(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 567 360 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
11.06.2025 Bulletin 2025/24

(21) Application number: **24217636.0**

(22) Date of filing: **05.12.2024**

(51) International Patent Classification (IPC):
F25J 3/04 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
F25J 3/04048; F25J 3/04236; F25J 3/04284; F25J 3/04303; F25J 3/04321; F25J 3/04412; F25J 3/0443; F25J 3/04454; F25J 2200/34; F25J 2200/50; F25J 2200/54; F25J 2215/56; F25J 2235/42; F25J 2245/02; F25J 2245/42;
(Cont.)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **06.12.2023 JP 2023206377**

(71) Applicant: **L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE
75007 Paris (FR)**

(72) Inventor: **HIROSE, Kenji
HYOGO, 651-0087 (JP)**

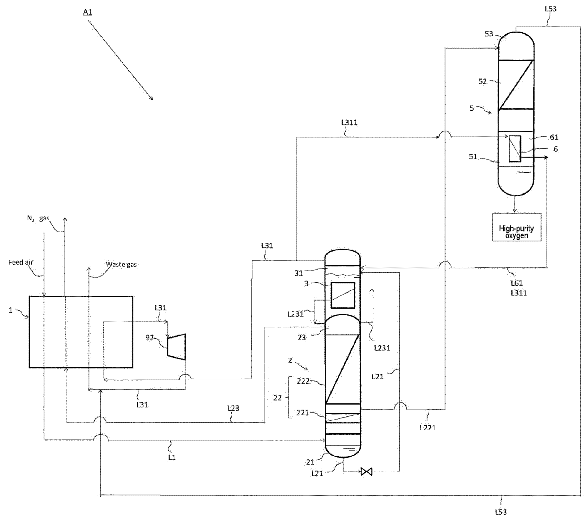
(74) Representative: **Air Liquide
L'Air Liquide S.A.
Direction de la Propriété Intellectuelle
75, Quai d'Orsay
75321 Paris Cedex 07 (FR)**

(54) **HIGH-PURITY OXYGEN PRODUCTION METHOD, AND AIR SEPARATION DEVICE FOR PRODUCING HIGH-PURITY OXYGEN**

(57) To provide an air separation device with which energy consumption can be reduced even while using a process gas as a heat medium for liquefied oxygen, so as to avoid high-purity oxygen production capacity constraints.

An air separation device A1 comprises: a main heat exchanger 1; a nitrogen rectification column 2; a nitrogen condensers 3 disposed in a top portion of the nitrogen rectification column 2; a high-purity oxygen rectification column 5; and an oxygen evaporator 6 disposed in a bottom portion 51 of the high-purity oxygen rectification column 5. An oxygen-containing fluid discharged from an intermediate stage of the nitrogen rectification column 2 is rectified in the high-purity oxygen rectification column 5 and is concentrated in the bottom portion 51 of the high-purity oxygen rectification column 5.

[Figure 1]



EP 4 567 360 A2

(52) Cooperative Patent Classification (CPC): (Cont.)
F25J 2250/10; F25J 2250/20

Description

[0001] The present invention relates to a high-purity oxygen production method and an air separation apparatus for producing high-purity oxygen.

[0002] As high-purity oxygen production methods in which components having a higher boiling point or a lower boiling point than oxygen are controlled to the order of ppm or less, there are known methods that employ cryogenic air separation. One such production method that can be cited is a method in which an oxygen-containing liquid or gas is discharged from a cryogenic air separation apparatus, and high-purity oxygen is rectified (see, for example, WO2018/219685 A1).

[0003] In order to rectify high-purity oxygen, a step is required in which feedstock liquefied oxygen is heated to vaporise low boiling point components such as nitrogen and argon, and as a heat medium for this process, it is known to use an oxygen-enriched liquid (WO2018/219685 A1), feed air (WO2014/173496 A2), recycled air (JP 2020-173041), and nitrogen gas (US11549747).

[0004] If a process liquid such as an oxygen-enriched liquid is used as the heat medium, as in WO2018/219685, since the sensible heat of the process liquid is used to provide the latent heat of vaporisation of the liquefied oxygen, a large molar flow rate is required, while at the same time the amount of heat supplied is limited by process balance constraints, and as a result there is a problem in that the amount of high-purity oxygen that can be recovered remains small.

[0005] In the methods of WO2014/173496 A2, JP 2020-173041 and US11549747, the flow rate of the feed air, recycled air, or nitrogen gas used to vaporise the liquefied oxygen can be increased, so there are no constraints on the high-purity oxygen production capacity, but there is another problem in that the methods involve a gas compression process, and thus energy consumption is high.

[0006] The present disclosure provides a high-purity oxygen production method and an air separation apparatus for producing high-purity oxygen, with which energy consumption is reduced even while a process gas is used as a heat medium for liquefied oxygen, so as to avoid high-purity oxygen production capacity constraints. US 2023/0038170 relates to a process for oxygen production at 99.8% content whereas the present invention allows oxygen to be produced with ppm order impurities. The liquid fed to the oxygen column comes from the liquid sump at the bottom of the column fed by the feed air, where hydrocarbons from feed air are accumulated.

[0007] According to the invention the feed (oxygen containing stream) to the pure oxygen column is comes from a section where hydrocarbons (eg. methane) have been removed.

[0008] When condensable gas is introduced as a heat source for oxygen reboil, the difference between the boiling point of oxygen and the ΔT of the heat exchanger determine the saturation temperature and pressure of the condensable gas. Principally, the lower the saturation pressure, the less energy is needed for reboil. The present invention uses oxygen-enriched gas for oxygen reboil, where the saturation pressure can be lower than pure nitrogen.

[0009] According to the invention, there is provided a method for producing high purity oxygen, comprising the following steps:

- a nitrogen and oxygen separation step of introducing a feed air cooled by a main heat exchanger to a lower section of a first nitrogen rectification column, and introducing oxygen-enriched liquid removed from the bottom of the first nitrogen rectification column into a rectification section of a second nitrogen rectification column and separating the feed air into a nitrogen-enriched component and an oxygen-enriched component in the first nitrogen rectification column and the second nitrogen rectification column;
- a first nitrogen condensation step of condensing vapor stream from the first nitrogen rectification column in a first nitrogen condenser;
- a second nitrogen condensation step of condensing vapor stream from the second nitrogen rectification column in a second nitrogen condenser;
- a high-purity oxygen production step of introducing an oxygen-containing fluid removed from the rectification section of the second nitrogen rectification column into a high-purity oxygen rectification column and producing high-purity product oxygen by using an oxygen evaporator; and
- a heating medium utilization step of using gas removed from the bottom of the second nitrogen rectification column as a heat medium for the oxygen evaporator which evaporates liquefied oxygen, and returning the gas to the second nitrogen condenser.

[0010] According to optional features, the method comprises:

- a partial feed air introduction step of compressing part of the feed air by a compressor, cooling the compressed part of the feed air in a main heat exchanger and expanding the feed air by an expansion turbine, and introducing the feed air into the second nitrogen rectification column;
- expanding in a turbine a vapor formed by vaporising liquid in the second condenser;
- pressuring nitrogen condensed in the second condenser in a pump and sending the pressurised condensed nitrogen to the top of the first nitrogen rectification column;
- the oxygen-containing fluid removed from the rectification section of the second nitrogen rectification column is introduced into the high-purity oxygen rectification column as the sole feed for the high-

purity oxygen rectification column;

- oxygen-enriched liquid removed from the bottom of the first nitrogen rectification column is introduced into a rectification section of a second nitrogen rectification column at a point below the point from which the oxygen-containing fluid removed from the rectification section of the second nitrogen rectification column;

In the present disclosure, a fluid that is discharged from a rectification stage of the rectification column above an introduction point of the feed air, recycled air, or oxygen-enriched liquid and that is introduced into the high-purity oxygen rectification column is referred to as oxygen-containing fluid, and a liquid discharged below the feed air introduction stage (for example, the bottom portion of the nitrogen rectification column) is referred to as oxygen-enriched liquid.

[0011] The oxygen-containing fluid may be a liquid or a gas-liquid mixture.

[0012] With this configuration, the nitrogen gas in the vapour stream is caused to exchange heat with the oxygen-enriched liquid in the nitrogen condenser, thereby vaporising the oxygen-enriched liquid to generate oxygen-enriched gas. The oxygen-enriched gas, which is utilised as a heat medium for the oxygen evaporator, has a pressure and composition sufficient to vaporise the rectified liquefied oxygen in the bottom portion of the high-purity oxygen rectification column using latent heat. In particular, since oxygen-enriched gas containing a large amount of oxygen can vaporise liquefied oxygen at a lower pressure than air or nitrogen, liquefied oxygen can be vaporised at the supply pressure from the nitrogen evaporator without the use of a com pressor.

[0013] The oxygen-containing gas condensed (re-liquefied) in the oxygen evaporator may be re-supplied to the nitrogen condenser.

[0014] With this configuration, recondensed oxygen enriched liquid obtained by condensing the oxygen enriched gas in the oxygen evaporator is re-supplied to a refrigerant side of the nitrogen condenser and vaporised through heat exchange with the vapour stream (nitrogen gas). The recondensed oxygen enriched liquid may be delivered to the nitrogen condenser by means of a head pressure utilizing a height difference between the oxygen evaporator and the nitrogen condenser.

[0015] If the oxygen evaporator is disposed at a lower position than the nitrogen condenser, delivery may be effected using a pump.

[0016] The nitrogen rectification column may include a rectification portion for separating high boiling-point components (for example, methane) from the oxygen contained in the supplied feed air, and for discharging an oxygen-containing liquid from an upper stage thereof.

[0017] With this configuration, the high boiling-point components contained in the feed air are concentrated in the liquefied oxygen. The oxygen-containing liquid serving as the feedstock for the high-purity oxygen is obtained by discharging some reflux liquid from above the feed air introduction portion of the nitrogen rectification column as the oxygen-containing liquid, the reflux liquid containing sufficient oxygen to serve as a feedstock for the high-purity oxygen while having high boiling-point components removed sufficiently. A rectification portion is disposed midway between the feed air introduction portion and the oxygen-containing liquid discharge portion, and is configured such that high boiling-point components removed from the feed air are transferred into the liquefied oxygen by gas-liquid contact and are concentrated in the lower portion of the rectification column.

[0018] The rectification portion may consist of rectification plates, structured packing, or random packing.

[0019] A high-purity oxygen production method includes:

- a nitrogen-oxygen separation step in which feed air cooled in (partially cooled by being discharged from an intermediate part of) a main heat exchanger (1) is introduced into an introduction portion in a lower part of a nitrogen rectification column, and the feed air is separated in first and second nitrogen rectification columns into a nitrogen-enriched component (nitrogen-enriched fluid) and an oxygen-enriched component (oxygen-enriched fluid);
- a first nitrogen condensation step in which a vapour stream (nitrogen-enriched gas) from the first nitrogen rectification column is condensed in a first nitrogen condenser;
- an oxygen-enriched liquid circulation step in which oxygen-enriched liquid discharged from a bottom portion of the nitrogen rectification column is passed through the main heat exchanger and is then sent to a rectification portion of the second nitrogen rectification column;
- a second nitrogen condensation step in which a vapour stream (nitrogen-enriched gas) from the second nitrogen rectification column is condensed in a second nitrogen condenser;
- a product nitrogen gas extraction step in which gas (nitrogen gas) discharged from a top portion of the first nitrogen rectification column is passed through the main heat exchanger and is extracted as product nitrogen gas;
- a waste gas extraction step in which gas (nitrogen gas) discharged from a top portion of the second nitrogen condenser is passed through a portion of the main heat exchanger, is then expanded and cooled in an expansion turbine, and is then passed through the main heat exchanger again and is extracted as waste gas;
- a high-purity oxygen production step in which an oxygen-containing fluid discharged from a rectification portion of the second nitrogen rectification column is introduced into a top portion of a high-purity oxygen rectification column, and an oxygen evaporator provided in a bottom portion is utilised to

produce high-purity oxygen;

- a heat medium utilisation step in which gas (oxygen-enriched gas) discharged from a bottom portion of the second nitrogen rectification column or a top portion of the first nitrogen condenser is utilised as a heat medium for the oxygen evaporator which vaporises liquefied oxygen, and is returned to the top portion of the nitrogen condenser; and
- a recycled gas introduction step in which gas discharged from the rectification portion of the second nitrogen rectification column is compressed by a compressor, is passed through the main heat exchanger, and is then introduced as recycled gas into a lower part of the first nitrogen rectification column.

[0020] A fourth high-purity oxygen production method includes:

- a partial feed air introduction step in which feed air compressed by a compressor is passed through (partially cooled by being discharged from an intermediate part of) a main heat exchanger, is expanded in an expansion turbine, and is introduced into a second nitrogen rectification column;
- a nitrogen-oxygen separation step in which feed air cooled in (partially cooled by being discharged from an intermediate part of) a main heat exchanger is introduced into an introduction portion in a lower part of a nitrogen rectification column, and the feed air is separated in first and second nitrogen rectification columns into a nitrogen-enriched component (nitrogen-enriched fluid) and an oxygen-enriched component (oxygen-enriched fluid);
- a first nitrogen condensation step in which a vapour stream (nitrogen-enriched gas) from the first nitrogen rectification column is condensed in a first nitrogen condenser;
- an oxygen-enriched liquid circulation step in which oxygen-enriched liquid discharged from a bottom portion of the first nitrogen rectification column is passed through the main heat exchanger and is then sent to a rectification portion of the second nitrogen rectification column;
- a second nitrogen condensation step in which a vapour stream (nitrogen-enriched gas) from the second nitrogen rectification column is condensed in a second nitrogen condenser;
- a product nitrogen gas extraction step in which gas (nitrogen gas) discharged from a top portion of the first nitrogen rectification column is passed through the main heat exchanger and is extracted as product nitrogen gas;
- a low-pressure nitrogen gas extraction step in which gas (nitrogen gas) discharged from a top portion of the second nitrogen rectification column is passed through the main heat exchanger and is extracted as low-pressure nitrogen gas;
- a waste gas extraction step in which gas (nitrogen gas) discharged from a top portion of the second nitrogen condenser is passed through the main heat exchanger and is extracted as waste gas;
- a high-purity oxygen production step in which an oxygen-containing fluid discharged from the rectification portion of the second nitrogen rectification column is introduced into a top portion of the high-purity oxygen rectification column, and an oxygen evaporator provided in a bottom portion is utilised to produce high-purity oxygen; and
- a heat medium utilisation step in which gas (oxygen-enriched gas) discharged from a bottom portion of the second nitrogen rectification column or a top portion of the first nitrogen condenser is utilised as a heat medium for the oxygen evaporator which vaporises liquefied oxygen, and is returned to the top portion of the second nitrogen condenser.

[0021] The first, second, third and fourth high-purity oxygen production methods may include a waste gas extraction step in which gas discharged from the top portion of the high-purity oxygen rectification column is passed through the main heat exchanger and is extracted as waste gas.

[0022] "High-purity oxygen" is oxygen having a concentration of at least 99.99% mol. According to the present invention, there is provided an air separation apparatus for producing high purity oxygen, comprising:

- a main heat exchanger;
- a first nitrogen rectification column;
- a second nitrogen rectification column;
- a first nitrogen condenser at the top of the first nitrogen rectification column;
- a second nitrogen condenser at the top of the second nitrogen rectification column;
- a high purity oxygen rectification column;
- an oxygen evaporator at the bottom of the rectification column;
- a conduit for introducing feed air cooled by a main heat exchanger to a lower section of a first nitrogen rectification column in order to separate the feed air into a nitrogen-enriched component and an oxygen-enriched component in the first nitrogen rectification column;
- a conduit for introducing oxygen-enriched liquid removed from the bottom of the first nitrogen rectification column into a rectification section of a second nitrogen rectification column in order to separate the oxygen enriched liquid into a nitrogen-enriched component and an oxygen-enriched component in the second nitrogen rectification column;
- a conduit for sending a nitrogen enriched vapor stream from the first nitrogen rectification column in the first nitrogen condenser;
- a conduit for sending a nitrogen enriched vapor stream from the second nitrogen rectification column in the second nitrogen condenser;

- a conduit for sending an oxygen-containing fluid removed from the rectification section of the second nitrogen rectification column into the high-purity oxygen rectification column and producing high-purity product oxygen at the bottom of the high purity oxygen rectification column and
- a conduit for sending gas removed from the bottom of the second nitrogen rectification column as a heat medium for the oxygen evaporator which evaporates liquefied oxygen, and returning the gas condensed in the oxygen evaporator to the second nitrogen condenser.

[0023] The air separation apparatus may comprise:

- an oxygen-enriched liquid pipeline through which oxygen-enriched liquid discharged from a bottom portion of the first nitrogen rectification column is passed partially through the main heat exchanger and is then sent to a rectification portion of the second nitrogen rectification column;
- an oxygen-containing fluid pipeline through which oxygen-containing fluid discharged from a middle-stage rectification portion of the second nitrogen rectification column is introduced into a top portion of the high-purity oxygen rectification column;
- a heat medium pipeline through which gas discharged from a lower-stage rectification portion of the second nitrogen rectification column is sent as a heat medium of the oxygen evaporator and is introduced as liquefied gas into the second nitrogen condenser;
- a recycled gas pipeline through which gas discharged from the middle-stage rectification portion of the second nitrogen rectification column is compressed by the compressor, is passed through the main heat exchanger, and is then introduced as recycled gas into the rectification portion of the first nitrogen rectification column;
- a waste gas extraction pipeline through which gas discharged from the top portion of the second nitrogen condenser is passed partially through the main heat exchanger, is then sent to the expansion turbine, is again passed through the main heat exchanger, and is extracted as waste gas;
- a turbine, a conduit for sending air to the turbine and a conduit for sending expanded air from the turbine to the second nitrogen rectification column;
- a turbine, a conduit for sending gas from the second nitrogen condenser to the turbine and a conduit for sending expanded gas from the turbine to the atmosphere;
- a compressor, a conduit for sending gas from between intermediate stages of the second nitrogen rectification column to the compressor and a conduit for sending compressed gas from the compressor to the bottom of the first nitrogen rectification column;
- an arrival point for the gaseous air in the first nitrogen rectification column is above an arrival point for the gas compressed in the compressor;
- the compressor is coupled to the turbine;
- means for sending condensed nitrogen from the second condenser to the top of the first nitrogen rectification column;
- means for sending a top gas from the oxygen rectification column to the main heat exchanger.

[0024] Further, a fourth air separation apparatus may comprise:

- a compressor for compressing a portion of the feed air, and
- an expansion turbine for expanding compressed air that has been compressed by the compressor, introduced into the main heat exchanger, and discharged from an intermediate part thereof.

[0025] The air separation apparatus may comprise:

- a feed air branch pipeline which sends a portion of the feed air to the compressor that compresses the feed air, sends the feed air compressed by the compressor to the main heat exchanger and discharges the same from an intermediate part thereof to the expansion turbine to expand the feed air, and then sends the feed air to the rectification portion of the second nitrogen rectification column;
- a low-pressure nitrogen gas extraction pipeline through which gas discharged from a top portion of the second nitrogen rectification column is extracted as low-pressure nitrogen gas; and
- a waste gas extraction pipeline through which gas discharged from the top portion of the second nitrogen condenser is extracted as waste gas.

[0026] The air separation apparatus may include:

- various measuring instruments such as flow rate measuring instruments, pressure measuring instruments, temperature measuring instruments, and liquid level measuring instruments;
- various valves such as control valves and gate valves; and
- piping that connects each element.

[0027] Energy consumption can be reduced even while using a process gas as a heat medium for liquefied oxygen, so as to avoid high-purity oxygen production capacity constraints.

[Figure 1] is a drawing illustrating an air separation apparatus according to a comparative example.
[Figure 2] is a drawing illustrating an air separation apparatus according to a comparative example.
[Figure 3] is a drawing illustrating an air separation apparatus according to the invention.

[Figure 4] is a drawing illustrating an air separation apparatus according to the invention.

[0028] The first air separation apparatus A1 according to a comparative example will be described with reference to Figure 1.

[0029] The first air separation apparatus A1 comprises a main heat exchanger 1, a nitrogen rectification column 2, a nitrogen condenser 3, an expansion turbine 92, a high-purity oxygen rectification column 5, and an oxygen evaporator 6.

[0030] The main heat exchanger 1 cools feed air introduced from a hot end and discharges the same from a cold end. The cooled feed air is introduced into the nitrogen rectification column 2 via a feed air pipeline L1.

[0031] The nitrogen rectification column 2 comprises a bottom portion 21, a rectification portion 22, and a top portion 23. The feed air pipeline L1 is connected to the bottom portion 21.

[0032] Oxygen-enriched liquid that collects in the bottom portion 21 is sent to a refrigerant phase 31 of the nitrogen condenser 3 via an oxygen-enriched liquid pipeline L21.

[0033] The nitrogen condenser 3 is provided above the top portion 23. A portion of nitrogen gas (vapour stream) discharged from the top 23 of the nitrogen rectification column 2 is introduced into the nitrogen condenser 3 via a reflux pipeline L231, and is cooled (condensed) through heat exchange with the oxygen-enriched liquid to form liquefied nitrogen. The liquefied nitrogen is returned to the top portion 23 of the nitrogen rectification column 2 as reflux liquid.

[0034] An oxygen-containing fluid is discharged from between intermediate portions 221, 222 of the rectification portion 22 of the nitrogen rectification column 2 via the oxygen-containing fluid pipeline L221 and is introduced into a top portion 53 of the high-purity oxygen rectification column 5.

[0035] Nitrogen gas discharged from the top portion 23 of the nitrogen rectification column 2 is sent via a product nitrogen gas extraction pipeline L23 to the main heat exchanger 1 and is extracted as product nitrogen gas.

[0036] Oxygen-enriched gas (oxygen-enriched liquid vapour) discharged from a top portion 31 of the nitrogen condenser 3 is introduced via a waste gas extraction pipeline L31 into the cold end of the main heat exchanger 1, is discharged from an intermediate part thereof, is then expanded and cooled in the expansion turbine 92, and is again sent to the main heat exchanger 1 and is extracted as waste gas.

[0037] A portion of the oxygen-enriched gas (oxygen-enriched liquid vapour) discharged from the top portion (refrigerant phase) 31 of the nitrogen condenser 3 is sent as a heat medium via a heat medium pipeline L311 to the oxygen evaporator 6, is re-liquefied, and is returned again to the top portion (refrigerant phase) 31 of the nitrogen condenser 3. The re-liquefied oxygen-enriched gas is supplied as a recycled oxygen-enriched liquid to the nitrogen condenser 3, as a refrigerant.

[0038] The high-purity oxygen rectification column 5 includes a bottom portion 51, a rectification portion 52, and a top portion 53.

[0039] Oxygen-containing liquid is introduced into the top portion 53 of the high-purity oxygen rectification column 5 and is rectified in the rectification portion 52, and liquefied oxygen collects in the bottom portion 51.

[0040] The oxygen evaporator 6 is provided in the bottom portion 51 of the high-purity oxygen rectification column 5. Liquid oxygen is converted into a vapour stream (oxygen gas) by the heat medium nitrogen gas in the oxygen evaporator 6, heat and material are exchanged in the rectification portion 52, and high-purity oxygen accumulates in the bottom portion 51. Gas discharged from the top portion 53 of the high-purity oxygen rectification column 5 passes through a pipeline L53 to merge with the waste gas extraction pipeline L31, is sent to the main heat exchanger 1, and is extracted as waste gas.

[0041] According to the air separation apparatus A1, coldness necessary to maintain the heat balance of the air separation apparatus can be supplied.

[0042] The second air separation apparatus A2 according to the comparative example will be described with reference to Figure 2. The same reference numerals as those in Figure 1 have the same functions, and therefore descriptions thereof may be omitted.

[0043] The second air separation apparatus A2 comprises the main heat exchanger 1, the nitrogen rectification column 2, a first nitrogen condenser 3, a second nitrogen condenser 4, a compressor 91, the expansion turbine 92, the high-purity oxygen rectification column 5, and the oxygen evaporator 6. Aspects of the configuration that differ from embodiment 1 will mainly be described.

[0044] The first nitrogen condenser 3 is disposed above the nitrogen rectification column 2, and the second nitrogen condenser 4 is disposed above the first nitrogen condenser 3. Some nitrogen gas (vapour stream) discharged from the top portion 23 of the nitrogen rectification column 2 is introduced into the first nitrogen condenser 3 via a first reflux pipeline L231, and is cooled (condensed) through heat exchange with the oxygen-enriched liquid to form liquefied nitrogen. The liquefied nitrogen is returned to the top portion 23 of the nitrogen rectification column 2 as reflux liquid. Some nitrogen gas (vapour stream) discharged from the top portion 23 of the nitrogen rectification column 2 is introduced into the second nitrogen condenser 4 via a second reflux pipeline L232, and is cooled (condensed) through heat exchange with the oxygen-enriched liquid to form liquefied nitrogen. The liquefied nitrogen is returned to the top portion 23 of the nitrogen rectification column 2 as reflux liquid.

[0045] An oxygen-enriched liquid pipeline L211 is a pipeline through which oxygen-enriched liquid discharged from the bottom portion 21 of the nitrogen rectification column 2 is passed partially through the main heat exchanger 1 and is then introduced into the second nitrogen condenser 4. The oxygen-enriched liquid from the second nitrogen condenser 4 is sent as a refrigerant to the first nitrogen condenser 3.

[0046] The compressor 91 compresses gas discharged from a top portion 41 of the second nitrogen condenser 4. A recycled gas pipeline L41 is a pipeline through which gas is discharged from the top portion 41 of the second nitrogen condenser 4, is compressed by the compressor 91, is passed through the main heat exchanger 1, and is then introduced as recycled gas into the rectification portion 22 of the nitrogen rectification column 2.

[0047] The third air separation apparatus A3 according to the invention will be described with reference to Figure 3. The same reference numerals as those in Figures 1 and 2 have the same functions, and therefore descriptions thereof may be omitted.

[0048] The third air separation apparatus A3 comprises the main heat exchanger 1, a first nitrogen rectification column 2, a second nitrogen rectification column 7, the first nitrogen condenser 3, the second nitrogen condenser 4, the compressor 91, the expansion turbine 92, the high-purity oxygen rectification column 5, and the oxygen evaporator 6. Aspects of the configuration that differ from Figure 2 will mainly be described.

[0049] Oxygen-enriched gas (vapour) generated in the first nitrogen condenser 3 and oxygen-enriched liquid discharged from the bottom portion 21 of the first nitrogen rectification column 2 are introduced into the second nitrogen rectification column 7. An oxygen-enriched liquid pipeline L212 is a pipeline through which oxygen-enriched liquid discharged from the bottom portion 21 of the first nitrogen rectification column 2 is introduced into the main heat exchanger 1, is discharged from an intermediate stage thereof, and is then introduced between intermediate stages 721 and 722 of the rectification portion of the second nitrogen rectification column 7.

[0050] An oxygen-containing liquid pipeline L723 is a pipeline that introduces oxygen-containing fluid discharged from between intermediate stages 722, 723 of the rectification portion of the second nitrogen rectification column 7 into the top portion 53 of the high-purity oxygen rectification column 5.

[0051] The position at which the oxygen-containing fluid is discharged into the oxygen-containing fluid pipeline L723 is above the position at which the oxygen-enriched liquid from the oxygen-enriched liquid pipeline L212 is introduced.

[0052] A heat medium pipeline L711 is a pipeline through which gas (oxygen-enriched gas) discharged from below the lower-stage rectification portion 721 of the second nitrogen rectification column 7 is sent as a heat medium to the oxygen evaporator 6, is re-liquefied, and is sent as a refrigerant phase 41 to the second nitrogen condenser 4 via pipeline L61.

[0053] A recycled gas pipeline L722 is a pipeline through which gas is discharged from between the intermediate stages 721 and 722 of the rectification portion of the second nitrogen rectification column 7, is compressed by the compressor 91, is passed through a portion of the main heat exchanger 1, and is then introduced as recycled gas into the rectification portion 22 of the first nitrogen rectification column 2.

[0054] A waste gas extraction pipeline L411 is a pipeline through which gas discharged from the top portion 41 of the second nitrogen condenser 4 is passed partially through the main heat exchanger 1, is then sent to the expansion turbine 92 to be expanded and cooled, is again passed through the main heat exchanger 1, and is extracted as waste gas, after mixing with top gas from the oxygen rectification column.

[0055] A vapour stream pipeline L731 is a pipeline through which a vapour stream that is discharged from a top portion 73 of the second nitrogen rectification column 7 and is sent to the second nitrogen condenser 4 and is returned in liquid form in part to the top portion 73 of the second nitrogen rectification column 7.

[0056] A pipeline L732 branches off from the liquid stream pipeline L731 downstream of the second nitrogen condenser 4 and feeds into the top portion 23 of the first nitrogen rectification column 2. A liquid transfer pump P1 is provided in the pipeline L732.

[0057] The fourth air separation apparatus A4 will be described with reference to Figure 4. The same reference numerals as those in figures 2 and 3 have the same functions, and therefore descriptions thereof may be omitted.

[0058] The fourth air separation apparatus A4 comprises the main heat exchanger 1, the first nitrogen rectification column 2, the second nitrogen rectification column 7, the first nitrogen condenser 3, the second nitrogen condenser 4, the compressor 911, the expansion turbine 921, the high-purity oxygen rectification column 5, and the oxygen evaporator 6. Aspects of the configuration that differ from figure 3 will mainly be described.

[0059] The compressor 911 compresses a portion of the feed air.

[0060] The expansion turbine 921 expands compressed air that has been compressed by the compressor 911, introduced into the main heat exchanger 1, and discharged from an intermediate part thereof.

[0061] A feed air branch pipeline L11 is a pipeline that branches off from the feed air pipeline L1 upstream of the main heat exchanger 1, sends a portion of the feed air to the compressor 911 that compresses the feed air, sends the feed air compressed by the compressor 911 to the main heat exchanger 1 and discharges the same from an intermediate part thereof to the expansion turbine 921 that expands the feed air, and then sends the feed air to the rectification portion of the second nitrogen rectification column 7.

[0062] A low-pressure nitrogen gas extraction pipeline L732 is a pipeline through which gas discharged from the top portion 73 of the second nitrogen rectification column

7 is extracted as low-pressure nitrogen gas.

[0063] A waste gas extraction pipeline L412 is a pipeline through which gas discharged from the top portion 41 of the second nitrogen condenser 4 is extracted as waste gas. The pipeline L53 merges with the waste gas extraction pipeline L412.

[0064] According to the fourth embodiment, coldness required for the heat balance is obtained by using the expansion turbine 921 to expand either a portion of the feed air or product nitrogen gas discharged from the first nitrogen rectification column 2 to the pressure of the second nitrogen rectification column 7. Motive power obtained by the expansion turbine 921 may be applied to the motive power of the compressor 911 that compresses the feed air. It should be noted that the same applies to figures 2 and 3.

[0065] The results of a physical simulation of the air separation apparatus of figure 4 are presented. Feed air (1000 Nm^3/h, 9.9 barA) was introduced.

[0066] 930 Nm3/h of the feed air was introduced into the hot end of the main heat exchanger 1, was cooled to -163°C, and was then introduced into the first nitrogen rectification column 2.

[0067] Another 70 Nm3/h of the feed air was compressed to 13 barA by the compressor 911, was introduced into the main heat exchanger 1, was cooled to -130°C, was expanded to 4.4 barA by the expansion turbine 921, and was introduced into the second nitrogen rectification column 7.

[0068] Nitrogen gas (330 Nm^3/h, 9.7 barA), liquefied nitrogen (48 Nm3/h, 9.7 barA), oxygen-enriched liquid (552 Nm^3/h, oxygen 35.3%) were discharged from the first nitrogen rectification column 2.

[0069] The liquefied nitrogen and oxygen-enriched liquid were introduced into the second nitrogen rectification column 7.

[0070] Low-pressure nitrogen gas (311 Nm3/h, 4.3 barA), oxygen-containing liquid (73 Nm3/h, 20.0 % O2), oxygen enriched gas (54Nm3/h, 4.3 barA, 36.3% O2), low-pressure oxygen enriched liquid (232 Nm3/h, 75.5% O2) were discharged from the second nitrogen rectification column 7.

[0071] The oxygen enriched gas was used as the heat medium in the oxygen evaporator 6, and was introduced to the second nitrogen condenser 4 as a coolant.

[0072] The low-pressure oxygen enriched liquid was introduced to the second nitrogen condenser 4 as a coolant.

[0073] The oxygen-containing liquid was introduced to the oxygen rectification column. The oxygen rectification column 5 was operated at 1.5 barA, and high-purity oxygen (10.8 Nm^3/h, 100%) collected in the bottom portion 51.

[0074] A comparison will be made with a case in which feed air was used as the heat medium in the oxygen evaporator 6, as presented in WO2014/173496.

[0075] In order to obtain the same nitrogen gas and high-purity oxygen liquid as in the above example (Figure 2), whereas the amount of feed air required in the present example was 1000 Nm^3/h, when feed air was used in the oxygen evaporators, 1027 Nm^3/h of feed air was required.

[0076] This is because the heat medium used in the oxygen evaporator 6 in the present example has a higher oxygen concentration than the feed air, thus allowing condensation to occur at a lower pressure such as 4.3 barA for the oxygen enriched gas instead of 9.9 barA for the feed air, and as a result reducing the compression energy required for the heat medium.

[0077] In addition, since it is not necessary to use the feed air as the heat medium, the amount of feed air that can be supplied to the first nitrogen rectification column 2 can be increased, also making it possible to improve the nitrogen gas recovery.

[0078] Another comparison will be made with a case of oxygen production at 99.8% content as presented in US 2023/0038170.

[0079] As an example, if there is 1 ppm methane (or hydrocarbon) in the air, methane is distributed to the oxygen stream in the comparative example process because there is no mechanism to separate methane from oxygen, and the methane concentration in oxygen will be more than 4.8 ppm when 11 Nm3/h of oxygen is produced from 1000 Nm3/h of feed air.

[0080] In the present invention, the oxygen-containing liquid supplied to the oxygen rectification column is derived from the methane-free reflux fluid above the location where the methane-containing fluid is supplied, so that an oxygen product with a methane content of less than 1 ppm can be produced.

(1) Although not explicitly stated, pressure regulating and flow rate control devices, etc. may be installed in each pipeline in order to regulate pressure and flow rate.
(2) Although not explicitly stated, control valves and gate valves, etc. may be installed in each line.
(3) Although not explicitly stated, pressure regulating and temperature measuring devices, etc. may be installed in each column in order to regulate pressure and temperature.

Claims

1. A method for producing high purity oxygen by cryogenic distillation of air, comprising steps:

- a nitrogen and oxygen separation step of introducing a feed air cooled by a main heat exchanger (1) to a lower section of a first nitrogen rectification column (2), and introducing oxygen-enriched liquid removed from the bottom of the first nitrogen rectification column into a rectification section (721, 722, 723) of a second nitrogen rectification column (7), separating the feed air

into a nitrogen-enriched component and an oxygen-enriched component in the first nitrogen rectification column and separating the oxygen enriched liquid into a nitrogen-enriched component and an oxygen-enriched component the second nitrogen rectification column;
• a first nitrogen condensation step of condensing vapor stream from the first nitrogen rectification column in a first nitrogen condenser (3) at the top of the first nitrogen rectification column;
• a second nitrogen condensation step of condensing vapor stream from the second nitrogen rectification column in a second nitrogen condenser (4) at the top of the second nitrogen rectification column;
• a high-purity oxygen production step of introducing an oxygen-containing fluid removed from the rectification section of the second nitrogen rectification column into a high-purity oxygen rectification column (5) and producing high-purity product oxygen by using an oxygen evaporator (6); and
• a heating medium utilization step of using gas removed from the bottom of the second nitrogen rectification as a heat medium for the oxygen evaporator which evaporates liquefied oxygen and liquefies the gas, and returning the liquefied gas to the second nitrogen condenser.

2. Method according to Claim 1 comprising a partial feed air introduction step of compressing part of the feed air by a compressor, cooling the compressed part of the feed air in a main heat exchanger.

3. Method according to Claim 2 comprising expanding the feed air by a expansion turbine (921), and introducing the feed air into the second nitrogen rectification column (7).

4. Method according to Claim 1 or 2 including the step of expanding in a turbine (92) a vapor formed by vaporising liquid in the second condenser (4).

5. Method according to any preceding claim including the step of pressuring nitrogen condensed in the second condenser (5) in a pump (P1) and sending the pressurised condensed nitrogen to the top of the first nitrogen rectification column (2).

6. Method according to any preceding claim wherein the oxygen-containing fluid removed from the rectification section of the second nitrogen rectification column (7) is introduced into the high-purity oxygen rectification column (5) as the sole feed for the high-purity oxygen rectification column.

7. Method according to any preceding claim comprising a waste gas extraction step in which gas discharged from the top portion (53) of the high-purity oxygen rectification column is passed through the main heat exchanger (1) and is extracted as waste gas.

8. An air separation apparatus for producing high purity oxygen by cryogenic distillation, comprising :

• a main heat exchanger (1)
• a first nitrogen rectification column (2)
• a second nitrogen rectification column (7)
• a first nitrogen condenser (3) at the top of the first nitrogen rectification column
• a second nitrogen condenser (4) at the top of the second nitrogen rectification column
• a high purity oxygen rectification column (5)
• an oxygen evaporator (6) at the bottom of the oxygen rectification column
• a conduit (L212) for introducing feed air cooled by a main heat exchanger to a lower section of a first nitrogen rectification column in order to separate the feed air into a nitrogen-enriched component and an oxygen-enriched component in the first nitrogen rectification column,
• a conduit for introducing oxygen-enriched liquid removed from the bottom of the first nitrogen rectification column into a rectification section of a second nitrogen rectification column in order to separate the oxygen enriched liquid into a nitrogen-enriched component and an oxygen-enriched component in the second nitrogen rectification column;
• conduit (L231) for sending a nitrogen enriched vapor stream from the first nitrogen rectification column in the first nitrogen condenser;
• a conduit (L731) for sending a nitrogen enriched vapor stream from the second nitrogen rectification column in the second nitrogen condenser;
• a conduit (L723) for sending an oxygen-containing fluid, preferably a liquid, removed from the rectification section of the second nitrogen rectification column into the high-purity oxygen rectification column and producing high-purity product oxygen at the bottom of the high purity oxygen rectification column and
• a conduit (L711, L61) for sending gas removed from the bottom of the second nitrogen rectification column as a heat medium for the oxygen evaporator which evaporates liquefied oxygen, and returning the gas condensed in the oxygen evaporator to the second nitrogen condenser.

9. Apparatus according to Claim 8 including a turbine (921), a conduit for sending air to the turbine and a conduit for sending expanded air from the turbine to the second nitrogen rectification column (7).

10. Apparatus according to Claim 8 including a turbine

(92), a conduit (L411) for sending gas from the second nitrogen condenser (4) to the turbine and a conduit for sending expanded gas from the turbine to the atmosphere.

11. Apparatus according to Claim 8 or 10 including a compressor (91), a conduit (L722) for sending gas from between intermediate stages (721, 722) of the second nitrogen rectification column (7) to the compressor and a conduit for sending compressed gas from the compressor to the bottom of the first nitrogen rectification column (2).

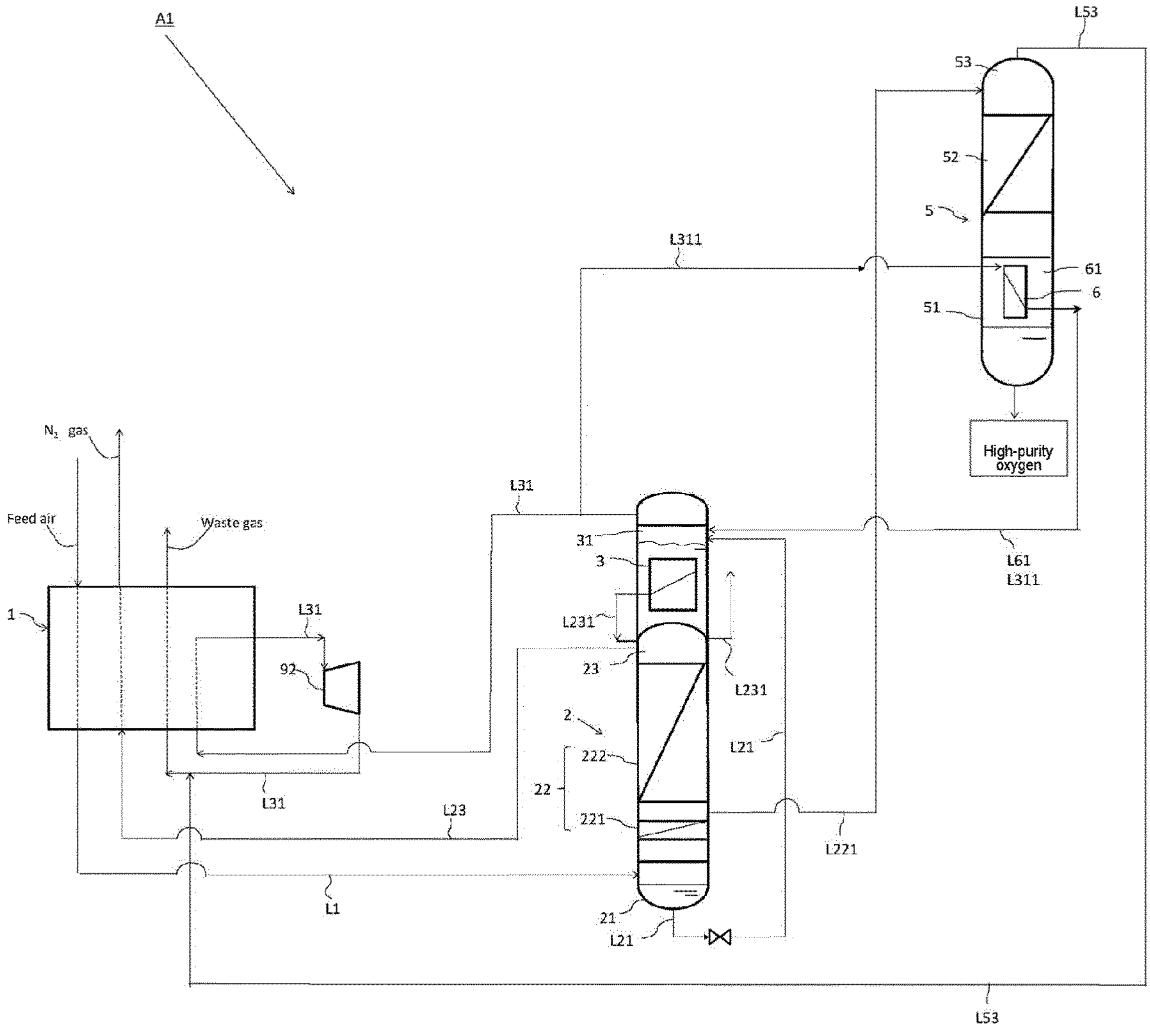
12. Apparatus according to Claim 11 where an arrival point for the gaseous air in the first nitrogen rectification column (2) is above an arrival point for the gas compressed in the compressor.

13. Apparatus according to Claims 10 and 11 wherein the compressor (91) is coupled to the turbine (92).

14. Apparatus according to one of Claims 8 to 13 including means (L732, P1) for sending condensed nitrogen from the second condenser (4) to the top of the first nitrogen rectification column (2).

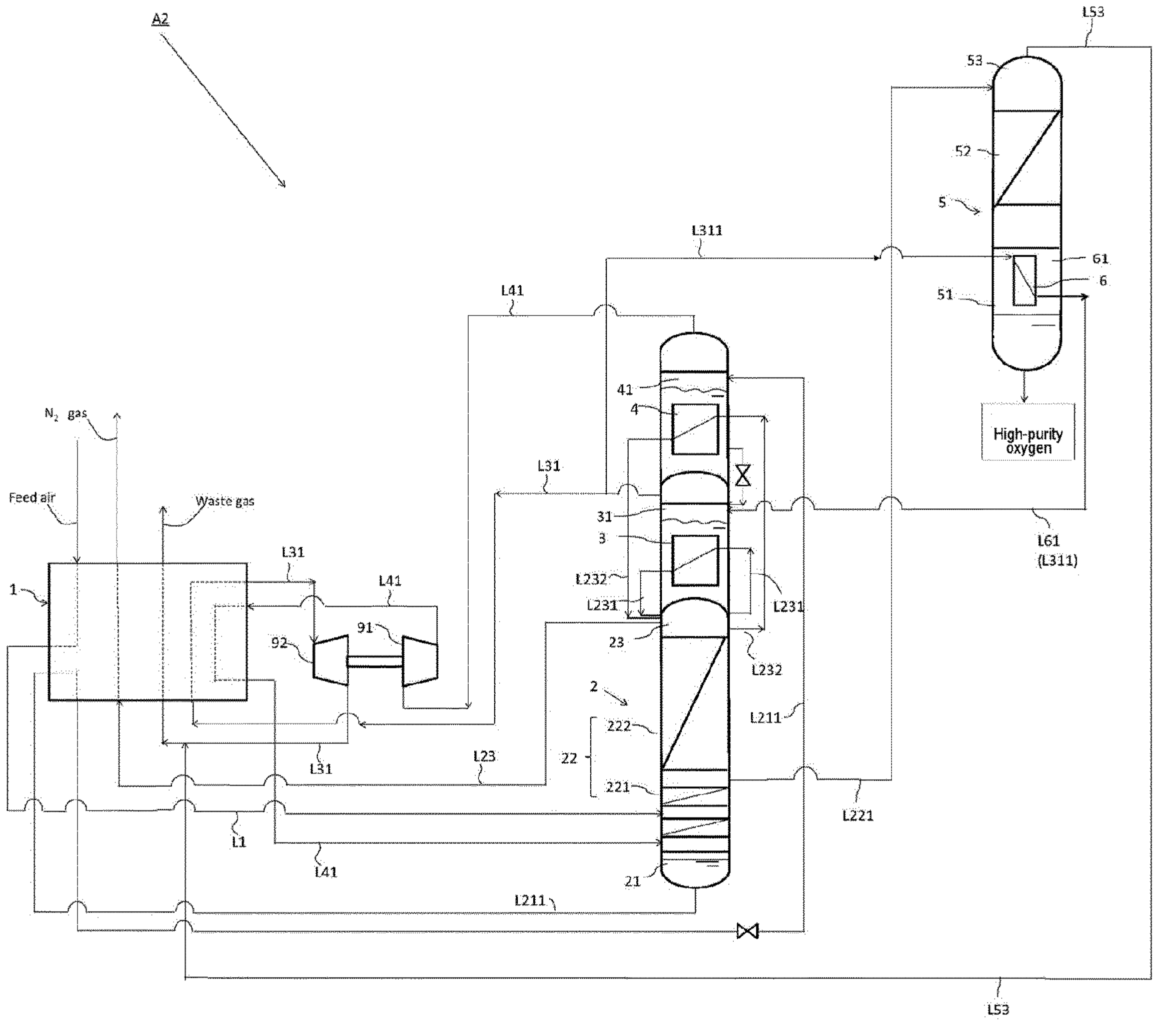
15. Apparatus according to one of Claims 8 to 14 including means for sending a top gas (L53) from the oxygen rectification column (5) to the main heat exchanger (1).

[Figure 1]

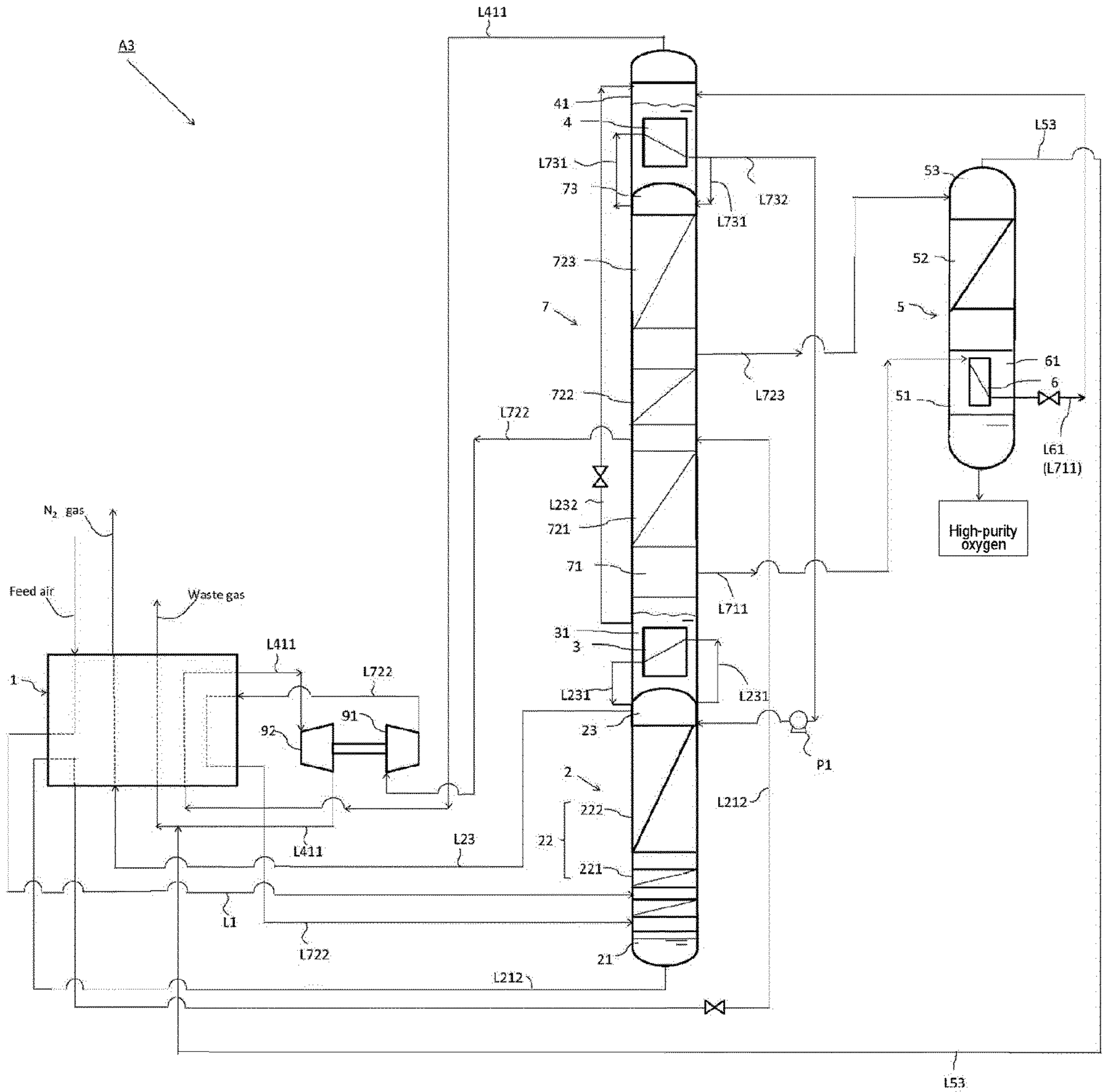


A1
L53
53
52
5
L311
61
6
51
High-purity oxygen
N_2 gas
Feed air
Waste gas
L31
31
3
L61
L311
1
L31
92
L231
23
L231
2
222
L21
22
221
L221
L31
L23
L1
21
L21
L53

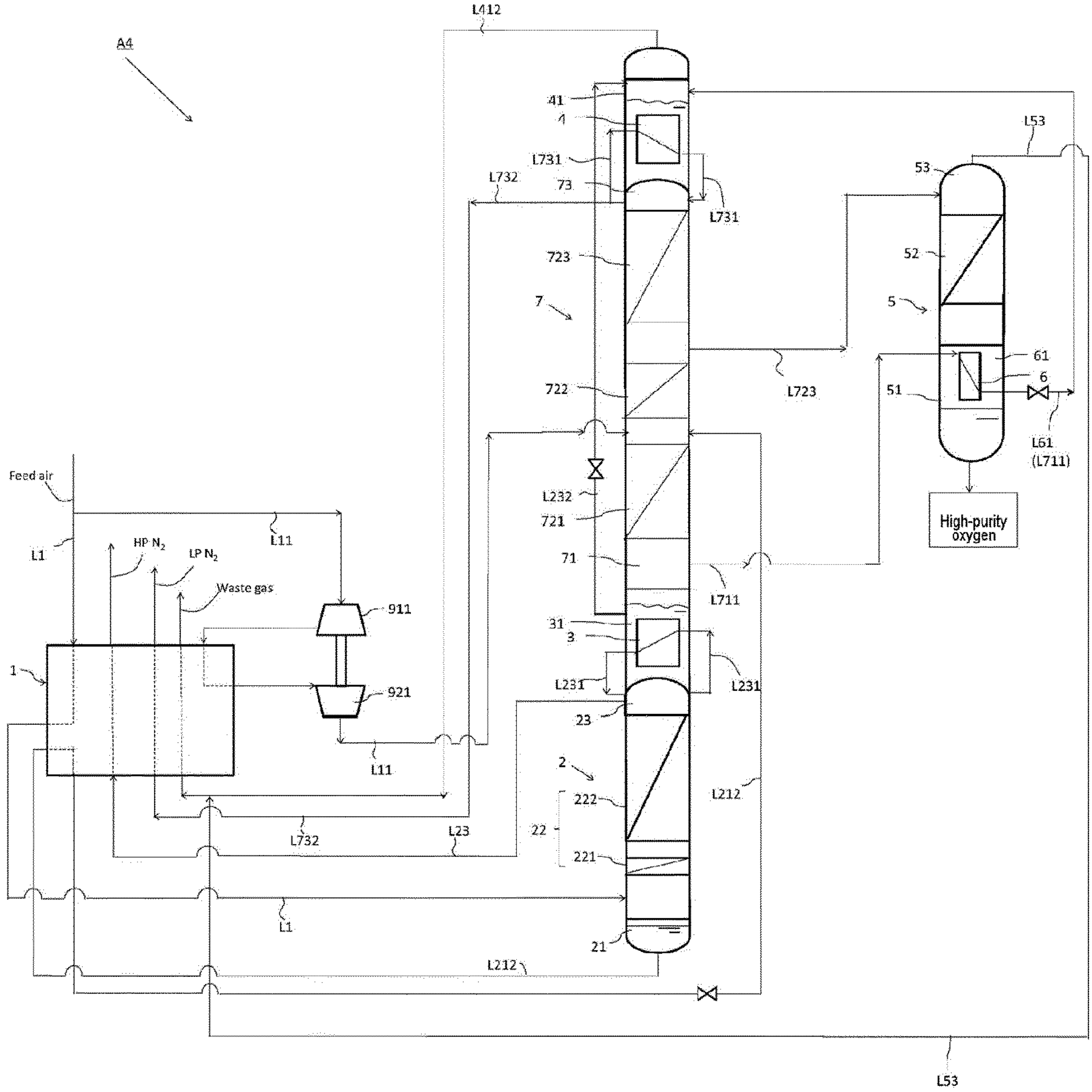
[Figure 2]


A2
L53
53
52
5
L311
61
6
51
L41
41
4
N2 gas
High-purity oxygen
L31
Feed air
Waste gas
31
3
L61
(L311)
1
L31
L41
L232
L231
91
92
L231
23
L232
2
222
L211
22
L23
L31
221
L221
L1
L41
21
L211
L53

[Figure 3]


A3
L411
41
4
L731
73
L732
L731
L53
53
52
5
723
7
722
L722
L723
61
6
51
L61
(L711)
L232
721
71
L711
High-purity oxygen
N2 gas
Feed air
Waste gas
1
L411
L722
91
92
31
3
L231
L231
23
P1
2
L212
222
22
221
L23
L411
L1
L722
21
L212
L53

[Figure 4]


A4
L412
41
4
L731
L732
73
L731
723
7
722
L232
721
71
L711
31
3
L231
L231
23
2
222
22
221
21
L212
L212
L1
L23
L732
L11
L53
53
52
5
61
6
51
L723
L61
(L711)
High-purity oxygen
Feed air
L1
HP N_2
LP N_2
L11
Waste gas
911
921
1
L53

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2018219685 A1 **[0002] [0003]**
- WO 2014173496 A2 **[0003] [0005]**
- JP 2020173041 A **[0003] [0005]**
- US 11549747 B **[0003] [0005]**
- WO 2018219685 A **[0004]**
- US 20230038170 A **[0006] [0078]**
- WO 2014173496 A **[0074]**