Dec. 24, 1957 A. ETIENNE 2,817,216

PROCESS AND APPARATUS FOR THE SEPARATION, BY RECTIFICATION, OF A GAS MIXTURE CONTAINING AT LEAST THREE COMPONENTS

Filed July 29, 1953 2 Sheets-Sheet 1

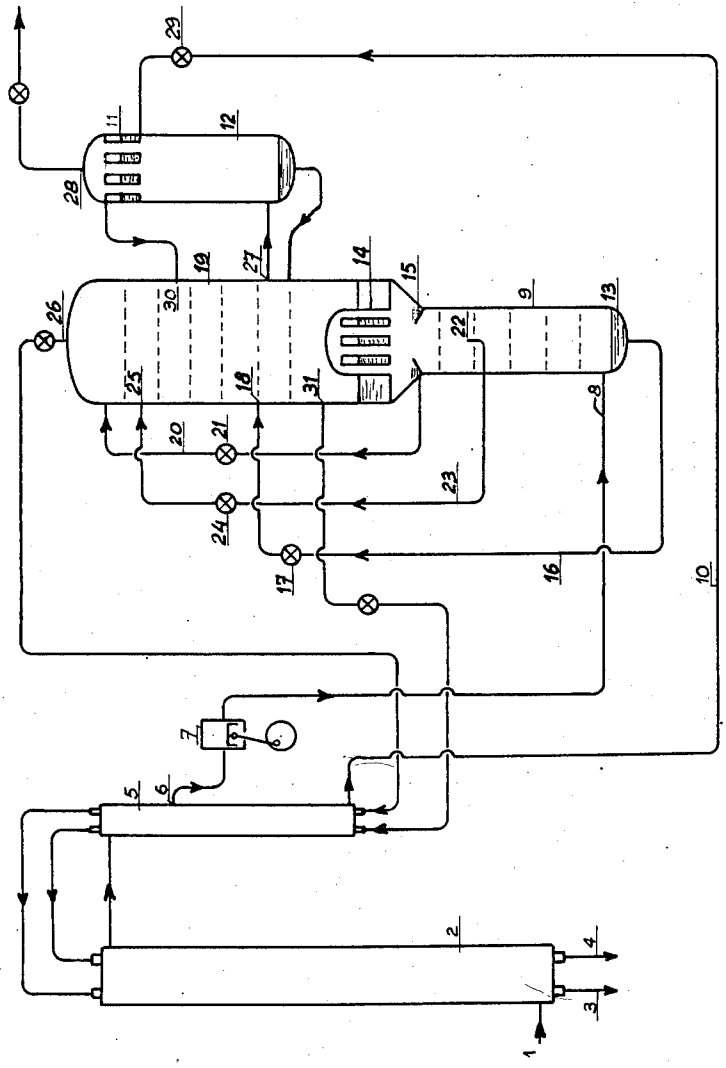

Fig. 1

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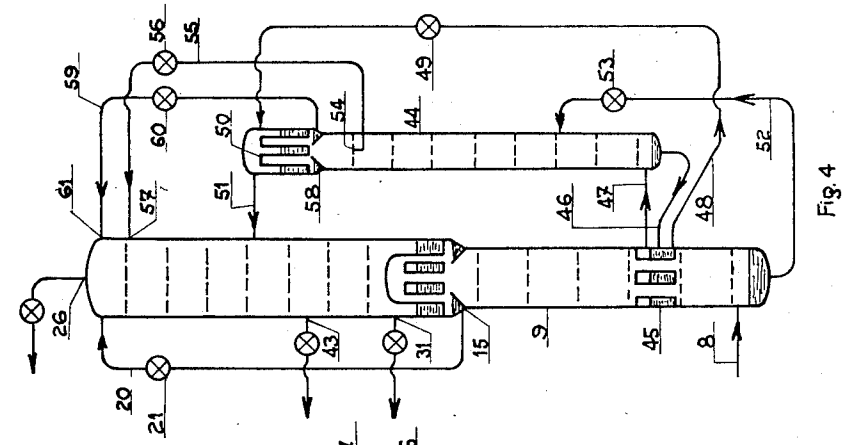

Fig. 4

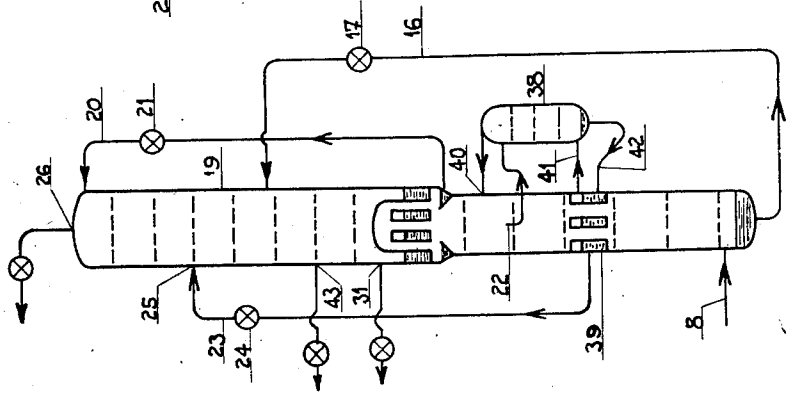

Fig. 3

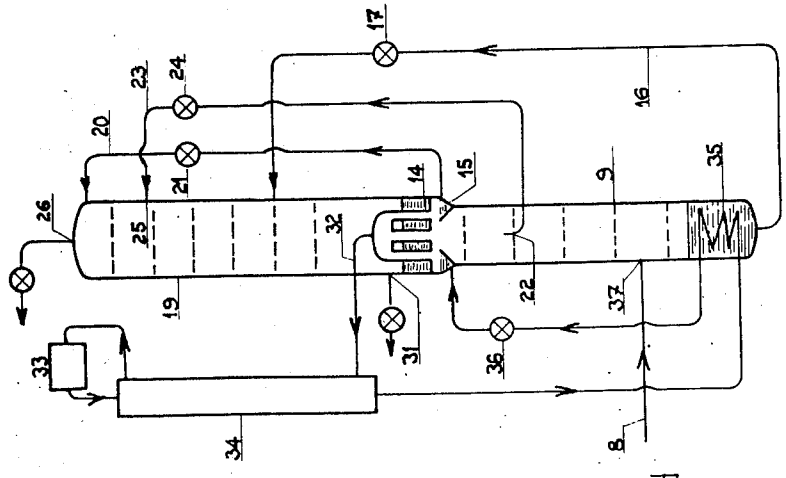

Fig. 2

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2,817,216

PROCESS AND APPARATUS FOR THE SEPARATION, BY RECTIFICATION, OF A GAS MIXTURE CONTAINING AT LEAST THREE COMPONENTS

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Claims priority, application France August 12, 1952

10 Claims. (Cl. 62—123)

The present invention relates to a process for the separation by rectification, of a gas mixture containing at least three components with different boiling points.

An object of the invention is to improve the purity of the most volatile product in the separation; another object is to allow an increase in the extraction yield of the component or components having intermediate boiling point.

The invention applies particularly to the separation of air, considered as a mixture of nitrogen, oxygen and argon; it allows to obtain nitrogen substantially deprived of argon, with a view, for instance, of supplying high purity nitrogen necessary for certain chemical syntheses; it also makes it possible to increase the extraction yield for argon by decreasing the amounts of argon lost with the outgoing nitrogen.

Another example of application of the present invention is given by the separation of mixtures of ethane, ethylene and acetylene obtained by condensation of coke oven gases or cracking gases of petrol refineries. It is known that in these mixtures, acetylene forms with ethane an azeotropic mixture with a boiling point intermediate between those of ethane and ethylene and which thus plays the part of argon in the mixture constituting air, while the ethylene takes the place of nitrogen. The invention makes it possible to extract from this mixture almost the whole of the ethylene in a condition of high purity.

When a mixture of two main components contains an impurity, the boiling point of which is intermediate between those of the main components, it is known to obtain, from the rectification column giving the final products collected outside, a mixture, in a gaseous or liquid condition, having the highest concentration possible in impurity. Thus when it is desired to obtain simultaneously pure oxygen and nitrogen by means of a separating apparatus using a double rectification, there is taken, from the column operating under the lowest pressure, the major part of the argon. If argon is considered simply as an impurity, the mixture thus obtained is evacuated outside of the installation; in spite of this relatively important loss, which decreases by that much the extraction yield for oxygen and nitrogen, it is not possible to obtain in this manner nitrogen practically free of argon.

If, on the contrary, argon is considered as a product meant to be used, the mixture thus obtained is concentrated in an auxiliary column so as to obtain pure argon. The extraction yield in oxygen and nitrogen is then bettered, but the nitrogen obtained remains contaminated by argon; therefore a good extraction yield for argon cannot be reached.

In the process according to the present invention, the gas mixture is rectified in two columns at least, the last one of which receives, at its top, a liquid rich in the most volatile component, condensed at the top of at least one previous column operating under a higher pressure than that of the last column. This process is characterized by the fact that there is collected, at least at

one point of said previous column, located below its top, a mixture which is in process of rectification.

The total number of plates of this previous column, the point at which this collecting is effected—in other words the number of plates arranged between that point and the top of the column—and the relative importance of this collecting may be so selected that the major part of the intermediate component which, but for this collecting, would be in the liquid condensed at the top of said previous column, be present in the mixture thus collected. There is thus obtained, at the top of said previous column, a condensed liquid practically free of the intermediate component; introduced at the top of the last column, this liquid acts as an efficient barrier against the ascent of the intermediate component at the top of that column and the product issuing at the top of said last column consists practically of the most volatile component, free of the intermediate component.

When there are several intermediate components, it may be necessary to effect several collectings at different points.

The mixture in process of rectification may be collected either in a liquid or in a gaseous condition; in the latter case, the mixture thus collected is evacuated outside the installation after having been expanded, preferably with a production of external work.

In accordance with the preferred form of embodiment of the invention, the mixture in process of rectification is collected in a liquid condition and is introduced after being expanded, in the last column at a point located underneath the inlet for the liquid rich in the most volatile component.

In a modification of this form of embodiment, the mixture, collected in a liquid condition, is introduced in an auxiliary concentration column, which operates at the same pressure as said previous column, and the heating of which is ensured by a vaporizer-condenser arranged in said previous column undereneath the outlet for the liquid thus collected, the vapour obtained being introduced into said previous column.

Preferably, the liquid obtained in the auxiliary concentration column is introduced, after expansion, at a point of the last column located below the inlet for the liquid rich in the most volatile component. If the intermediate component, however, is not a product which it is desired to use, the liquid obtained in the auxiliary concentration column may be vaporized by means of a vaporizer arranged in one of the rectification columns, and led outside the installation, after possibly recuperating its cold; this solution makes it possible to simplify the installation and to cut down the number of plates in the columns.

In a second modification of the preferred form of embodiment, there is collected, at the top of said previous column an uncondensed vapour, consisting of the most volatile component in a practically pure condition, and it is made to go through a cycle during which it is compressed to a pressure higher than that of said previous column, and liquefied in indirect contact with a liquid of said previous column, the liquid obtained being introduced, after expansion, at the top of one of the two columns in question.

When using, for the rectification of the gas mixture only two columns operating at different pressures, the so-called "previous column" is that in which the gas mixture is introduced directly after cooling.

On the contrary, when using, for the rectification of the gas mixture, three columns, operating under different, decreasing pressures, the so-called previous column is that which operates under the pressure intermediate between those of the two other columns. In the latter case, if the intermediate component is not wanted for

use as a product, the liquid in process of rectification, collected in the intermediate column, may be vaporized by means of a vaporizer arranged in one of the three columns and led outside the separation installation after possibly recuperating its cold; this allows a simplification of the apparatus and a decrease in the number of plates in the columns.

The intermediate component may be evacuated with the least volatile component. One can, however, according to need, use jointly with the various forms of embodiment of the invention mentioned above, any one of the already known processes for obtaining pure products. Thus, if the least volatile component is desired in a practically pure condition, there is collected, at an intermediate point of the last column, a mixture which is enriched in the intermediate component. If the intermediate component is itself desired for use as a product, the mixture enriched in the intermediate component issuing from the last column is rectified in an auxiliary column operating at the same pressure as the last column, so as to obtain the intermediate component at a high concentration.

By way of example, there is shown, in the appended drawing, four types of embodiment of the invention applied mainly to the separation of air considered as a mixture of nitrogen, oxygen and argon.

Figure 1 shows, diagrammatically, a complete installation for the production of nitrogen, oxygen and argon according to the preferred type of embodiment of the invention.

Figure 2 represents, diagrammatically, a double column apparatus according to a modification of this preferred type of embodiment, which is also applicable to the separation of gas mixtures of ethane, ethylene and acetylene.

Figure 3 shows, diagrammatically, a double column apparatus according to another modification of the preferred type of embodiment.

Figure 4 shows, diagrammatically, a three column apparatus also operating in accordance with the invention.

In Figure 1, the air, previously compressed, for instance to about 10 atmospheres absolute, and cooled in a known manner, is brought in by the pipe **1**; it goes through the exchanger **2** in counter-current to the nitrogen and oxygen issuing from the installation through the pipes **3** and **4**; the air then goes through the liquefier **5**, still in counter-current to the nitrogen and oxygen issuing from the apparatus. At a point **6** of the liquefier, air is collected in a gaseous condition, which is expanded in the expansion machine **7** and introduced, through the pipe **8**, at the base of the column **9** operating under a pressure higher than the atmospheric pressure. The remainder of the compressed air is collected in a liquid condition and sent, through the pipe **10** to the condenser-vaporizer **11** of an auxiliary column **12** which will be referred to later.

The air introduced at the base of column **9** is separated, there, in a known manner, into a so-called "rich liquid," containing practically all the oxygen, which gathers at the bottom of column **9** at **13**, and a so-called "poor liquid," containing practically pure nitrogen, condensed at the top of column **9** in the condenser-vaporizer **14** and collected at **15**. The rich liquid is sent up through the pipe **16**, expanded through the valve **17** and introduced at an intermediate point **18** of the second column **19** operating under a pressure slightly higher than the atmospheric pressure. The poor liquid is sent up through the pipe **20**, expanded through the valve **21** and introduced at the top of the column **19**.

According to the invention, there is collected, at a point **22** of the first column **9**, a mixture, in the liquid condition, in which the argon content is important with respect to the oxygen content and this liquid is sent up through the pipe **23**, expanded through the valve **24** and

introduced at a point **25** of the second column **19** below the top of said second column.

The number of plates in the first column **9** is preferably larger than that of a column of the same type comprising no tapping off at **22**. In this manner, the liquid collected at **15** contains practically no argon, any more. The two washing liquids tapped off at **15** and **22** are poured to different levels in the second column **19** so as to allow an efficient use of their difference in composition. It is thus possible to extract, at **26**, at the top of column **19**, nitrogen gas practically free of argon.

In Figure 1, the argon is extracted at a high concentration by means of the auxiliary column **12**, operating at the same pressure as column **19**. There is tapped off at a point **27** of column **19** a gas mixture rich in argon, which is introduced at the base of column **12**. The mixture is separated in a known manner; there is collected at the base of column **12** a heavy liquid, free of argon, which is introduced in column **19** substantially at the same point **27** where the gas mixture rich in argon is tapped off, and there is collected at **28**, at the top of column **12** a gas highly concentrated in argon. The reflux liquid is obtained in that column, by means of the tubular bundle **11** in which is vaporized the liquid air brought through the pipe **10** and previously expanded through the valve **29**. The vaporized air is introduced into the column **19** at a suitable point **30**. Practically pure oxygen gas is extracted at **31**. Instead of liquid air, one may also use, in the tubular bundle **11** part of the rich liquid tapped off at **13**; in such a case, liquid air is introduced in a known manner in column **9**.

Only the separation apparatus proper has been shown in Figure 2. This apparatus comprises an auxiliary nitrogen cycle designed for obviating the insufficient reflux at the top of the second column **19**. The tapping off of liquid at **22** in the first column, **9**, is compensated by the decrease in the amount of liquid sent up through the pipe **20**; it is accompanied, therefore, by a decrease in the amount of reflux liquid used at the upper portion of the second column **19** and, in some cases, for instance for obtaining a complete separation of the components and their production in a condition of high purity, the amount of washing liquid thus used may be insufficient for obtaining the desired result.

For obtaining a supplement of washing liquid, there is tapped off from the top of the condenser **14** a gas consisting of pure nitrogen practically free of argon, and it is sent through the pipe **32** to a compressor **33**. An exchanger **34** cools the compressed nitrogen by indirect contact with the cold nitrogen coming from the condenser **14**. The compressed nitrogen then goes through a coil **35** immersed in the rich liquid at the bottom of column **9** and its pressure is sufficient for its liquefaction. The liquid nitrogen thus obtained is expanded through the valve **36** and introduced at the top of column **9**, at **15**. The liquefying of nitrogen in the coil **35** is accompanied by the vaporization of the rich liquid of column **9**. The heating of the bottom of column **9** thus obtained makes it possible to increase the power of rectification of the first column; consequently the compressed air is introduced at a point **37** placed slightly above the base of column **9**, a few plates being arranged between that point **37** and the base.

In this apparatus, the production of argon is not contemplated. There is no auxiliary column **12**; the argon is simply evacuated with the oxygen at **31**, while pure nitrogen, free of argon is extracted through **26**.

It should be noted that the auxiliary nitrogen cycle could be realized by tapping off pure nitrogen at the top of the second column **19**.

The apparatus just described with reference to Figure 2, is also suitable for the separation of mixtures of ethane, ethylene and acetylene in a gaseous condition. In such a case, the auxiliary cycle is an ethylene cycle and the

azeotropic mixture of acetylene and ethane comes out with the ethane at 31.

In Figure 3, there is shown another double column separation apparatus according to the invention, in which one remedies to the insufficiency of the washing liquid at the top of the second column 19 not by means of a cycle of pure nitrogen but by means of an auxiliary concentration column 38, operating at the same pressure as column 9. The liquid tapped off at 22, instead of being taken up directly in column 19 at 25 as in the two previous figures, is introduced at the top of the auxiliary column 38, the heating of which is ensured by a tubular bundle 39 arranged in column 9 at a suitable place, and playing in the latter the part of an intermediate condenser.

The liquid tapped off at 22 is separated, in that column 38, into a heavy liquid which gathers at the bottom of column 38 and a vapour which is collected at the top of said column and introduced into column 9 at a point 40 corresponding to its composition. This vapour increases, in the top of column 9 the amount of the most volatile product and consequently that of the reflux liquid collected at 15. A piping 42 supplies the bundle 39 with liquid from the bottom of column 38, while a piping 41 ensures the return, to said column 38, of the portion of said liquid which is vaporized in bundle 39. The non vaporized portion is sent up through the pipe 23, expanded at 24 and introduced at a point 25 of the second column 19 like, previously, thet liquid tapped off at 22, but the liquid thus treated is more concentrated in argon than the liquid tapped off at 22 in the cases of the first two figures. On Figure 3, the column 19 comprises a third outlet 43 for the evacuation of the argon in a dilute condition.

Figure 4 shows a three column separation apparatus. In addition to the above described columns 9 and 19, this apparatus comprises a third column 44 operating at a pressure which is intermediate between those of the two other columns. This intermediate column 44 is heated by means of an intermediate condenser 45 consisting of a tubular bundle arranged in column 9; to this effect, a piping 46 supplies the condenser 45 with liquid from the bottom of the auxiliary column 44 and a piping 47 brings back to the bottom of said column the vaporized portion of that liquid, while the non vaporized portion is sent up through the piping 48, expanded at 49 and introduced into the tubular bundle 50 of the top of the auxiliary column 44; a piping 51 introduces the vapour produced into the column 19 at a level corresponding to its composition.

The intermediate column 44 is supplied with rich liquid from the column 9 through a piping 52 after expansion at 53. The poor liquid collected at 15, on the contrary, is sent up directly to the top of column 19. But no intermediate tapping off is effected as in the previous figures at 22. The tapping off is effected, according to the invention, on the intermediate column 44, at a point 54 arranged underneath the top of this latter column. The liquid thus tapped off is sent up through the piping 55, expanded at 56 and introduced into the column 19 at a point 57 arranged underneath the top of this column. There is collected at 58, underneath the tubular bundle 50 a portion of the reflux liquid constituted by pure nitrogen, practically free of argon. This liquid is sent up through the piping 59, expanded at 60 and introduced at 61 at the top of the column 19.

In order that the liquid collected at 15 be also constituted by nitrogen practically free of argon, the first column 9 must be given a number of plates allowing a complete separation of argon and consequently higher than that which corresponds to the complete separation of oxygen alone. Further, the amount of reflux liquid in column 9 must be sufficient to cause all the argon to pass into the rich liquid collected at the bottom of the column; this amount, higher than the one used previously, is obtained by means of the use of the third column 44.

The amounts of liquid nitrogen sent up through the pipes 55 and 59 decrease by the same amount the amount of liquid nitrogen to be taken from 15 under the condenser of the column 9.

There is thus extracted from the top of the column 19, at 26, pure nitrogen gas practically free of argon, at the base of the column 19 at 31 practically pure oxygen gas and, through a third outlet, at 43, impure nitrogen containing oxygen and argon.

The above described devices may, of course, be used in various combinations; thus in the case of Figure 4, which comprises three columns, it may be convenient to effect a tapping off of the mixture in process of rectification on the first column 9; similarly, all the apparatus described may be provided with an auxiliary column for argon, of the type of column 12 in Figure 1; they may also be modified so as to produce, in a known manner, one or more of the components in a liquid condition.

What I claim is:

1. A process for obtaining the volatile constituent free from any constituent of intermediate volatility from a gaseous mixture containing three components with different boiling points, by successive fractionation at low temperatures in two successive rectifying columns, comprising condensing at the top of the column operating under a pressure higher than that of the last column, a first liquid rich in the most volatile component, introducing said first liquid into the last column as the final reflux liquid, withdrawing from the column in which the first liquid is condensed a second liquid rich in the least volatile component and introducing it into the last column at a low elevation, withdrawing further from the column in which the first liquid is condensed at the point of maximum concentration of the constituent of intermediate volatility a third liquid and introducing it in to the last column at an intermediate point as a wash liquid.

2. A process for obtaining the volatile constituent free from any constituent of intermediate volatility from a gaseous mixture containing three components with different boiling points, by successive fractionation at low temperatures in two successive rectifying columns, comprising condensing, in the top of the column operating under a pressure higher than that of the last column, a first liquid rich in the most volatile component, introducing said first liquid into the last column, at its top as the final reflux liquid, withdrawing from the lower portion of the column in which the first liquid is condensed a second liquid rich in the least volatile component, and introducing it into the last column at a low elevation, withdrawing further from the column in which the first liquid is condensed at the point of maximum concentration of the constituent of intermediate volatility a third liquid and introducing it into the last column as a wash liquid at a point below that at which the first liquid is introduced.

3. An apparatus for the separation, by rectification, of a gas mixture containing at least three components with different boiling points, comprising a high pressure rectifying column and a low pressure rectifying column having a reboiler, means for transferring heat from the top of the high pressure column to the reboiler of the low pressure column to condense a first liquid rich in the most volatile component at the top of the high pressure column, piping means for introducing said first liquid into the last column, at its top, piping means for withdrawing from the bottom of the column in which the first liquid is condensed a second liquid rich in the least volatile component, and introducing it into the last column, and further piping means for withdrawing from the column in which the first liquid is condensed, at an intermediate point of said column located under its top, a liquid substantially richer than the first one in at least one intermediate component, and piping means for introducing said liquid in the last column, at a point located underneath the inlet for the first liquid, as a wash liquid.

4. An apparatus for separating a gaseous mixture containing at least three components with different boiling points, by successive fractionation at low temperatures, comprising a high pressure fractionating column, a low pressure fractionating column, means for condensing, at the top of the high pressure column, a first liquid rich in the most volatile component, piping means for introducing said first liquid into the top of the low pressure column, piping means for withdrawing from the bottom of the high pressure column a second liquid rich in the least volatile component, and introducing it into the low pressure column, piping means for withdrawing from the high pressure column, at an intermediate point located underneath its top, a third liquid substantially richer than the first one in at least one intermediate component, means for introducing said third liquid into the low pressure column as a wash liquid, further comprising piping means for withdrawing at the top of the high pressure column a vapor consisting of the most volatile component in a practically pure condition, a compressor for compressing said vapor, heat exchanging means for cooling said compressed vapor, arranged in the bottom of the high pressure column, the pressure of said compressed vapor being sufficient for its liquefaction in said heat exchanging means, and piping means for introducing said liquefied vapor at the top of one of said columns.

5. A process for separating air into its components, by successive liquefaction and fractionation at low temperatures under pressure in two successive rectifying columns, comprising condensing at the top of the rectifying column operating under a pressure higher than that of the last rectifying column, a first liquid rich in nitrogen, introducing said first liquid into the last column as a final reflux liquid, withdrawing from the column in which the first liquid is condensed a second liquid rich in oxygen and introducing it into the last column at a low elevation, withdrawing further from the column in which the first liquid is condensed at the point of maximum concentration of argon a third liquid and introducing it into the last column as a wash liquid.

6. A process for separating air into its components, by successive liquefaction and fractionation at low temperatures under pressure in several successive rectifying columns, operating under successively lower pressures, comprising condensing, at the top of the column before the last one, a first liquid rich in nitrogen, introducing said first liquid into the last column as a first reflux liquid, withdrawing from the column in which the first liquid is condensed a second liquid rich in oxygen and introducing it into the last column at a low elevation, withdrawing further from the column in which the first liquid is condensed at the point of maximum concentration of the constituent of intermediate volatility a third liquid and introducing it into the last column as a wash liquid.

7. An apparatus for the separation, by rectification, of air, comprising a high pressure rectifying column and a low pressure rectifying column having a reboiler, means for transferring heat from the top of the high pressure column to the reboiler of the low pressure column to condense a first liquid rich in nitrogen at the top of the high pressure column, piping means for introducing said first liquid into the last column, at its top, piping means for withdrawing from the bottom of the column in which the first liquid is condensed a second liquid rich in oxygen, and introducing it into the last column, and further piping means for withdrawing from the column in which the first liquid is condensed, at an intermediate point of said column located under its top, a liquid substantially richer than the first one in argon, and feeding it to the last column as a wash liquid.

8. An apparatus for the separation, by rectification, of air, comprising a high pressure rectifying column and a low pressure rectifying column having a reboiler, means for transferring heat from the top of the high pressure column to the reboiler of the low pressure column to condense a first liquid rich in nitrogen at the top of the high pressure column, piping means for introducing said first liquid into the last column, at its top, piping means for withdrawing from the bottom of the column in which the first liquid is condensed a second liquid rich in oxygen, and introducing it into the last column, and further piping means for withdrawing from the column in which the first liquid is condensed, at an intermediate point of said column located under its top, a third liquid substantially richer than the first one in argon, and piping means for introducing said liquid in the last column, at a point located underneath the inlet for the first liquid, as a wash liquid.

9. An apparatus for separating air by successive fractionation at low temperatures, comprising a high pressure fractionating column, a low pressure fractionating column having a reboiler, means for transferring heat from the top of the high pressure column to the reboiler of the low pressure column to condense a first liquid rich in nitrogen at the top of the high pressure column, piping means for introducing said first liquid into the top of the low pressure column, piping means for withdrawing from the bottom of the high pressure column a second liquid rich in oxygen, and introducing it into the low pressure column, further piping means for withdrawing from the high pressure column, at an intermediate point located underneath its top, a third liquid substantially richer than the first one in argon and means for introducing said third liquid into the low pressure column as a wash liquid.

10. A process for separating a gaseous mixture containing at least three components of different boiling points, by successive rectification at low temperatures in at least two successive rectifying columns, comprising condensing, in at least one of the columns operating under a pressure higher than that of the last column, a first liquid rich in the most volatile component, introducing said first liquid into the last column, withdrawing from the column in which the first liquid is condensed a second liquid rich in the least volatile component and introducing it into the last column, withdrawing further from the column in which the first liquid is condensed a third liquid substantially richer than the first one in at least one intermediate component and introducing it into the last column as a wash liquid, still further withdrawing in the column in which the first liquid is condensed a vapor consisting of the most volatile component in a practically pure condition, compressing said vapor, liquefying said compressed vapor by heat exchange with a liquid rich in the least volatile component of the column in which the first liquid is condensed, and introducing said liquefied vapor as a reflux liquid in at least one of said columns.

References Cited in the file of this patent

UNITED STATES PATENTS

1,083,988	Claude	Jan. 13, 1914
1,471,832	Davis	Oct. 23, 1923
1,512,268	Barbet	Oct. 21, 1924
1,880,981	Pollitzer et al.	Oct. 4, 1932
2,411,711	De Baufre	Nov. 26, 1946
2,577,701	Deming et al.	Dec. 4, 1951