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(54) METHOD AND APPARATUS FOR PRODUCING AIR PRODUCTS FROM AN OXYGEN FRACTION

(57) In a method and an apparatus for producing air products comprising the steps of a liquid feed mixture (1) comprising krypton, xenon and more than 50 mol-% oxygen is provided. The liquid feed mixture (1) is subjected to a rectification in a krypton-xenon rectification system providing a first fraction (2) depleted in oxygen and enriched in krypton and xenon relative to the feed mixture (1) and a second fraction (3) enriched in oxygen and depleted in krypton and xenon relative to the feed mixture (1). The first fraction (2) and the second fraction (3) are withdrawn from the krypton-xenon rectification system comprising a rectification column arrangement (14), the rectification column arrangement (14) being arranged in a coldbox (300) that does not contain further separation columns not being part of the krypton-xenon rectification system.

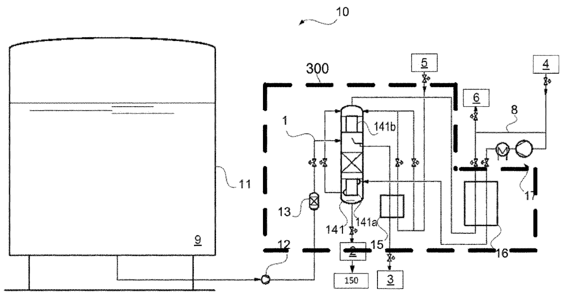

Fig. 1

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Description

[0001] The present invention relates to a method and to an apparatus for producing air products, particularly including a krypton/xenon mixture and oxygen.

Field of the invention

[0002] The production of air products in liquid or gaseous state by cryogenic separation of air in air separation units is well known and described, for example, in H.-W. Häring (ed.), Industrial Gases Processing, Wiley-VCH, 3006, especially sections 2.2.5, "Cryogenic Rectification" and 3.3 "Recovery of Krypton and Xenon". Unless expressly defined otherwise, the terms used below have the meanings customary in the technical literature.

[0003] The noble gases krypton and xenon, which are contained in atmospheric air at concentrations of about 1 ppm and about 0.09 ppm can be obtained by processing considerable amounts of air in air separation units. The boiling temperatures of krypton and xenon are well above the boiling temperatures of nitrogen and oxygen. The task of producing krypton and/or xenon products includes an enrichment to obtain a krypton/xenon mixture and separating said mixture as further explained below.

[0004] It is an object of the present invention to improve the processing of mixtures particularly including a krypton/xenon mixture and oxygen, particularly to provide additional or improved air products. According to prior art, that is done by a krypton-xenon enrichment column integrated in the main air separation plant for separating nitrogen and oxygen. Such enrichment column is, however, not installed in about 95 % of the existing air separation units. Therefore, they cannot be used for the production of krypton and xenon. The direct oxygen product (upstream a possible krypton-xenon enrichment column) contains only traces of krypton, which is not profitable to be transported to a separate krypton-xenon recovery unit.

[0005] In prior art, adding a krypton-xenon recovery to an air separation plant not yet having a krypton-xenon enrichment column by means would require opening the coldbox of the plant and other heavy intrusions into the original installation. Such steps would require months of shut-down of the main air separation plant meaning large production losses. Such shut-down is typically not acceptable to the customer. The invention seeks for a possibility to add a krypton-xenon recovery with moderate effort to an existing air separation which was previously not adapted for krypton-xenon recovery plant, in particular with minimum or no shut-down time of the main plant.

Summary of the invention

[0006] Against this background, the present invention provides a method and an apparatus for producing air products, particularly including a krypton/xenon mixture and oxygen, comprising the features of the independent claims, such features being able to be connected to an existing air separation plant without changing the air separation plant itself and providing an enrichment of krypton and xenon which is worth to be transported to a separate krypton-xenon enrichment unit. Embodiments are subject of the dependent claims and of the explanations that follow hereinbelow.

[0007] A method for producing air products comprising the step of providing a liquid or gaseous oxygen feed mixture is proposed; normally, a liquid feed mixture is provided. In an example, the feed mixture may comprise:

Krypton

- less than 120 ppm
- preferably less than 50 ppm
- more preferably 1 to 50 ppm

Xenon

- less than 15 ppm
- preferably less than 10 ppm
- more preferably 0.3 to 10 ppm

[0008] Most of the remainder of the feed mixture is usually oxygen. The invention works with oxygen concentrations in the feed mixture of more than 50 mol-%. Preferably the feed mixture comprises more than 90 mol-%, more preferably more than 98 mol-%, even more preferably more than 98 mol-%, for example 98 to 99.9 mol-% oxygen. The liquid feed mixture or a part thereof is subjected to a rectification providing a first fraction depleted in oxygen and enriched in krypton and xenon relative to the feed mixture and a second fraction enriched in oxygen and depleted in krypton and xenon relative to the feed mixture.

[0009] The first fraction and the second fraction are withdrawn from a rectification column arrangement used in the rectification in liquid form, the liquid feed mixture or the part thereof subjected to the rectification is introduced with a proportion of liquid of 90% or more, particularly of 95% or more or 99% or more, particularly in an essentially liquid form, into the rectification column arrangement, and a total feed to the rectification column arrangement is made up to at least 90%, particularly of at least 95% or 99%, particularly essentially completely, by the liquid feed mixture or the part thereof subjected to the rectification.

[0010] In most cases, the feed mixture will be (at least partly) in liquid state. Firstly, such a liquid is easier to transport and to store than a gas; secondly it can be directly used as a reflux liquid in the krypton-xenon rectification system.

[0011] In the invention, the rectification system for krypton-xenon has its own coldbox, enclosing the column(s) of such rectification system only and no other separation columns, in particular not of the main air separation plant for nitrogen-oxygen separation. Such coldbox may, however, enclose other parts of the rectification system like heat exchangers, pipelines, valves and/or possibly other cold parts, e.g. a cryogenic adsorption system. Thus, the krypton-xenon rectification system of the invention is retrofit-ready, i.e. it can be added to an existing tank or air separation unit without opening the insulation of the tank or the ASU.

[0012] A "coldbox" is an insulating enclosure having walls normally made of metal sheets and having an insulation in the walls (e.g. vacuum insulation) or at the inner surface of the walls or by filling its interior (outside the apparatus parts themselves) with powder or granulate material like perlite. The insulation methods mentioned may, of course be combined.

[0013] Terms such as "essentially comprising", "essentially consisting of", etc., when used herein to describe constituents of a composition, fluid, stream, etc., shall indicate that,

[0014] in addition to one or more specified constituents, one or more further constituents may be present in the composition, fluid, stream, etc., but that the essential features of the composition, stream, etc., in terms of at least one of physical properties, chemical properties, reactivity in one or more reaction units, treatability in one or more treatment units, compatibility with one or more materials, etc., are not significantly, not practically, or neglectably changed by the one or more further constituents. In this connection, the one or more specified constituents may make up at least 90%, particularly at least 95%, 99%, 99.9%, 99.99% or 99.999% of the composition, stream, etc. Terms such as "essentially free from", etc., may refer to one or more constituents being present in a composition, fluid, stream, etc., in minor amounts which likewise do not influence the essential features referred to above, such as in amounts of less than 10%, 5%, 1%, 0.1%, 0.01% or 0.001%.

[0015] Similarly, a reference to a composition, fluid, stream, etc., being made up from, or being formed by, etc., "essentially" one or more other compositions, fluids, streams, etc., shall indicate that such a composition, fluid, stream, etc., may also include parts from other sources, i.e., compositions, fluids, streams, etc., but that these generally only contribute to a small part to the overall amount. That is, the one or more compositions, fluids, streams, etc., specified as being made up from, or being formed by, "essentially" one or more specified compositions, fluids, streams, etc., may be provided from the one or more specified compositions, fluids, streams, etc., by at least 90%, particularly at least 95% or 99%. All percentage values indicated herein, if not otherwise indicated or excluded by the technical understanding of the skilled person, may refer to volume, weight, mass, or molar proportions.

[0016] In an embodiment of the present invention, the liquid feed mixture comprises 4 to 7 or 5 to 6 ppm by volume krypton, 0.2 to 0.6 or 0.3 to 0.5 ppm by volume xenon, and 99.5 to 99.9 % by volume oxygen. Embodiments of the present invention may therefore be used for treating liquid oxygen withdrawn from the sump of a low-pressure column of an air separation unit as generally known from the prior art.

[0017] In an embodiment of the present invention, the liquid feed mixture is provided using a liquid withdrawn from a cryogenic storage tank. This advantageously allows for collecting such liquid from one or more air separation units. The storage tank may be the usual liquid oxygen product and/or backup tank which belongs to an air separation plant or a set of air separation plants. There is no need for a separate tank feeding the krypton-xenon system.

[0018] According to an embodiment of the present invention, the liquid withdrawn from the cryogenic storage tank comprises one or more hydrocarbons and providing the liquid feed mixture comprises removing at least a part of the hydrocarbons from the liquid withdrawn from the cryogenic storage tank. Removal of hydrocarbons may be performed upstream the rectification column arrangement using methods as known in the prior art which may be adapted to the proposed process if necessary according to the understanding of the skilled person.

[0019] An embodiment of the present invention includes that the liquid withdrawn from the cryogenic storage tank is at least in part made up by a liquid produced in one or more air separation units and stored in the cryogenic storage tank, as mentioned.

[0020] The cold needed for driving the rectification system is preferably provided by liquid nitrogen e.g. taken from a LIN tank, a nearby nitrogen liquefier or an air separation plant producing liquid nitrogen. Such LIN tank may be filled by a remote source or by an air separation plant that delivers the liquid feed mixture or fills the LOX tank, the liquid feed mixture is taken from. In embodiments of the present invention, the rectification column arrangement comprises a rectification column with sump evaporator and a head condenser. This rectification column is referred to herein as a "first" rectification column at certain places, even if it may be the sole rectification column in the rectification column arrangement. In this embodiment, the sump evaporator may be heated using gaseous nitrogen and/or wherein the head condenser may be cooled using liquid nitrogen. In a preferred embodiment, the same fraction, e.g. nitrogen, is used for both purposes.

[0021] Alternatively, the liquid nitrogen is or produced by a recycle attached to the rectification column arrangement and made up by external gaseous nitrogen from a nitrogen pipeline connected to a pipeline network or to a near air separation plant producing pressurized nitrogen. Such air separation plant may or may not be the one delivering the feed mixture.

[0022] In embodiments of the present invention, the gaseous nitrogen used for heating the sump evaporator is, after having been used for heating the sump evaporator, at least in part expanded into the head condenser, more precisely into an evaporation space thereof, to form a part of the liquid nitrogen used for cooling the head condenser. The gaseous nitrogen used for heating the sump evaporator may be cooled during said heating the sump evaporator to an extent that it is partly or completely liquefied or brought close to the liquefaction temperature at an elevated pressure. Expansion into the head condenser then may cause (further) liquefaction.

[0023] The gaseous nitrogen after use for cooling the head condenser may at least in part be subjected to a compression step and a cooling step before being used for heating the sump evaporator. Suitable pressure and temperature levels are used as required to perform a satisfactory separation.

[0024] In embodiments of the present invention, a nitrogen cooling cycle may be formed. That is, gaseous nitrogen may be withdrawn from the head condenser, more precisely from an evaporation space thereof, and used at least in part used as the gaseous nitrogen used for heating the sump evaporator. Said gaseous nitrogen withdrawn from the head condenser may, together with gaseous makeup nitrogen, be subjected to the compression and cooling steps mentioned.

[0025] In embodiments of the present invention, liquid nitrogen used for cooling the head condenser be provided from a source of liquid nitrogen external to the first rectification column, either as the sole liquid nitrogen source, or in addition to another liquid nitrogen source, e.g. the above compression cooling cycle.

[0026] In embodiments of the present invention, the rectification column arrangement may comprise a second rectification column with a sump evaporator, wherein a feed provided to the second rectification column may be formed using a sump liquid of the first rectification column and wherein the first fraction may be withdrawn as a sump liquid from the second rectification column. Such embodiments may be used to further purify a product provided by a corresponding arrangement.

[0027] In such configurations, the sump evaporator of the second rectification column may be heated using further gaseous nitrogen which is thereafter at least in part expanded into the head condenser of the first rectification column. This allows for the same nitrogen source being used for both heating tasks.

[0028] Furthermore, in arrangements with a second rectification column, the sump liquid of the first rectification column used to form the feed to the second rectification column may be sent to a cryogenic adsorption step to remove N2O and/or CO2. In contrast to upstream treatment of the feed to the first rectification column, such a configuration is advantageous as a lower amount of liquid has to be treated.

[0029] In another embodiment of the invention, a purge liquid is withdrawn from the evaporation space of a condenser-evaporator in a distillation column system for nitrogen-oxygen separation and the liquid feed mixture is provided using such purge liquid. Such providing of the liquid feed mixture may be realized by a direct introduction, possibly through a purification step into the rectifications system, or by using a liquid tank as described above.

[0030] The "distillation column system for nitrogen-oxygen separation" (air separation unit, ASU) may be a classical double-column unit, the evaporation space of the main condenser being the source for the feed mixture. Alternatively, the ASU may be a single-column plant for nitrogen production having a top condenser, the feed mixture originating from evaporation space such top condenser. (The term "condenser" is a short form of "condenser-evaporator" in both cases.) The single-column plant may have a recycling of the gaseous fraction from the evaporation space of the top condenser to the single column, in particular by a cold compressor, in particular driven by a waste gas turbine (SPECTRA™ plant, see e.g. EP 412793 B1, EP 773417 B1, US 2007204652 , US 2008289362 A1, US 2009120128 A1, US 2009107177 A1, US 2010242537 A1, EP 2662653 A1, US 10209004 B2).

[0031] The rectification column arrangement may comprise a first rectification column and a second rectification column, the top fraction of the first rectification column being at least partially liquefied, a portion of the at least partially liquefied top fraction of the first rectification column being introduced into the second rectification column, the first fraction enriched in krypton and xenon being withdrawn from the first column and the second fraction enriched in oxygen being withdrawn from the second column. The first and second (upper) columns may be arranged as a double column with common condenser evaporator in the bottom of the second column; additionally the first column may have a bottom reboiler and the second column may have a top condenser; both may be operated by nitrogen as described above.

[0032] In the invention, the first fraction enriched in krypton and xenon is transported to a downstream separation unit for further enrichment of krypton and xenon not enclosed by the coldbox of the krypton-xenon rectification column arrangement. The transport may be performed continuously by a pipeline or intermittently by tank vehicles, depending on the distance between krypton-xenon rectification system and downstream separation unit.

[0033] Preferably, such embodiment is configured according to claim 10. This arrangement is not to be confused with a classical ASU configuration in a distillation system for nitrogen-oxygen separation, but it works according to similar principles but for oxygen-krypton/xenon separation.

[0034] An apparatus for producing air products is also provided, the apparatus being adapted to perform the steps of providing a liquid feed mixture comprising 1 to 10 ppm by volume krypton, 0.1 to 1 ppm by volume xenon, and 99 to 99.9 % by volume oxygen, and subjecting the liquid feed mixture or a part thereof to a rectification providing a first fraction depleted in oxygen and enriched in krypton and xenon relative to the feed mixture and a second fraction enriched in oxygen and depleted in krypton and xenon relative to the feed mixture. The apparatus is adapted to withdraw the first fraction and the second fraction from a rectification column used in the rectification in liquid form, introduce the liquid feed mixture or the part thereof subjected to the rectification with a proportion of liquid of 90% or more into the rectification column, and make up a total feed to the rectification column to at least 90% by the liquid feed mixture or the part thereof subjected to the rectification.

[0035] As to further details and advantages of such an apparatus, reference is made to the explanations above in connection with the method according to the present invention and its embodiments. Particularly, such an apparatus provided according to the present invention may comprise means adapted to perform a method according to any of the embodiments of the present invention.

Brief description of the Figures

[0036] Embodiments of the invention will now be described, by way of example only, with reference to accompanying drawings, in which:

Figure 1 illustrates a unit for processing of a mixture containing krypton, xenon and oxygen in a configuration usable according to an embodiment of the present invention.

Figure 2 illustrates a unit for processing of a mixture containing krypton, xenon and oxygen in a configuration usable according to an embodiment of the present invention.

Figure 3 illustrates another embodiment of the present invention.

Figure 4 shows a further embodiment of the present invention having a split feed line and a single integrated heat exchanger.

Embodiments of the invention

[0037] Krypton and xenon production based on cryogenic air separation may be performed in three sub-units or steps which are often referred to as C1, C2 and C3. The C1 unit or step is typically a part of, or performed in, an air separation unit as described at the outset and it produces so-called crude krypton/xenon which has comparatively low concentrations of krypton and xenon and contains about 99.3% oxygen. Crude krypton/xenon from several air separation units may be collected and transported to the C2 unit or step, in which a purification is performed, mainly by removing the oxygen. The product of the C2 unit or step is essentially a krypton/xenon mixture with traces of impurities. The removed oxygen is conventionally used as a gaseous oxygen product at low pressure. From several C2 units or steps, the krypton/xenon mixture may be passed on to a C3 unit or step to produce pure krypton and xenon. The designation of units or steps as C1, C2, C3 is not limiting and the present invention can be used with other arrangements of apparatus units or method steps.

[0038] Figure 1 illustrates an apparatus 10 according to an embodiment of the present invention which may be used as a C1 unit or in a C1 step. More generally, the apparatus 10 illustrated in Figure 1 may be used in connection with producing air products, particularly including a krypton/xenon mixture and oxygen from liquid oxygen which is withdrawn from a sump of a low pressure column of an air separation unit or a comparable liquid in cryogenic state.

[0039] Apparatus 10 comprises a cryogenic storage tank 11 which may be supplied with cryogenic liquid 9 from one or more air separation units, e.g. by tank trucks. Such a liquid 9 may be withdrawn from the cryogenic storage tank 11 using a pump 12. and provides a liquid feed mixture 1.

[0040] A rectification column arrangement 14 which comprises, in the embodiment illustrated in Figure 1, a single rectification column 141, is part of apparatus 10 and is adapted to perform a rectification providing a first fraction 2 depleted in oxygen and enriched in krypton and xenon relative to the feed mixture 1, which may be supplied to a C2 unit as may be known to the skilled person, or any other subsequent processing step or steps, and a second fraction 3 enriched in oxygen and depleted in krypton and xenon relative to the feed mixture 1. Second fraction 3 may essentially consist of oxygen and some impurities already mentioned above.

[0041] The first fraction 2 and the second fraction 3 are withdrawn from the rectification column arrangement 14, i.e. from the rectification column 141, in liquid form, the liquid feed mixture 1 or the part thereof subjected to the rectification is introduced with a proportion of liquid of 90% or more into the rectification column arrangement 14, and a total feed to the rectification column arrangement 14 is made up to at least 90% by the liquid feed mixture 1 or the part thereof subjected to the rectification. Particularly, only liquid in form of the feed mixture 1 is introduced into rectification column arrangement 14, and liquid oxygen is withdrawn at an upper position in form of the second fraction 3.

[0042] The rectification column 141 of the rectification column arrangement 14 comprises a sump evaporator 141a and a head condenser 141b, wherein the sump evaporator 141a is heated using gaseous nitrogen 4 and wherein the head condenser 141b is cooled using liquid nitrogen 5 which both, in parts, are provided from external source in the example illustrated. The gaseous nitrogen used for heating the sump evaporator 141a is, in the example shown, after having been used for heating the sump evaporator 141a, at least in part expanded into the head condenser 141b to form a part of the liquid nitrogen used for cooling the head condenser 141b.

[0043] In the example shown, the gaseous nitrogen 4 used for heating the sump evaporator 141a is at least in part subjected to a compression step in a compression unit 17 and a cooling step in counterstream heat exchangers 16 and 15 before being used for heating the sump evaporator 141a. Gaseous nitrogen is withdrawn from the head condenser 141b and used at least in part used as the gaseous nitrogen used for heating the sump evaporator 141a, i.e. it is, in the example shown, combined with the gaseous nitrogen 4 from the external source and compressed and cooled together therewith as shown for a stream 8. A part may also be vented to the atmosphere or used otherwise, as shown for a fraction 6 in Figure 1.

[0044] Coldbox 300 is schematically shown in Figure 1 as a dotted line. It encloses all cold parts of the krypton-xenon rectification system. It encloses a single column, the rectification column 141 and other cold parts like condenser-evaporators 141a, 141b and gas-gas or liquid-liquid heat exchangers 15, 16. The coldbox 300 does not enclose further separation columns not being part of the krypton-xenon rectification system, in particular not a column of a main plant like an air separation plant for nitrogen-oxygen separation, in particular not a column of the air separation unit, the feed mixture may come from. Thus, the krypton-xenon rectification system is retrofit-ready, i.e. it can be added to an existing tank or air separation unit without opening the insulation of the tank or the ASU.

[0045] In Figure 2, an apparatus 20 according to a further embodiment of the present invention is illustrated which can be used for essentially the same purposes as the apparatus 10 according to Figure 1. Some of the elements, which may have essentially the same or a comparable function and configuration, are not again described for reasons of clarity. For reasons of clarity and generality, furthermore, storage tank 11 which is illustrated in Figure 1 is not illustrated in Figure 2.

[0046] Apparatus 20 according to Figure 2 comprises a rectification column arrangement 14 which, however, comprises two rectification columns 141 and 142. Rectification column 141 may essentially be provided as described before in connection with apparatus 10 shown in Figure 1. Rectification column 142 may be provided to further treat sump liquid of rectification column 141. Different from what is shown in Figure 1 for apparatus 10, furthermore, adsorption unit 13 of apparatus 20 shown in Figure 2 is arranged at a different position to treat the sump liquid of rectification column 141 fed into rectification column 142. A side stream of the gaseous nitrogen 4 is used to heat a sump evaporator 142a of rectification column 142, forming a condensate which is also expanded into head condenser 141b of rectification column 141.

[0047] The columns of the rectification column arrangement (14) of all embodiments may have an inlet for gaseous oxygen in order to introduce gases losses from a tank or a filling process for transporting one or more products, in particular products from the rectification column arrangement.

[0048] The various embodiments described herein are presented only to assist in understanding and teaching the claimed features. These embodiments are provided as a representative sample of embodiments only and are not exhaustive and/or exclusive. It is to be understood that advantages, embodiments, examples, functions, features, structures, and/or other aspects described herein are not to be considered limitations on the scope of the invention as defined by the claims or limitations on equivalents to the claims, and that other embodiments may be utilised, and modifications may be made without departing from the scope of the claimed invention. Various embodiments of the invention may suitably comprise, consist of, or consist essentially of, appropriate combinations of the disclosed elements, components, features, parts, steps, means, etc., other than those specifically described herein. In addition, this disclosure may include other inventions not presently claimed, but which may be claimed in future.

[0049] Coldbox 300 is schematically shown in Figure 2 as a dotted line. It encloses all cold parts of the krypton-xenon rectification system. It encloses a single column, the rectification column 141 and other cold parts like condenser-evaporators 141a, 141b and gas-gas or liquid-liquid heat exchangers 15, 16. The coldbox 300 does not enclose further separation columns not being part of the krypton-xenon rectification system, in particular not a column of a main plant like an air separation plant for nitrogen-oxygen separation, in particular not a column of the air separation unit, the feed mixture may come from. Thus, the krypton-xenon rectification system is retrofit-ready, i.e. it can be added to an existing tank or air separation unit without opening the insulation of the tank or the ASU.

[0050] In Figure 3, an apparatus, and a process according to a further embodiment of the present invention is illustrated which can be used for essentially the same purposes as those shown in Figures 1 and 2. As Figure 2, it comprises two separation columns 141, 143, having, however, a slightly different operating regime. Some of the elements, which may have essentially the same or a comparable function and configuration, are not again described for reasons of clarity.

[0051] Liquid oxygen 9 containing krypton and xenon, is supplied from a cryogenic storage tank or one or more air separation units, in particular by impure LOX (LOX imp) having an oxygen concentration of less than 99.5 mol-%, in particular 70 to 90 mol-% and into a coldbox 300. A least a portion of the mixture 9 may be subcooled in a nitrogen heat exchanger 316. The subcooled feed mixture 309 is purified in adsorption unit 13, having two switchable vessels in this example. The purified liquid constitutes a liquid feed mixture 1 to a rectification column arrangement 14 comprising a first column 141 for krypton-xenon concentration and a second column 143 for high-purity oxygen production. The second column (upper column) is specifically used to separate oxygen from other (lighter) gases such as nitrogen, argon, hydrogen and/or carbon monoxide. Those two columns 141/143 are arranged one above the other according to a classical double column, the top condenser of the lower column 141 simultaneously operating as bottom reboiler of the upper column 143. Those two columns 141, 143 are the only separation columns in the krypton-xenon rectification system of this embodiment. The coldbox 300 does not contain any further column, in particular no separation column für nitrogen-oxygen separation.

[0052] The rectification column arrangement 14 is adapted to perform a rectification providing a first fraction 2 depleted in oxygen and enriched in krypton and xenon relative to the feed mixture 1, which may be supplied to a C2 unit as may be known to the skilled person, or any other subsequent processing step or steps, and a second fraction 3 enriched in oxygen and depleted in krypton and xenon relative to the feed mixture 1. Second fraction 3 may essentially consist of oxygen and some impurities already mentioned above.

[0053] The first fraction 2 and the second fraction 3 are withdrawn from the rectification column arrangement 14, i.e. from the rectification columns 141 resp. 143, in liquid form, the liquid feed mixture 1 or the part thereof subjected to the rectification is introduced with a proportion of liquid of 90% or more into the rectification column arrangement 14, and a total feed to the rectification column arrangement 14 is made up to at least 90% by the liquid feed mixture 1 or the part thereof subjected to the rectification. Particularly, only liquid in form of the feed mixture 1 is introduced into rectification column arrangement 14, and liquid oxygen is withdrawn at an upper position in form of the second fraction 3. In special cases, the feed mixture may be gaseous.

[0054] The rectification column 141 of the rectification column arrangement 14 comprises a sump evaporator (bottom reboiler) 141a and a head condenser (top condenser) 141b, wherein the sump evaporator 141a is heated using gaseous nitrogen 4 and wherein the head condenser 141b is cooled using liquid oxygen collecting in the bottom of the second column 143. Thereby, top condenser 141b works as bottom reboiler of the second column 143 as well. The gaseous nitrogen used for heating the sump evaporator 141a is, in the example shown, after having been used for heating the sump evaporator 141a and thereby liquefied, at least in part expanded into the top condenser 143b of the second column 143 to form a part of the liquid nitrogen used for cooling the head condenser 141b. Before expansion, it may be subcooled in the nitrogen heat exchanger 316.

[0055] In the example shown, the gaseous nitrogen 4 is supplied from a pressurized nitrogen pipeline 320 (PGAN pipeline). (Alternatively, it may be taken pressureless and then compressed in a nitrogen compressor - not shown in the drawing. The low pressure nitrogen from the reboiler/condenser cycle in the coldbox can be "recycled" to the feed of the compressor (recycle compressor) to reduce the required amount of nitrogen from the pipeline.) A first portion 322 of the gaseous nitrogen 321 is cooled in the nitrogen heat exchanger 316 and taken as the heating medium 4 for the bottom reboiler 141a. A second portion 323 is used for regenerating the adsorption unit 13.

[0056] Gaseous nitrogen is withdrawn from the head condenser 143b, fully warmed in the nitrogen heat exchanger 316 and rejected, e.g. vented to the atmosphere or used otherwise. (As an Alternative, a nitrogen recycle as in Figures 1 or 2 could be used for heating and cooling evaporator-condenser 141a and 143b.

[0057] The feed mixture to the second column 143 is provided by the top fraction of the lower column 325 after liquefaction in the condenser-evaporator 141b. A non-condensed portion 326 of the top fraction of the upper column 143 is taken as oxygen-rich waste gas, fully warmed in the nitrogen heat exchanger 316 and rejected, e.g. vented to the atmosphere or used otherwise. A small amount of liquid 327 is withdrawn from the top condenser 143b as a purge fraction. Addition liquid nitrogen (PLIN) 328 may be introduced as a cooling medium into the top condenser 413b; it may be taken from a liquid storage tank.

[0058] Coldbox 300 is schematically shown in Figure 3 as a dotted line. It encloses all cold parts of the krypton-xenon rectification system. It encloses a single column, the rectification columns 141 and 143 and other cold parts like condenser-evaporators 141a, 141b, 143b and gas-gas and heat exchanger 316 without phase changes. The coldbox 300 does not enclose further separation columns not being part of the krypton-xenon rectification system, in particular not a column of a main plant like an air separation plant for nitrogen-oxygen separation, in particular not a column of the air separation unit, the feed mixture may come from. Thus, the krypton-xenon rectification system is retrofit-ready, i.e. it can be added to an existing tank or air separation unit without opening the insulation of the tank or the ASU.

[0059] Figure 4 depicts a variant of Figure 1 having two main differences. Firstly, the liquid feed mixture 1 is split into a first portion 1A and a second portion 1B before being introduced into the single rectification column 141. The first portion 1A is fed to the top of the column like in Figure 1, the second portion is introduced into the bottom of column 141. As a second main difference, the two heat exchangers 15, 16 of Figure 1 are integrated into a single heat exchanger 15A.

Claims

1. A method for producing air products comprising the steps of

    - providing a liquid feed mixture (1) comprising krypton, xenon and more than 50 mol-% oxygen and

- subjecting the liquid feed mixture (1) or a part thereof to a rectification in a krypton-xenon rectification system providing a first fraction (2) depleted in oxygen and enriched in krypton and xenon relative to the feed mixture (1) and a second fraction (3) enriched in oxygen and depleted in krypton and xenon relative to the feed mixture (1),

characterized in that

- the first fraction (2) and the second fraction (3) are withdrawn from the krypton-xenon rectification system comprising a rectification column arrangement (14), the rectification column arrangement (14) being arranged in a coldbox (300) that does not contain further separation columns not being part of the krypton-xenon rectification system.

2. The method according to claim 1, wherein the liquid feed mixture (1) is provided using a liquid withdrawn from a cryogenic storage tank (11).

3. The method according to claim 2, wherein the liquid withdrawn from the cryogenic storage tank (11) is at least in part made up by a liquid produced in one or more air separation units and delivered via an oxygen product line to the cryogenic storage tank (11), the oxygen product line and the line for the feed mixture being the only flow connection between the one or more air separation units and the rectification system .

4. The method according to any of the preceding claims, wherein the rectification column arrangement (14) comprises a first rectification column (141) with a sump evaporator (141a) and a head condenser (141b).

5. The method according to claim 4, wherein the sump evaporator (141a) is heated using gaseous nitrogen (4) and wherein the head condenser (141b) is cooled using liquid nitrogen (5), the gaseous nitrogen used for heating the sump evaporator (141a) is, after having been used for heating the sump evaporator (141a), at least in part expanded into the head condenser (141b) to cool the head condenser (141b).

6. The method according to claim 6 or 5, wherein the gaseous nitrogen (4) used for cooling the head condenser (141b) is at least in part subjected to a compression step and a cooling step before being used for heating the sump evaporator (141a).

7. The method according to any of according to any of the preceding claims, wherein the rectification column arrangement (14) comprises a second rectification column (142) with a sump evaporator (142a), wherein a feed provided to the second rectification column (142) is formed using a sump liquid of the first rectification column (141) and wherein the first fraction (2) is withdrawn as a sump liquid from the second rectification column (142)..

8. The method according to claim 7, wherein the sump evaporator (142a) of the second rectification column (142) is heated using gaseous nitrogen which optionally is thereafter at least in part expanded into the head condenser (141b) of the first rectification column.

9. The method according to claim 1 or 2, wherein a purge liquid is withdrawn from the evaporation space of a condenser-evaporator in a distillation column system for nitrogen-oxygen or argon-oxygen separation and the liquid feed mixture (1) is provided using such purge liquid.

10. The method according to claim 9, wherein the rectification column arrangement (14) comprises a first rectification column (141) and a second rectification column (143), the top fraction of the first rectification column (141) is at least partially liquefied, a portion (325) of the at least partially liquefied top fraction of the first rectification column is introduced into the second rectification column (143), the first fraction (2) enriched in krypton and xenon is withdrawn from the first column and the second fraction (3) enriched in oxygen is withdrawn from the second column (143).

11. The method according to any of according to any of the preceding claims, wherein the first fraction (2) enriched in krypton and xenon is transported to a downstream separation unit for further enrichment of krypton and xenon which is not enclosed by the coldbox (300) of the krypton-xenon rectification column arrangement (14).

12. The method according to claims 1 or 9, wherein

- the rectification column system comprises

  - a lower column having an LC bottom reboiler,
  - an upper column having an UC head condenser and
  - a main condenser bringing lower and upper columns in heat-exchange relationship,

- the liquid feed mixture is introduced into an intermediate section of the lower column,
- the first fraction (2) is withdrawn from the bottom of the lower column and the second fraction (3) is withdrawn from the upper column.

13. The method according to any one of the preceding claims, wherein the liquid feed mixture (1) comprises at most 99.9 % by volume oxygen.

14. An apparatus (10, 20) for producing air products, the apparatus (10, 20) being adapted to perform the steps of

- providing a liquid feed mixture (1) comprising krypton, xenon and more than 50 mol-% oxygen and
- subjecting the liquid feed mixture (1) or a part thereof to a krypton-xenon rectification system providing a first fraction (2) depleted in oxygen and enriched in krypton and xenon relative to the feed mixture (1) and a second fraction (3) enriched in oxygen and depleted in krypton and xenon relative to the feed mixture (1),

characterized in that the apparatus (10) is adapted to

- withdraw the first fraction (2) and the second fraction (3) from the krypton-xenon rectification system comprising a rectification column arrangement (14) used in the rectification in liquid form,
- the rectification column arrangement (14) being arranged in a coldbox (300) that does not contain further separation columns not being part of the krypton-xenon rectification system.

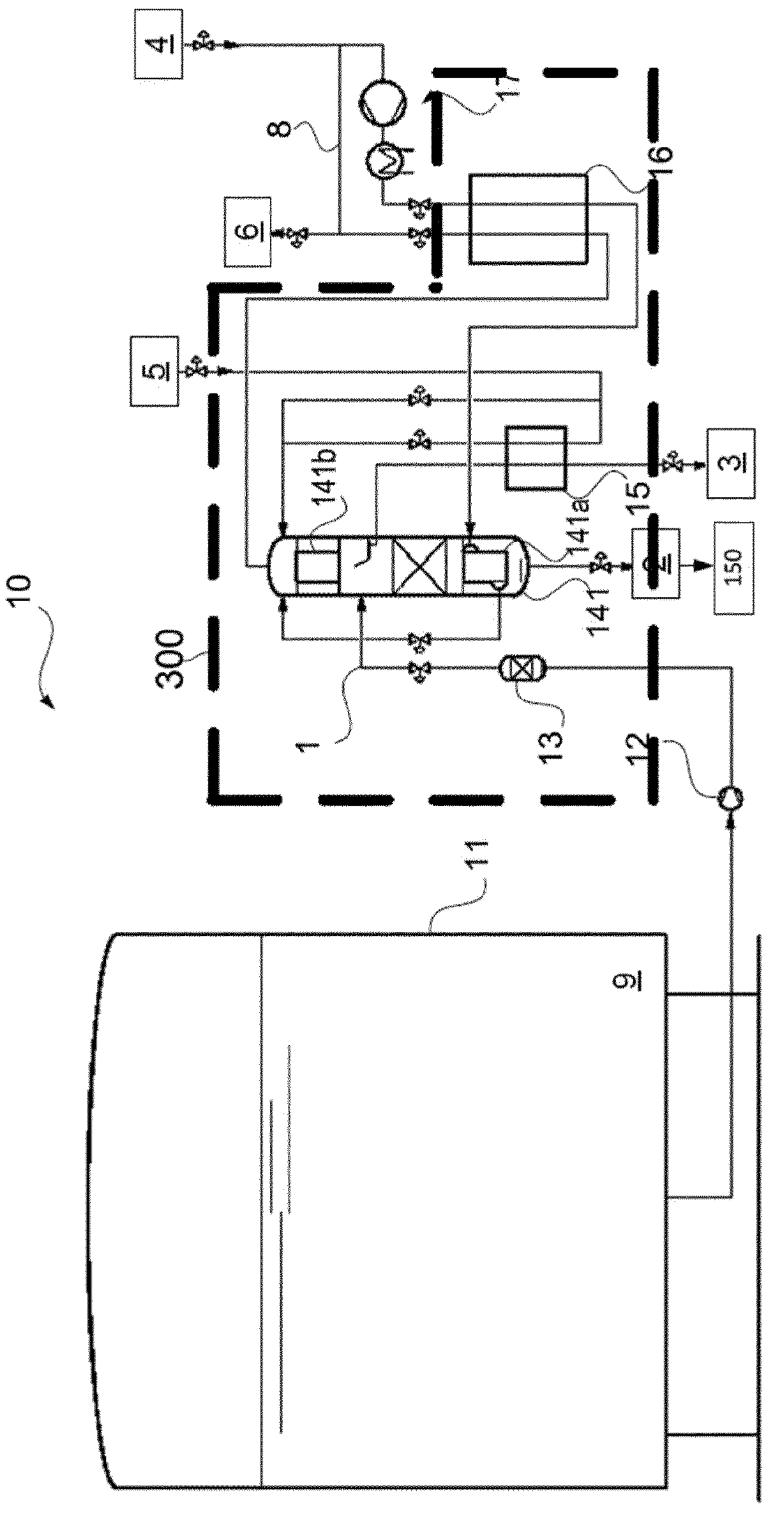

Fig. 1

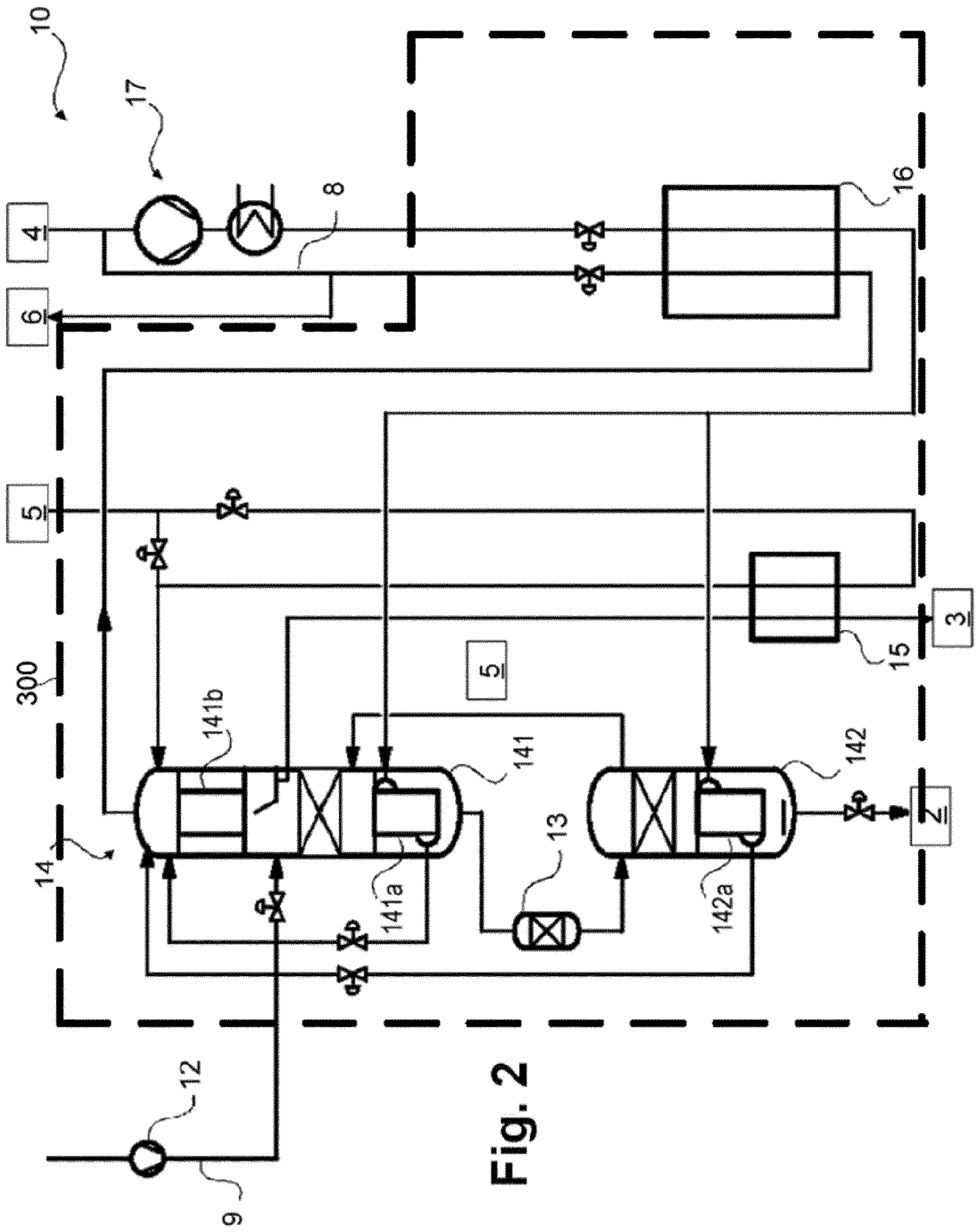

Fig. 2

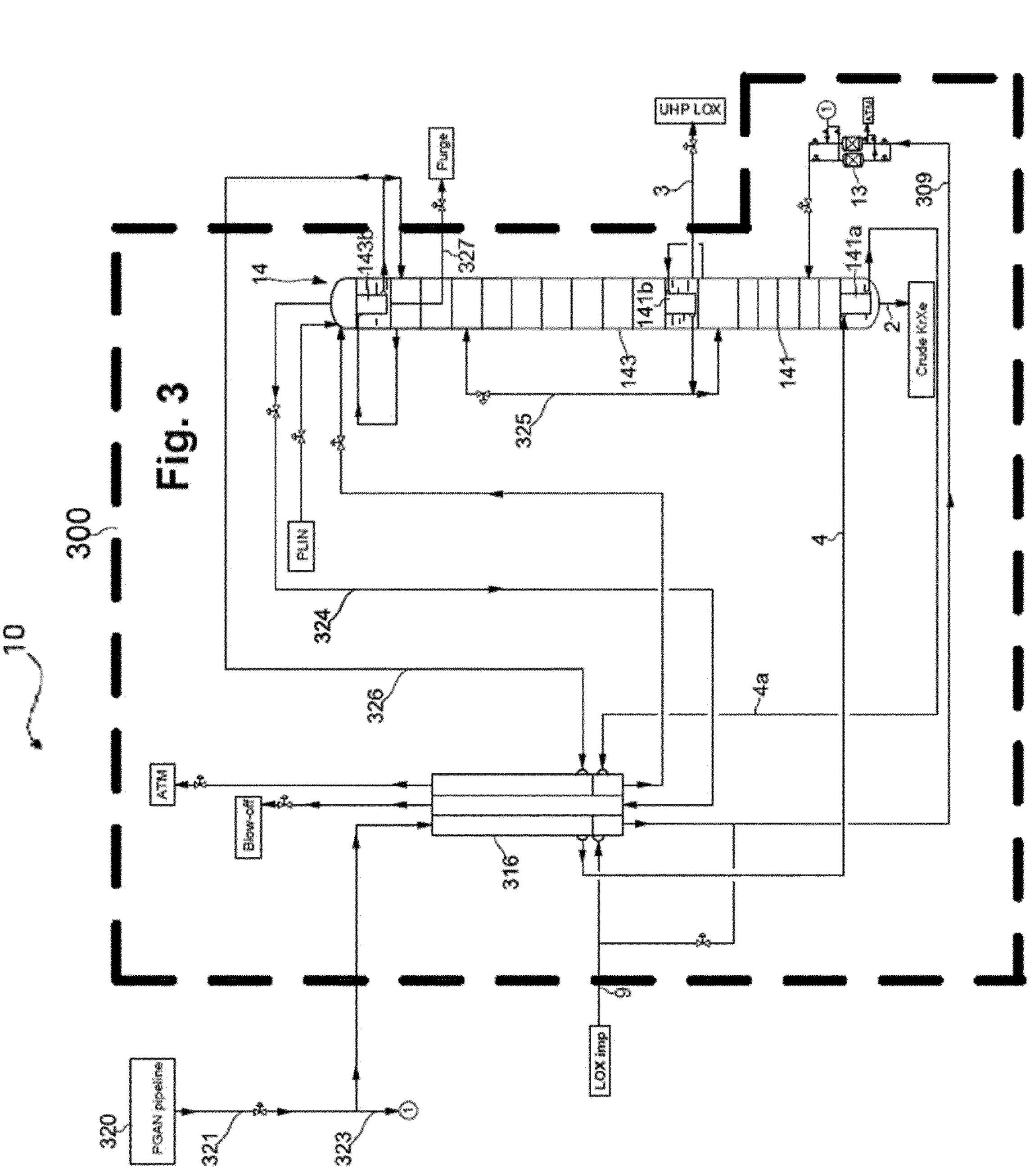
10
300
PGAN pipeline
320
321
323
LOX imp
9
316
ATM
Blow-off
326
324
PLIN
325
4a
4
14
143b
327
Purge
143
141b
UHP LOX
3
141
141a
2
Crude KrXe
13
ATM
309

Fig. 3

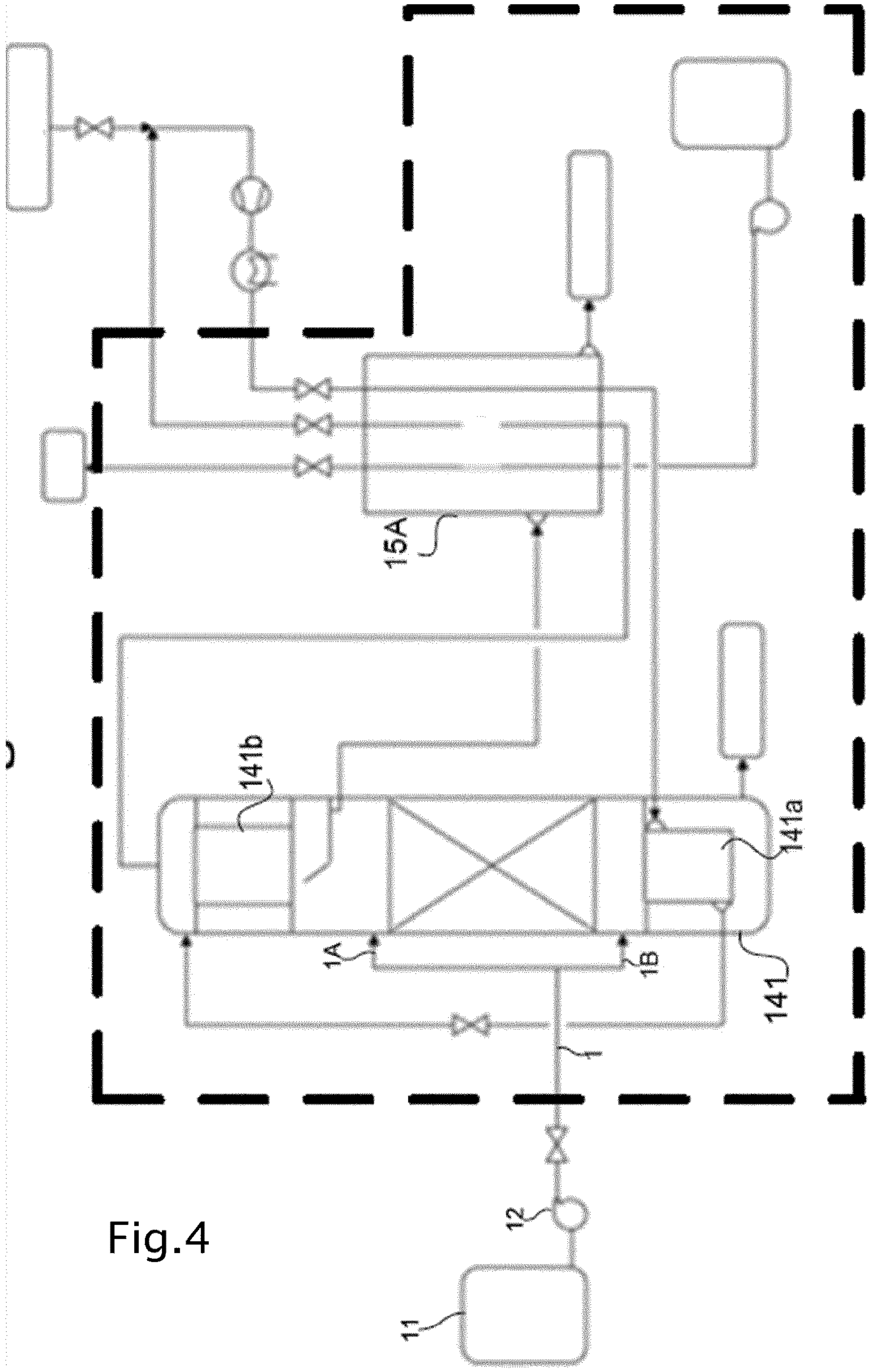

Fig.4

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EUROPEAN SEARCH REPORT

Application Number
EP 23 02 0291

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	FR 2 640 032 A1 (TEISAN KK [JP]) 8 June 1990 (1990-06-08) * page 3, lines 7-11; figure 1 * * page 4, lines 6-12 * * page 5, line 34 - page 6, line 33 *	1,4-8, 13,14 2,3,8,11	INV. F25J3/04 F25J3/08
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			TECHNICAL FIELDS SEARCHED (IPC)
			F25J

~~The present search report has been drawn up for all claims~~

1

Place of search	Date of completion of the search	Examiner
Munich	14 November 2023	Göritz, Dirk

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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Application Number

EP 23 02 0291

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

3-8(completely); 1, 2, 11, 13, 14(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 23 02 0291

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 3-8(completely); 1, 2, 11, 13, 14(partially)

A method for producing air products comprising the steps of
- providing a liquid feed mixture comprising krypton, xenon and more than 50 mol-% oxygen,
- subjecting the liquid feed mixture or a part thereof to a rectification in a krypton-xenon rectification system providing a first fraction depleted in oxygen and enriched in krypton and xenon relative to the feed mixture and a second fraction enriched in oxygen and depleted in krypton and xenon relative to the feed mixture,
- the first fraction and the second fraction are withdrawn from the krypton-xenon rectification system comprising a rectification column arrangement, the rectification column arrangement being arranged in a coldbox that does not contain further separation columns not being part of the krypton-xenon rectification system,

wherein inter alia the rectification column arrangement comprises a first rectification column with a sump evaporator and a head condenser.

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2. claims: 9, 10, 12(completely); 1, 2, 11, 13, 14(partially)

A method for producing air products comprising the steps of
- providing a liquid feed mixture comprising krypton, xenon and more than 50 mol-% oxygen,
- subjecting the liquid feed mixture or a part thereof to a rectification in a krypton-xenon rectification system providing a first fraction depleted in oxygen and enriched in krypton and xenon relative to the feed mixture and a second fraction enriched in oxygen and depleted in krypton and xenon relative to the feed mixture,
- the first fraction and the second fraction are withdrawn from the krypton-xenon rectification system comprising a rectification column arrangement, the rectification column arrangement being arranged in a coldbox that does not contain further separation columns not being part of the krypton-xenon rectification system,

wherein inter alia the rectification column arrangement comprises a first rectification column and a second rectification column, the top fraction of the first rectification column is at least partially liquefied, a portion of the at least partially liquefied top fraction of the first rectification column is introduced into the second rectification column, the first fraction enriched in krypton and xenon is withdrawn from the first column and the second fraction enriched in oxygen is withdrawn from the second column.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 02 0291

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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14-11-2023

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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