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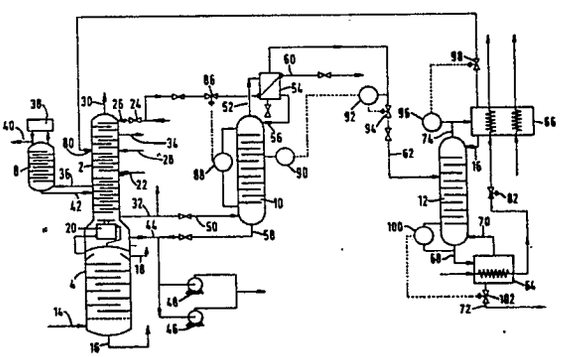
(54) Air separation.

(57) A gaseous feed of oxygen containing both light and heavy impurities is introduced through inlet 50 into a first liquid-vapour contact column 10 thereby producing a first fraction having an enhanced concentration of heavy impurities and a second fraction having a reduced concentration of heavy impurities. A gaseous first stream of the second fraction is condensed in a condenser 54 and returned to the column 10 as reflux through inlet 56. A second stream of the second fraction is fed into a second liquid-vapour contact column 12 having a reboiler 64 in which light impurities are stripped from the feed by ascending vapour. The second stream is introduced into the column 12 at a level above which there are liquid-vapour contact surfaces whereby there is produced at the top of the column 12 a fraction having a substantially greater concentration of light impurities than the feed to that column. A portion of this fraction is condensed in condenser 66 and used to provide reflux for the column 12, while another such portion is subjected to further fractionation in columns 2 and 8 to produce an argon product.



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AIR SEPARATION

This invention relates to air separation. In particular, it relates to the production of what is sometimes termed "ultra high purity" or "ultra pure" oxygen.

Many tens of thousands of tons of high purity oxygen are produced per year worldwide. The oxygen is produced by the well-known process of fractionally distilling air at cryogenic temperatures. The oxygen produced typically has a purity in the range of 99.5 - 99.9%. This purity makes it suitable for use in a large number of industrial processes.

The main impurity in the high purity oxygen is argon. However, there is typically in the order of 10 volumes per million (vpm) of methane. The presence of methane, in particular, may be undesirable in a few processes, for example, the fabrication of micro-electronic products. Accordingly, there is a demand for oxygen of a higher purity than that normally provided.

One way of meeting the demand is to subject the oxygen to a process of catalytic combustion so as to remove traces of methane. However, in some instances, this process is not suitable because the gas becomes contaminated with particles generated from the catalyst granules. Alternative purification methods are known. These generally involve subjecting the normal high purity oxygen to two further cryogenic separation stages, the first involving removal of heavy impurities, such as methane, having a vapour pressure less than oxygen, and the second the removal of light impurities having a vapour pressure greater than oxygen. See, for example, US patent specifications 3 363 427 and 4 755 202.

The process described in US patent 4 755 202 produces from the column removing light impurities a first gaseous product comprising ultra high purity oxygen having a minimum of impurities and second an oxygen product having a level of impurities which makes it acceptable as normal high purity oxygen. This second oxygen product does, however, contain a significant proportion of argon which is itself a valuable commercial product. The invention relates to a process in which at least some of the argon can be recovered.

According to the present invention there is provided a process for producing ultra pure oxygen from a gaseous feed containing oxygen, light impurities and heavy impurities, comprising:

(a) introducing the gaseous feed into a first liquid-vapour contact column, absorbing heavy impurities into descending liquid, and thereby producing a first fraction having an enhanced concentration of heavy impurities and a second fraction having a reduced concentration of heavy impurities;

(b) condensing a first gaseous stream of said second fraction and supplying resulting condensate to the first column as reflux;

(c) withdrawing a second steam of said second fraction from the first column and introducing it into a second liquid-vapour contact column in which light impurities are stripped from descending liquid by ascending vapour, said second column being provided with a reboiler, characterised in that:

(i) the second stream is introduced into the second column at a level above which there are liquid-vapour contact surfaces for the fractionation for the gas whereby there is produced at the top of the column a fraction having a substantially greater concentration of light impurities than the incoming feed;

(ii) condensing a portion of the fraction enriched in light impurities and returning thus formed condensate to the second column as reflux; and

(iii) subjecting a stream of the fraction enriched in light impurities to further fractionation in at least one column other than said first and second columns and recovering an argon product therefrom.

The invention also provides apparatus for performing this process.

Preferably, the stream for further fractionation to recover the light impurity (argon) product is returned to the same column from which the gaseous oxgyen feed is taken. This column is typically the lower pressure column of a conventional double column arrangement and is fitted with a "side column" which receives an argon-enriched feed from the lover pressure column and fractionates that feed to produce a crude argon product and an argon-depleted fluid that is returned to the lower pressure column.

Preferably, the stream taken for further fractionation contains at least 5% by volume of argon.

Preferably, the said second stream is introduced into the said second column as a gas or vapour and not a liquid. This helps to reduce the amount of refrigeration required for the condenser associated with the first column.

Preferably, when the oxygen feed is produced by fractionation of air in a conventional double column, the condenser associated with the said first column is refrigerated by a part of the oxygen-poor liquid ("PL") withdrawn from the higher pressure column of the double column arrangement. We have found that in any conventional double column arrangement, the top of the lower pressure column is typically provided with excessive reflux. This reflux is normally provided by the PL. By taking a portion of the PL to provide

condensation for the said first column, a more suitable rate of supplying reflux to the lower pressure column can be attained.

Preferably, heat for the reboiler associated with the said second column and cooling for the condenser associated with the said second column can be provided by a heat pump circuit in which the working fluid is air.

The process and apparatus according to the invention will now be described by way of example with reference to the accompanying drawing which is a schematic circuit diagram illustrating an air separation plant.

Referring to the drawing, there is shown an arrangement of columns separating air into oxygen, nitrogen and argon products and for producing and ultra pure oxygen product typically containing less than ten volumes per million of impurities. Incoming air feed typically at its dew point is subjected to distillation in a double column 2 comprising a higher pressure column 4 and a lower pressure column 6. The double column 2 provides oxygen and nitrogen products and a feed of argon-enriched oxygen to a side column 8 in which the argon-enriched oxygen is subjected to further separation to produce a crude argon product. The arrangement of columns shown in the drawing also includes a first purification column 10 for purifying gaseous oxygen produced by the double column 2 and a second purification column 12 which provides further purification and produces an ultra high purity oxygen product typically containing less than 1 volume per million of impurities.

The double column 2 and the side column 8 and their operation are generally conventional (save for the return of a stream from the column 12 to the column 6 which will be described herein below). It will be appreciated that the heat exchangers that are normally employed in association with the columns 2 and 8 are omitted from the drawing for purposes of ease of illustration. For one typical arrangement of such heat exchangers and for a description of the operation of a double column, with a side column for producing crude argon, attention is directed to Figure 1 of European patent application 296 342 A and the description thereof. Since this invention is primarily concerned with the purification of the oxygen product from the double column 2, only an abbreviated description will be given herein of its operation and of the operation of the column 8.

Air is introduced into the higher pressure column 4 through an inlet 14. It is separated into oxygen-enriched liquid ("RL") and oxygen-poor liquid ("PL"). The column 4 is provided with a condenser 20 at its top which provides liquid nitrogen reflux for it and which also provides reboil for the lower pressure column 6. A stream of oxygen-rich liquid is withdrawn from the bottom of the column 4 through an outlet 16 and after subcooling (by means not shown) is introduced into the lower pressure column 6 through an inlet 22. The fluid that is thus introduced into the column 6 is separated into oxygen and nitrogen fractions. To provide liquid nitrogen reflux for the lower pressure column 6 a stream of PL is withdrawn from the higher pressure column 4, is subcooled (by means not shown) and is then divided into two sub-streams, one of which is passed through a Joule Thomson valve 24 and then through an inlet 26 leading into the top of the lower pressure column 6.

If desired, air may be introduced directly into the lower pressure column 6 through an inlet 28. This air is known as "Lachmann air" and its use is well known in the art. Oxygen and nitrogen fractions are produced, both typically of a purity between 99.0 and 99.9%. A gaseous nitrogen product is withdrawn from the top of the column 6 through an outlet 30 and a gaseous oxygen product from the bottom of the column 6 through an outlet 32. In addition, the waste nitrogen stream is withdrawn from the column 6 through an outlet 34 (and is used for the purposes of regenerating a reversing heat exchanger or other purification unit for removing water vapour and carbon dioxide from the air feed). An argon-enriched oxygen vapour stream is withdrawn from the column 6 through an outlet 36 and is introduced into the column 8 which is provided with a condenser 38 and which separates the argon-enriched oxygen into a crude argon fraction which collects at the top of the column 8 and is typically withdrawn in liquid state through the outlet 40. In addition, a liquid oxygen stream is returned from the bottom of the column 8 through the outlet 42 to the column 6.

As well as producing a gaseous oxygen product, the double column 2 may if desired be used to produce a liquid oxygen product and a stream of liquid oxygen may be withdrawn from the column 6 through an outlet 44 and then pumped to storage by means of pumps 46 and 48.

A part of the gaseous oxygen product produced by the column 2 is introduced as a stream into the first purification column 10 at its bottom. In this column heavy impurities, particularly methane, are stripped from the gaseous oxygen by being adsorbed into the liquid phase. Accordingly, as the vapour ascends the column 10 so it becomes leaner in heavy impurities until at the top of the column it is essentially free of them. A stream of vapour is withdrawn from the top of the column 10 through the outlet 52 and a part of it is condensed in a condenser 54 and is returned to the top of the column 10 through the inlet 56. As the

liquid descends the column 10 so it becomes progressively richer in heavy impurities. A liquid oxygen fraction containing essentially all the heavy impurities thus collects at the bottom of the column 10 and a stream of such liquid oxygen is withdrawn through the outlet 58. Since typically the oxygen feed to the column 10 will include in the order of 10 volumes per million of methane, it will be appreciated that the liquid oxygen withdrawn through the outlet 58 will still be of an acceptable purity for use in most commercial applications and accordingly it is united with the liquid oxygen product withdrawn from the column 2 through the outlet 44.

Refrigeration for the condenser 54 is provided by a stream of the PL from the column 4. This stream is vaporised as it passes through the condenser 54 and the resulting nitrogen vapour leaves the condenser 54 through an outlet 60 and is typically united with the gaseous nitrogen withdrawn from the column 2 through the outlet 30.

Not all the oxygen essentially free of heavy impurities withdrawn from the column 10 through the outlet 52 is condensed in the condenser 54. A stream of uncondensed oxygen free of heavy impurities is withdrawn from the condenser 54 (or may by-pass the condenser 54 altogether) and is introduced into the second purification column 12 through an inlet 62 located at an intermediate level thereof. The column 12 is operated so as to separate the oxygen into a fraction that is essentially free of low boiling point impurities (and is thus capable of forming an ultra-high purity oxygen product) and a fraction which is enriched more than ten-fold in argon compared with the argon content of the oxygen entering the column 12 through the inlet 62. The column 12 is thus provided with a reboiler 64 and a condenser 66. The reboiler 64 provides an upward flow of vapour through the column and the condenser 66 provides a downward flow of liquid. Accordingly the vapour becomes progressively richer in light impurities (argon) as it ascends the column 12 and the liquid becomes progressively leaner in light impurities (argon) as it descends the column 12. A liquid oxygen fraction essentially free of both light and heavy impurities (ie. containing no more than 1 vpm of impurities) collects at the bottom of the column 12. A stream of this ultra high purity oxygen is withdrawn from the bottom of the column 12 through an outlet 68 and passed through the reboiler 64 in which it is partially reboiled. The vapour thus formed is returned to column 12 through an inlet 70 while the residual liquid is passed through pipe 72 to storage (not shown).

In addition to the withdrawal of liquid through the outlet 68, a stream of vapour enriched in argon is withdrawn from the top of the column 12 through an outlet 74. This stream is then passed into the condenser 66 in which it is partially condensed. The condensate is returned to the top of the column 12 through an inlet 76 while the uncondensed vapour is returned to the lower pressure column 6 through an inlet 80. Since typically the fraction collecting at the top of the column contains at least 5% by volume of argon, this recycling of the vapour from the column 12 to the column 6 enhances the total yield of argon from the process. Since also the temperature of this stream tends to be lower than the average temperature in the column 6, cold is also recovered. Typically, inlet 80 is situated at the same level as the inlet 28 for Lachmann air.

Heating for the reboiler 64 and cooling for the condenser 66 are preferably provided by means of a heat pump cycle that uses air as the working fluid. The air is typically taken from the stream that is fed to the column 4 and is introduced into the reboiler 64 at a temperature of 102 K under pressure of approximately 6.5 bar absolute. The air is fully condensed in the condenser 64 and is then flashed through a Joule-Thomson valve 82 so as to reduce its temperature. This reduced temperature condensate then flows through the condenser 66 so as to provide at least part of the cooling for that condenser. If further condenser duty is required, this may be provided by passing a further stream of PL from the column 4 through the condenser 66. The nitrogen (now gaseous) exiting the condenser 66 may be united with the gaseous nitrogen product withdrawn from the column 6 through the outlet 30, while the air leaving the condenser 66 may be warmed in the main heat exchanger(s) (not shown) of the plant and vented to the atmosphere.

It will be appreciated that the columns 4, 6, 8, 10 and 12 will all contain means for producing intimate contact between ascending vapour and descending liquid. Typically, such means are provided by sieve trays although other contacting apparatus such as a packing may be used. In the process according to the invention, the first purification column 10 typically has from 6 to 10 theoretical trays and operates at a reflux or L/V ratio of about 0.5 while the second purification column 12 includes from 60 to 80 theoretical trays operating at a reflux ratio of approximately 60. The inlet 62 is positioned at a level 21 trays from the top of the column. Further, in this example about one third of the vapour withdrawn from the column 10 through the outlet 52 is returned to the column as reflux while the remaining two thirds are condensed and introduced into the column 12 as feed.

If desired, the columns 10 and 12 and associated condensers and reboiler can be retro-fitted to an existing air separation plant including the columns 4, 6 and 8.

In order to control operation of the first purification column 10, two main controls may be employed. The first control adjusts the flow of PL to the condenser 54 by adjusting the setting of the flow-control valve 86. The setting of the valve is controlled by sensing the pressure drop encountered by the rising vapour in the column 10 which is monitored by a pressure sensor 88. The arrangement allows for a constant pressure drop to be maintained and therefore for the oxygen free of heavy impurities to be withdrawn from the column 10 at a constant rate equal to the required design rate.

The purity of the stream withdrawn through the outlet 52 is maintained indirectly. An analyser-cum-controller analyses the hydrocarbon content of the vapour apart way up the column 10. This analyser 90 biases as valve controller 92 so as to control the setting of a flow control valve 94 in a conduit through which the gaseous oxygen free of heavy impurities flows on its way to the inlet 62 to the column 16. Adjustment of the position of the valve 94 will adjust the exact proportion of the fluid entering the condenser 54 that is returned to the column 10 as reflux through the inlet 56. Accordingly, the arrangement of the analyser 90, controller 92 and valve 94 is able to maintain the sensed hydrocarbon concentration in the vapour at a chosen level such that the level of hydrocarbon impurity in the gas withdrawn through the outlet 52 of the column 10 does not exceed a chosen level.

Two main controls are also used for the column 12. First, an analyser-cum-controller 96 analyses the argon concentration in the oxygen leaving the top of the column 12 through the outlet 74 and adjusts the setting of a flow control valve 98 in the conduit returning the argon-enriched oxygen to the column 6 near the inlet 80. This accordingly adjusts the amount of vapour to be condensed and hence the reflux rate. Accordingly, any fluctuation in the purity at the top of the column 74 can be corrected. The control of the flow rate of the ultra high purity oxygen withdrawn through the outlet 68 of the column 12 is effected by means of a controller 100 which by adjusting a flow control valve 102 in the ultra high purity oxygen outlet pipeline 72 enables a constant head of liquid to be maintained in the reboiler 64 so that there is a constant product withdrawal rate.

We have performed a computer simulation of the operation of the plant shown in the drawing and have obtained the results set out in Table 1 below.

TABLE 1

		Column 10		Column 12	
	Feed to Inlet 14	Top Outlet 52	Bottom Outlet 58	Recycled Ar-enriched O_2	Ultra High purity O_2 product
Flowrate as % of feed to inlet 14	100	67	33	2	64
Temperature [K]	95.5	94.6	95.5	94	96
Pressure [Bara]	1.61	1.54	1.61 (+ head)	1.45	1.6 (min)
Physical state	VAP	VAP	LIQ	VAP	LIQ
Impurities:					
Methane	10vpm	5ppb	55vpm	0ppb	6ppb
Argon	0.3%	0.3%	0.3%	8%	100ppb
Krypton	7vpm	0ppb	25vpm	0ppb	0ppb
KEY: ppb = volumes per billion (thousand million)					
vpm = volumes per million					

Claims

1. A process for producing ultra pure oxygen from a gaseous feed containing oxygen, light impurities and heavy impurities, comprising:

(a) introducing the gaseous feed into a first liquid-vapour contact column, absorbing heavy impurities

into descending liquid, and thereby producing a first fraction having an enhanced concentration of heavy impurities and a second fraction having a reduced concentration of heavy impurities;

(b) condensing a first gaseous stream of said second fraction and supplying resulting condensate to the first column as reflux;

(c) withdrawing a second stream of said second fraction from the first column and introducing it into a second liquid-vapour contact column in which light impurities are stripped from descending liquid by ascending vapour, said second column being provided with a reboiler, characterised in that:

(i) the second stream is introduced into the second column at a level above which there are liquid-vapour contact surfaces for the fractionation for the gas whereby there is produced at the top of the column a fraction having a substantially greater concentration of light impurities than the incoming feed;

(ii) condensing a portion of the fraction enriched in light impurities and returning thus formed condensate to the second column as reflux; and

(iii) subjecting a stream of the fraction enriched in light impurities to further fractionation in at least one column other than said first and second columns and recovering an argon product therefrom.

2. A process according to claim 1, in which the stream for further fractionation to recover the light impurity (argon) product is returned to the same column from which the gaseous oxgyen feed is taken.

3. A process according to claim 2, in which said same column is typically the lower pressure column of a conventional double column arrangement and is fitted with a "side column" which receives an argon-enriched feed from the lower pressure column and fractionates that feed to produce a crude argon product and an argon-depleted fluid that is returned to the lower pressure column.

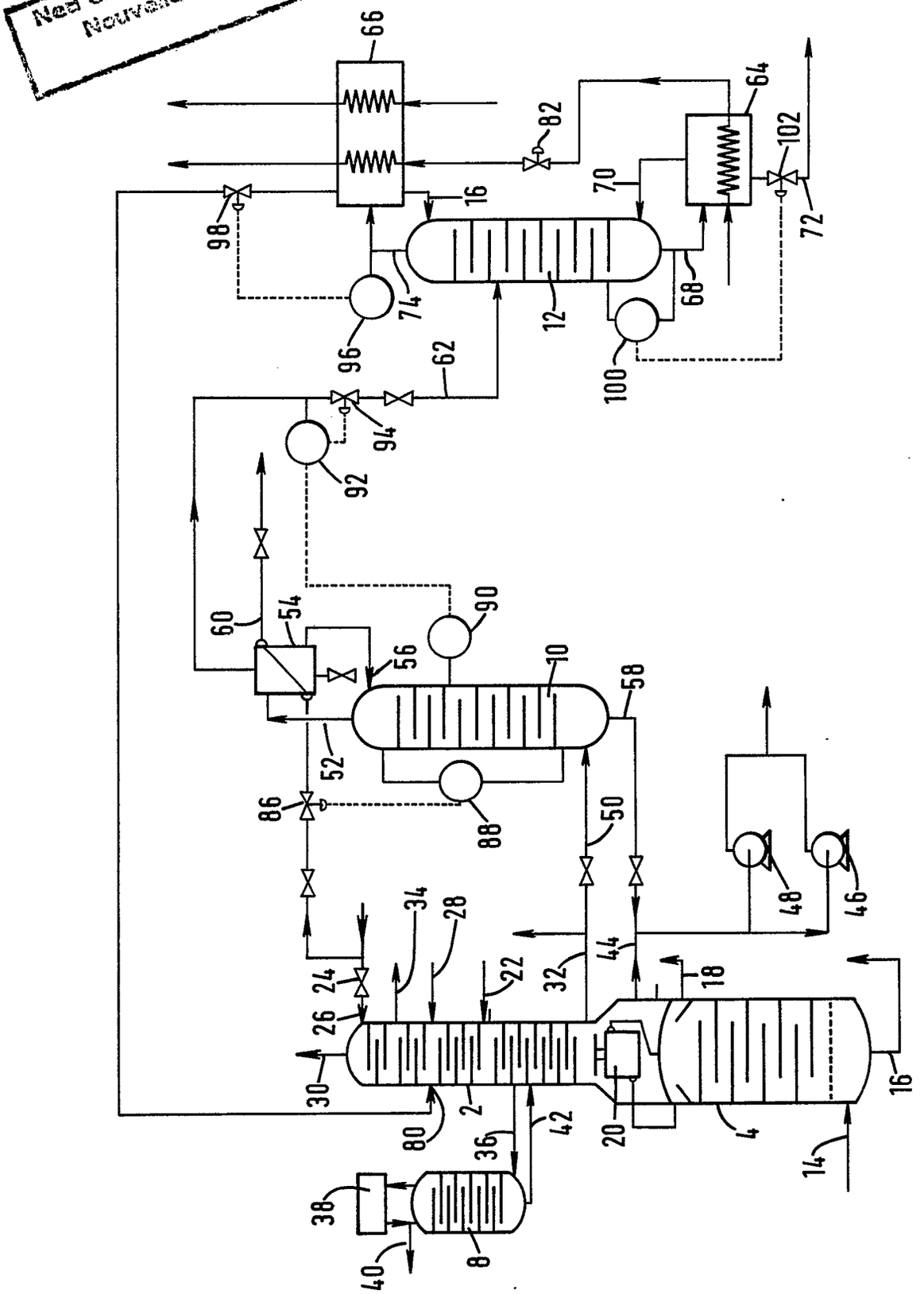
4. A process according to claim 3, in which the condenser associated with said first column is refrigerated by a part of the oxygen-poor liquid withdrawn from said higher pressure column

5. A process according to any preceding calim, in which the stream taken for further fractionation contains at least 5% by volume of argon.

6. A process according to any preceding claim, in which the said second stream is introduced into the said second column as a gas or vapour and not a liquid.

7. A process according to any preceding claim, in which heat for the reboiler associated with the said second column and cooling for the condensation associated with the said second column can be provided by a heat pump circuit in which the working fluid is air.

8. A process for producing ultra high purity substantially as herein described with reference to the accompanying drawings.



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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2011

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 94, no. 6, February 1981, abstract no. 33046p, Columbus, Ohio, US; "Producing high-purity oxygen", & SU-A-757 817 (S.S. BUDNEVICH et al.) * Complete abstract; figure 2; column 4, lines 9-14 *	1,2,7,8	F 25 J 3/04 F 25 J 3/08
D,X	US-A-3 363 427 (E.R. BLANCHARD et al.) * Column 1, lines 11-13; column 2, lines 57-70; column 3, lines 29-36; column 13, line 32 - column 5, line 52; figure 5 *	1,6,8	
P,X	US-A-4 867 772 (D.V. EYRE)(filed: 29-11-1988, publ.: 19-09-1989) * Abstract; figure 3; column 6, lines 11-14; column 10, line 62 - column 12, line 31; column 13, table 1: "Composition of Waste oxygen" in "line 230" *	1-6,8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

F 25 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-04-1990	SIEM T.D.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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