regardless of the absolute operation pressures.

Figure 1 shows, diagrammatically, an embodiment of the invention in its simplest form applied to a double rectification column as it is generally used in the separation of air. The cycle is in this case supported by the more volatile fraction resulting from the rectification under the lowest pressure and provides only reboiling at the base of the high pressure column and cooling of the low pressure column.

The mixture to be separated, either in a gaseous condition and preferably close to its dew point, or partly liquefied by known means, not shown, enters at A the high pressure column C_1, which is heated at its base as will be explained hereafter. It is topped by a column C_2, operated at a lower pressure, for instance at atmospheric pressure, both columns being connected with a condenser-reboiler B wherein the reboiling necessary at the base of the low pressure column C_2 is performed by calories released by the condensation of the reflux at the top of the high pressure column C_1. Part of the liquid produced by this condensation is collected and led, through a tube T_1, provided with an expansion valve V_1, to the top of the column C_2. This column receives also through a tube T_2 and an expansion valve V_2 the less volatile liquid, which has been separated in the column C_1, issued from the base thereof, and cooled in an exchanger E_3. These two liquids enter the column C_2 at different levels, by reason of their different compositions. From the column C_2 issue, in a gaseous condition, respectively at the base through a pipe S_1 and at the top through a pipe C_2, the two fractions separated. The less volatile fraction, issuing by pipe S_1, is collected outside, its low temperature being utilized in an exchanger, not shown. The more volatile fraction, issuing through pipe C_2, is utilized according to the invention, in a cycle providing here, on the one hand, the reboiling

in the base of the high pressure column and, on the other hand, the formation of the liquid reflux at the top of the low pressure column. Accordingly, this fraction provides in succession the cooling of the liquid reflux of the column C_2 in an exchanger E_1, then the cooling of the fraction issuing at the base of the column C_1, in an exchanger E_3. It is then compressed by a compressor K, the resulting gas being cooled in an exchanger E_2 by the same gas before its compression, then liquefied in a coil W, placed at the base of the column C_1. The calories released in this liquefaction insured the reboiling in column C_1. The liquid condensed in the coil W is cooled in the exchanger E_1, then expanded by a valve V_3 and used as a liquid reflux at the top of the column C_2. The portion making up the final product is extracted by a pipe S_3 upon issuing from the exchanger E_2.

Figure 2 shows another embodiment of the invention. In this embodiment, the two columns stand side by side, being not connected through a condenser-reboiler. This arrangement is advantageous in some cases, especially because it does not require so much height in the shops.

The gas mixture to be separated, partly liquefied if necessary by known means not shown, enters column C_1 at A_1, the column C_1 being under pressure. The reboiling and the cooling of the gas mixture are ensured as will be explained hereafter. The relatively little volatile liquid resulting from the rectification in the column C_1 feeds the low pressure column C_2 at A_2 through a tube T_2, having therein an expansion valve V_2. The column C_2 is also fed at a higher level by a more volatile fraction which leaves the high pressure column C_1 at its top in a gaseous condition, through a tube T_4. This fraction is first liquefied in a coil W_2, thus reboiling the liquid in the bottom of the column C_2; it is then expanded by a valve V_1 and enters the column C_2 through a tube T_1. The less volatile fraction of the mixture issues from column C_2 through tube S_1, and the more volatile fraction issues through tube S_2, both fractions being in a gaseous condition. This more volatile fraction runs through two exchangers E_1 and E_2, the functions of which are explained hereafter. A portion making up a final product is extracted by a pipe C_3, the remainder being compressed in a compressor K, cooled in the exchanger E_2 by the same gas not yet compressed, and liquefied in the coil W_1, thus providing the necessary heat for the reboiling at the base of column C_1. The liquid produced in the coil W_1 is cooled again in the exchanger E_1 and divided into two portions, the first one of which passes through a tube T_3 and an expansion valve V_3 and is used as a reflux liquid in the low pressure column C_2, while the other one passes through a tube T_5 and an expansion valve V_5 and enters a condenser D_1 thereby condensing, by indirect contact, the reflux necessary for the operation of the column C_1. It then re-enters the cycle, being joined with the gases issuing by the pipe S_2 from the top of the column C_2.

Figure 3 shows an application of the invention to the separation of a mixture formed, for instance, of 70% ethane and 30% ethylene. The separation of such a mixture is considered to be relatively difficult not only because the closeness of the boiling points of the components (respectively —89° C. and —103° C.) but chiefly through the low percentage of the lower boiling component, i. e. ethylene. The separation of such a mixture is frequently accomplished because of the use of ethylene as a raw material for the chemical industries.

The mixture to be separated, close to its dew point or partly liquid, enters at A_1 a high pressure column C_1, wherein it is separated into a gas fraction, formed of substantially pure ethylene which issues at S_4 from the top of the column C_1 and a liquid fraction, leaving the column at its base. The liquid fraction passes through a tube T_2 and an expansion valve V_2 to the low pressure column C_2, which is operated at atmospheric pressure and which it enters at A_2. In this column the separation is achieved, the ethylene issuing from the top as a gas through a pipe S_2 and the ethane from the base, as a liquid through a pipe S_1.

A part of the gaseous ethylene leaving the column C_2 by the pipe S_2 is utilized in an exchanger E_1 for cooling the refluxing liquids of both columns C_1 and C_2, is then compressed to about 8 atmospheres in a compressor K, is cooled by heat exchange with the gas not yet compressed in an exchanger E_2 and liquefied in a tubular heat exchanger W_1 placed at the base of the column C_1. This provides the heat for the column C_1. The ethylene thus liquefied is divided into three portions of which the first one is expanded through a valve V_5 to the pressure of the column C_1 and serves as a reflux liquid in that column, the second one is expanded by a valve V_3 to the atmospheric pressure and passes through a tube T_3 to column C_2 where it is used as liquid reflux, the third one is expanded through an expansion valve V_6, is united with a part of the ethylene issuing from the column C_2, the whole issuing as the final product by the pipe S_3.

The gaseous fraction resulting from the rectification in the column C_1 leaves the column through a pipe S_4, passes through a tube T_4, and is liquefied in the tubular heat exchanger W_2 placed at the base of the column C_2. This provides the heat for the column C_2. It is then expanded by a valve V_1 and used as a liquid reflux at the top of the column C_2 jointly with the fraction expanded by valve V_3.

The separated ethylene making up one of the final products is extracted from the cycle by the pipe S_3, coming, on the one hand directly from the column C_2, on the other hand from the portion returning in liquid reflux through the tube T_3 at the top of this same column and expanded by the valve V_6. The ethane is drawn either in a gaseous condition or in a liquid condition, in this embodiment, from the base of the column C_2 through a pipe S_1.

It will be seen that in this embodiment, the characteristic cycle is supported by the most volatile product resulting from the separation, i. e. ethylene, and this provides the heating of the base of the high pressure column and the cooling of the top of both columns, the heating being indirect and the cooling, on the contrary, being indirect.

In the example of Figure 4, the cycle is supported, not by the most volatile product resulting from the separation but by the least volatile product. This embodiment of the invention is of interest in the event the most volatile product is either in a relatively small proportion in the mixture, or is highly valuable and must not be exposed to being partly lost in leaks which are difficult to avoid in a complex cycle.

The mixture to be treated, previously cooled to the vicinity of its dew point, enters under pressure at A_1 the high pressure column C_1, wherein it separates into a less volatile fraction issuing from the base at S_5 and a more volatile fraction issuing from the top at S_4. The first mentioned fraction feeds, through a tube T_2 and an expansion valve V_2, the column C_2, which is operated at a lower pressure than C_1 but is preferably higher than atmospheric pressure.

The second fraction is first cooled in an exchanger E_1, then expanded by a valve V_1 and enters the column C_2 near its top. The most volatile fraction resulting from the rectification in the column C_2 issues at S_2 at the top thereof, and is utilized in the exchanger E_1 for cooling the fraction issuing at S_4 from the column C_1. It is then collected outside by a pipe S_3. The least volatile fraction leaves the column C_2 near its base in a gaseous condition, at S_6. It is expanded to atmospheric pressure by a valve V_6 and is warmed up in an exchanger E_2. A portion of it, making up a final product, is withdrawn by a pipe S_1. The remaining part is compressed by a compressor K, cooled in the exchanger E_2, and liquefied in a coil W_1, located in the bottom of the column C_1. It

is then partly expanded by a valve V_4 to a pressure intermediate between the pressures of the columns C_1 and C_2 and is vaporized in a coil D_1 located in the upper part of the column C_1, supplying therein the necessary reflux. It liquefies again in a coil W_2 providing the heat for the boiling in the bottom of the column C_2, is then expanded to atmospheric pressure by a valve V_3 and vaporized in a coil D_2 located in the upper part of the column C_2 before re-entering the cycle at P.

Although the invention refers essentially to the separation of a mixture into two fractions, it may be applied in some cases to a separation into three fractions when the mixture includes, besides the two components with close volatilities, a third component, substantially more volatile than the two others, and which can, for example in an apparatus similar to the one of Figure 1, be extracted in a gaseous condition from the condenser B, at the top of the high pressure column C_1, through the tube T_3 shown in dotted lines.

This would be the case, for instance, for a mixture of hydrogen, nitrogen and carbon oxide produced from a coke oven gas. The hydrogen would issue at T_3, nitrogen at S_3 and carbon oxide at S_1.

For greater simplicity, the figures do not show the devices providing the general cold maintenance of the apparatus, independently from the cycle characterizing the invention. The cold output may be obtained by any known means, as the expansion of compressed gas with production of external work, the utilization of conventional frigorific cycles, etc.

What I claim is:

A process for separating at a sub-atmospheric temperature a substantially binary mixture, made up with two components with close boiling points into said components, which process involves higher and lower pressure rectification stages, with heat exchanges between these stages, and comprises withdrawing as final product a portion of the lowest boiling component issuing in a gaseous state from the lower pressure stage, compressing the remaining portion of said component, liquefying it by indirect contact with the highest boiling fraction resulting from the higher pressure rectification, expanding the so obtained liquid and using it by direct contact as cooling liquid in both rectification stages, furnishing the whole of the heat necessary for operating the lower pressure rectification stage by liquefying the lowest boiling fraction resulting in a gaseous condition from the higher pressure rectification, expanding the resulting liquid and introducing it into the lower pressure rectification stage.

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