

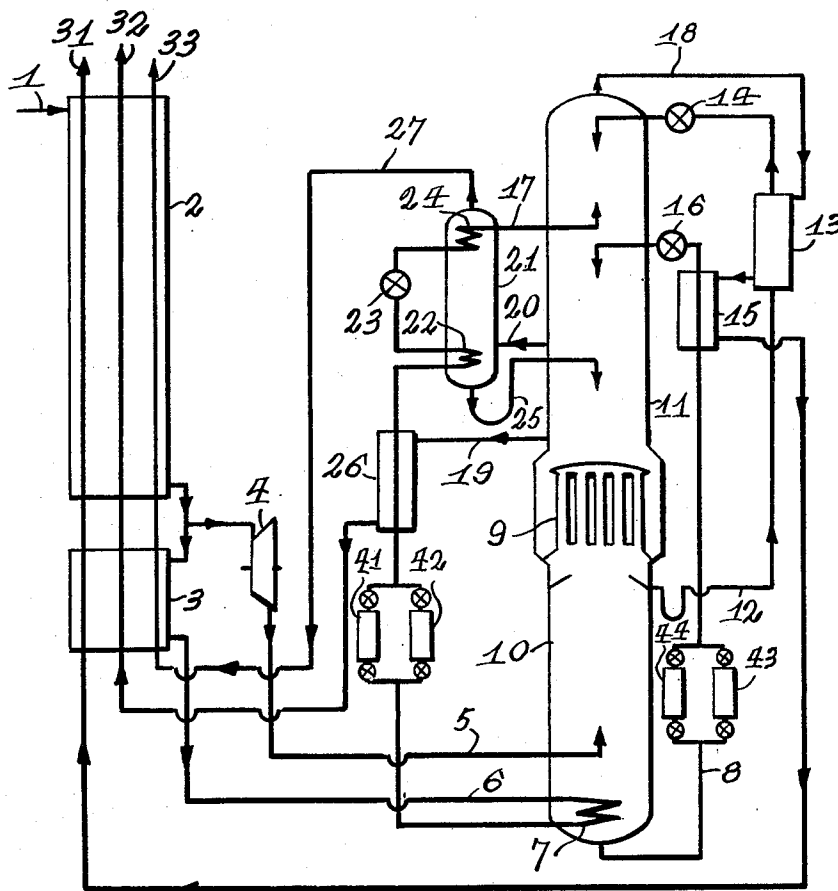
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LOW TEMPERATURE SEPARATION OF GASEOUS MIXTURES

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## LOW TEMPERATURE SEPARATION OF GASEOUS MIXTURES

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The present invention has for an object a process of separating by rectification a gaseous mixture containing at least three constituents, having different equilibrium constants, for example, air considered as a mixture of oxygen, nitrogen, and argon, the latter being of vapor-pressure (equilibrium constant) intermediate the other two. For the sake of clarity, the invention will be explained, using air as an example.

In known procedures, air is separated by rectification into nitrogen and oxygen in acceptable degrees of purity, using an apparatus having two rectification columns operating at different pressures and in mutual connection with a heat exchange mechanism, including means acting as a condenser at the top of the high pressure column and as a vaporizer at the base of the low pressure column. In these procedures there has been extracted from the low pressure column a mixture of the major part of the argon contained in the air to be separated, as well as part of at least one of the other principal components, oxygen and nitrogen, and this mixture has been rectified in an auxiliary column, operating at a pressure in the neighbourhood of that of the low pressure column of the principal assembly. The rectification carried out in the auxiliary column yields a concentrated fraction of argon, which can then be purified by chemical or physical processes.

This fraction is generally a mixture made up essentially of oxygen and argon, the latter constituting about 10% of the mixture which feeds the auxiliary column.

Considering the closeness of the boiling points of oxygen and argon  $-182, 95^{\circ}$  C. and  $-185, 65^{\circ}$  C. respectively, the separation of these two components presents difficulties, and in practice separation is always imperfect. The essential difficulty resides in obtaining sufficient reflux ratio at the top of the auxiliary column to cause the argon, scarcely more volatile than the oxygen, to leave the top of the auxiliary column relatively free of oxygen.

To obtain this reflux, various solutions have been proposed as, for example, the use of a cooling cycle fed either by argon or by nitrogen. Another solution, simpler, but leading to inferior yields, consists in drawing in gaseous state, a part of the nitrogen produced by the principal column at the greatest pressure, in liquefying this nitrogen in an exchanger placed at the base of the auxiliary column, and vapourizing it, after expanding it in an exchanger placed at the top of the auxiliary column. The quantity of nitrogen thus taken from the main column is consequently lacking at the top of the low pressure column, where the required reflux is provided by nitrogen drawn in the liquid state from the high pressure column, then expanded. Only a limited quantity of this nitrogen can be disposed of to assure operation of the auxiliary column, if the operation of the main column is not to be interfered with. The yield of argon is, as a result mediocre, and the concentration of the argon fraction obtained is low.

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The present invention permits on the contrary the yield, without an auxiliary cycle and with a relatively simple apparatus, of almost all the argon in concentrated form and simultaneously the oxygen and the nitrogen in a high degree of purity.

The present invention employs the generally known arrangement, on one hand of two columns functioning at different pressures and mutually connected with a heat exchange apparatus forming a condenser at the top of the highest pressure column and a vaporizer at the base of the lowest pressure column, and on the other hand an auxiliary column fed by an intermediate fraction drawn from the lowest pressure column and containing all or a part of the argon of the air to be separated.

These three columns are hereafter called respectively, the high pressure column, the low pressure column, and auxiliary column.

The invention embodies the following features. All air to be separated, compressed to a pressure greater than that of the high pressure column, and cooled by exchange with the products of its separation to a temperature appreciably higher than its temperature of liquefaction under the said pressure, is divided into two parts. One of these parts is introduced into the high pressure column with an expansion effected, preferably with performance of external work, to the pressure of this column. The other part is cooled to the temperature of liquefaction, and partially liquefied by heat exchange with the products of separation. The liquefaction is then completed in a coil located at the bottom of the high pressure column. The liquid thus obtained is used, after expansion, to cause by its vaporization, cooling by indirect contact with the upper part of the auxiliary column. Optionally, the liquid from the coil at the bottom of the high pressure column may first be passed through a coil at the bottom of the auxiliary column. The gas resulting from this vaporization is introduced into the low pressure column.

There is thus extracted in the apparatus, on the one hand argon at the top of the auxiliary column, and on the other hand nitrogen and oxygen respectively at the top and at the bottom of the low pressure column.

The following example, which is not intended to be limiting, illustrated by reference to the attached drawing of a preferred apparatus, will make the principle of the invention better understood.

The air to be separated into oxygen, nitrogen and argon, previously freed by known methods of entrained humidity and carbon dioxide and compressed to about 15 atmospheres and at ambient temperature enters at 1 a first heat exchanger 2 cooled by separated gases leaving in the neighbourhood of atmospheric pressure. Thus cooled to around  $-140^{\circ}$  C. in the exchanger 2, the air is divided into two parts. A first part representing approximately 70% of the air to be separated is expanded by the turbine 4 to a pressure of approximately five atmospheres and enters at this pressure, by the tube 5, into the high pressure column 10, several trays above the bottom. The second part is cooled in a heat exchanger 3 to a temperature of about  $-158^{\circ}$  C., and enters by the tube 6 into a coil 7 located at the lower part of the column 10.

The column 10, according to the usual arrangement, is surmounted by a column 11 functioning in the neighbourhood of atmospheric pressure. The two columns are thermally connected by the vapourizer-condenser 9 forming a condenser at the top of the column 10 and a vapourizer at the base of the column 11.

Part of the air to be separated, introduced into the column 10 and forming, as already stated, approximately 70% of the total amount of the starting air, is rectified in this column yielding on the one hand nitrogen which

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is condensed in total to the liquid state at the top of the column in the condenser 9, and on the other hand a liquid containing all the oxygen and the argon of the air, and having an oxygen content of approximately 50%. One part of the condensed nitrogen and all the liquid rich in oxygen leaves the column 10 respectively by the tubes 12 and 8 to enter the low pressure column 11. The condensed nitrogen is super-cooled in the exchanger 13 then expanded by the valve 14 and enters the top of the column 11, where it is used as a washing liquid. The liquid rich in oxygen is super-cooled in the exchanger 15, expanded by the valve 16 and enters the column 11 half-way up the latter.

The column 11 also receives, as will be explained later, the fraction of the air to be separated, not introduced into the high pressure column, and which is liquefied in the coil 7. This fraction having about 30% of the total of the air, enters the column 11 in a gaseous state by the tube 17.

The following products are extracted by the column 11:

- (a) At the top by the tube 18, gaseous nitrogen,
- (b) At the bottom by the tube 19, gaseous oxygen,
- (c) Laterally, by the tube 20, a gaseous fraction formed of about 10% argon and 90% oxygen with only traces of nitrogen.

This last fraction is introduced into the auxiliary column 21 near the base. The column 21 functions at the same pressure as the column 11. The column 21 is heated at the bottom on the one hand by a gaseous fraction having its origin in the column 11 (stream 20), and on the other hand optionally by a coil 22 into which there passes the air liquefied previously in the coil 7 and having been preferably subjected to sub-cooling of several degrees in the exchanger 26 cooled by oxygen drawn from the column 11. After its passage into the coil 22, this air is expanded by the valve 23 to the pressure of the column 11. It is vaporized in the coil 24, located at the top of the column, causing by this vapourization the formation of the required reflux, then it is introduced into the tube 17 in the column 11, substantially at the same height as the liquid rich in oxygen arrives by the tube 8. From the top of the auxiliary column 21 there is drawn a gaseous fraction containing about 90% argon of the air to be separated, and not having more impurities than about 3% oxygen and about .5% nitrogen. From the base of the auxiliary column 21 there flows a liquid made up of oxygen and argon which returns by the tube 25 to the column 11.

The oxygen drawn in gaseous state from the column 11 is preferably used to cool, in the exchanger 26, the air under pressure of approximately 15 atmospheres which has been liquefied in the coil 7, and then is caused to leave by the conduit 32 after having been reheated in the exchanger 3 and 2 in counter-current with the entering air. Alternatively, the exchanger 26 may be omitted and the oxygen (stream 19) carried directly from the column 11 to the exchanger 3.

The gaseous nitrogen leaving the top of the column 11 cools successively, in the exchanger 13 and 15, the liquid nitrogen and the liquid rich in oxygen, all having their origin in the column 10, then leaves by the tube 31 after being reheated, as is the oxygen, in the exchangers 3 and 2.

The argon leaving the top of the column 21 by the tube 27 is equally reheated in the same exchangers and leaves by the tube 33.

Since oxygen usually contains hydrocarbon impurities, it is preferable to include filtration means to remove these impurities when the oxygen is in the liquid state. One set of filters 41, 42 is shown between the coil 7 and the heat exchanger 26. Another set of filters 43, 44 is shown in the pipe line 8. Two filters are shown in each case so that one can be operated while the other is re-

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generated. These filters are preferably of the type in which the impurities are adsorbed on a solid adsorbent.

The comparison of the apparatus described above, with known apparatuses makes the following points clear. The yield in argon separated is better. The argon fraction is substantially pure. The oxygen obtained is substantially pure.

In the usual systems, there is generally introduced the major part of the air, if not all, in the gaseous state at the base of the high pressure column. Consequently, the oxygen is furnished in the form of a liquid of which the oxygen content is at a maximum, the attendant content of the liquid in equilibrium with atmospheric air at 21% oxygen, an amount which is, to be more exact, about 40% under a pressure of 5 atmospheres.

In the apparatus described above, the portion of the air to be separated which enters the high pressure column enters into it several trays above the bottom, this bottom being heated in indirect contact by condensation in the coil 7 of the other portion of the air. The liquid leaving the column 10 by the tube 8 can thus have an amount of oxygen greater than its usual amount, for example, about 50%. Containing more oxygen, this liquid contains less nitrogen. The latter leaves then at the top of the high pressure column in greater quantity. As a result of this it is possible, even though only a part of the air is separated in the high pressure column, for substantially the same quantity of liquid nitrogen to leave the column as in the usual process where all the air enters the high pressure column. The higher part of the low pressure column receiving then the same quantity of washing liquid at the same purity, functions according to normal conditions and furnishes gaseous nitrogen of the usual purity. On the other hand the lower part of the low pressure column being heated by condensation of the same quantity of nitrogen, the yield at the base of this column is equally satisfactory.

The oxygen obtained will be all the more pure since almost the total amount of argon leaves the column 11 by the tube 20, the oxygen being entrained with the argon returning to the column 11 by the tube 25.

Considering that a high proportion (about 30%) of the air to be separated does not pass through the expansion turbine 4, the lowering of the refrigeration which results from it, should be compensated for by a rise of the initial air pressure, a pressure that is around 15 atmospheres where 12 atmospheres suffices for the conventional type of apparatus.

I claim:

1. A process for the separation by liquefaction and rectification, of a gaseous mixture having three principal constituents, utilizing a main column made up of two rectification zones in mutual heat exchange relationship and under different pressures, and an auxiliary column receiving a fraction having its origin in the lower pressure rectification zone and in which a part of the mixture to be separated previously compressed to a pressure higher than that of the higher pressure rectification zone is expanded to the higher pressure and introduced into the higher pressure zone, comprising liquefying another part of the compressed gaseous mixture by indirect heat exchange with a liquid from the higher pressure rectification zone, then utilizing said other part for cooling by indirect contact with the auxiliary column and introducing said other part into the lower pressure zone.

2. A process according to claim 1 in which part of the gaseous mixture under pressure which has been liquefied by indirect heat exchange with a liquid from the high pressure rectification zone is first utilized for heating by indirect contact with the lower part of the auxiliary column, before serving for cooling the upper part of the auxiliary column.

3. A process according to claim 1 in which the said other part is sub-cooled by a gaseous fraction from the

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low pressure column prior to its use for cooling the auxiliary column by indirect contact.

4. A process according to claim 1 in which the said other part is sub-cooled by a gaseous fraction from the low pressure chamber prior to its use for cooling the auxiliary column by indirect contact, and in which the said other part is then utilized for heating by indirect contact with the lower part of the auxiliary column before serving for cooling the upper part of the auxiliary column.

5. A process according to claim 1 in which the gaseous mixture is air and the three principal constituents are oxygen, nitrogen, and argon.

6. A process according to claim 1 in which the gaseous mixture is air and the other constituents are air, nitrogen, and argon and in which part of the oxygen which has been liquefied by indirect heat exchange with a liquid from the high pressure rectification zone is first utilized for heating by indirect contact with the lower part of the auxiliary column, before serving for cooling the upper part of the auxiliary column.

7. A process for the separation by liquefaction and rectification of a gaseous mixture having high, low and intermediate equilibrium constants and utilizing a main column made up of two rectification zones in mutual heat exchange relationship and under different pressures, and an auxiliary column receiving a fraction having its origin in the lower pressure rectification zone and in which a part of the mixture to be separated previously compressed to a pressure higher than that of the higher pressure rectification zone is expanded to the higher pressure and introduced into the higher pressure zone, comprising liquefying another part of the gaseous mixture by indirect heat exchange with a liquid from the higher pressure rectification zone, then utilizing said other part

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for cooling by indirect contact with the auxiliary column thereby to concentrate the constituent of intermediate vapor pressure, and simultaneously vaporizing at least in part said other part.

8. A process according to claim 7 in which the gaseous mixture is air and the three constituents are oxygen, argon and nitrogen.

9. A process according to claim 7, in which part of the gaseous mixture under pressure which has been liquefied by indirect heat exchange with a liquid from the higher pressure rectification zone is first utilized for heating by indirect contact with the lower part of the auxiliary column, before serving for cooling in the auxiliary column.

10. A process according to claim 7, in which the said other part is sub-cooled by a fraction from the low pressure zone prior to its use for cooling in the auxiliary column.

11. A process according to claim 7, in which the said other part is sub-cooled by a fraction from the low pressure zone prior to its use for cooling in the auxiliary column, and in which the said other part is then utilized for heating by indirect contact with the lower part of the auxiliary column before serving for cooling in the auxiliary column.

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