



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.06.2024 Bulletin 2024/26

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

(21) Application number: **22020618.9**

(52) Cooperative Patent Classification (CPC):
**F25J 3/0409; F25J 3/04224; F25J 3/04357;
F25J 3/04412; F25J 3/04678; F25J 3/04727;
F25J 3/048; F25J 2280/02**

(22) Date of filing: **20.12.2022**

(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:
KH MA MD TN

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(54) **PROCESS AND APPARATUS FOR PRODUCING ARGON BY CRYOGENIC AIR SEPARATION**

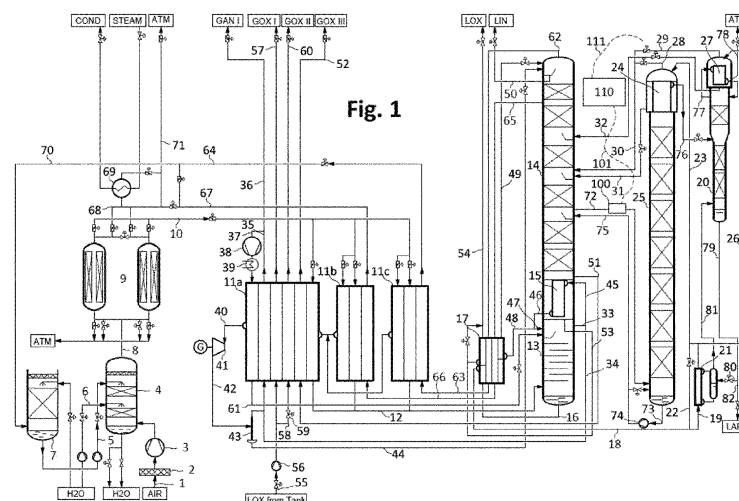
(57) The process for producing an argon-enriched fraction by cryogenic air separation comprises

- introducing feed air into a distillation system for oxygen-nitrogen separation comprising a low-pressure column,
- withdrawing an argon-containing fraction from the low-pressure column and introducing it into a crude argon column having a crude argon top condenser being indirectly cooled by a cryogenic working fluid,
- withdrawing an argon-enriched fraction from an upper section of the crude argon column,
- measuring the oxygen content in the argon-containing

fraction,
characterized in that

- measuring the nitrogen content in the argon-containing fraction,
- predicting the nitrogen content in the crude argon condenser on the basis of the measured nitrogen content and
- controlling the operation of the crude argon column depending on such corrected estimated argon concentration depending on such predicted nitrogen content in the crude argon condenser.

A respective apparatus is claimed as well.



Description

[0001] This invention regards to a process for controlling a process for producing argon by air separation and a respective apparatus according to the introductory parts of the independent claims.

[0002] The "distillation system for oxygen-nitrogen separation" of the invention can be a classical Linde double column. Other systems, e.g. with two or more columns side by side or three- or more-column system may be used.

[0003] Cryogenic air separation plant have nitrogen and/or oxygen as their main product. If the plant is large enough, frequently argon is produced as an additional product. A usual configuration of such a plant having a double column as "distillation system for oxygen-nitrogen separation" and a crude argon column is shown in Häring, Industrial Gas Processes, 2008, Figure 2.3A on page 22. For a high argon yield, the crude argon columns has to be controlled. For that purpose, it is known to measure the oxygen content in the argon-containing fraction feeding the crude argon column, in particular by a standard oxygen analyser.

[0004] It is the object of the invention to improve the argon yield of such a system. that is done by the features of the second part of claim 1.

[0005] The invention does not use the classical means of influencing the product yield of a distillation product, i.e. changing the number of theoretical trays or the type of mass exchange element, or stationarily change reflux or the like. During the invention it has been surprisingly found that the classical control leads to instabilities and that those instabilities can be considerably reduced by a nitrogen measurement, such feature indirectly improving argon yield.

[0006] As the argon-containing fraction (also called argon transition fraction) does not contain so much nitrogen, so that the use of nitrogen content for control is not natural. A typical composition of such fraction is 90 mol-% argon, 10 mol-% oxygen and 150 mol-ppm nitrogen. On the other side, even fast nitrogen analysers make measurement in a frequency of some minutes. They were not to be expected to be able to help in the control with much shorter response time.

[0007] Nevertheless, in the invention, it was shown that using the nitrogen values for correcting the known oxygen-based control gives a considerable improvement in argon yield. The benefit on argon recovery can be up to 1 % and, depending on product state (liquid or gaseous), ASU configuration is based on exploiting of design margins. The surplus in recovery can be produced by installation of a control concept based on the nitrogen measurement in the vapor feed to the crude argon column. The advantage of the nitrogen control concept over existing concepts is that the source of an inert gas potentially blocking the crude argon condenser is monitored at the inlet to the system. Whereas the existing measurements with the same purpose are located further up-

stream in the low pressure column or downstream the crude argon condenser. These measurements are indirect, have delay times and can have other reasons for value change. In contrast, the invention provides a direct measurement having nearly no delay.

[0008] Preferably, a gas chromatograph is used for measuring the nitrogen content, in particular a fast gas chromatograph. An average gas chromatograph delivers the measurement result after a delay time of 10 s. A fast gas chromatograph would be one with typically 30 s delay time.

[0009] According to a further aspect of the invention, the control action(s) is/are performed depending on the predicted nitrogen content in the crude argon condenser. Preferably, nitrogen and oxygen concentration are directly measured in the argon-containing fraction, predicted in the condenser and the argon concentration is computed from those values. The control action(s) may be one or more of the following.

- Correction of the setpoint of the controller for the oxygen content in the argon-containing fraction.
- Initiation of a blow off of crude argon from the top of the crude argon column, from the crude argon top condenser or from the crude argon product line to avoid instability in the crude argon top condenser.
- Adaptation of the crude argon condenser duty to optimize the recovery, such adaption preferably done by controlling the feed to the crude argon column.

[0010] As another aspect of the invention, alternatively or additionally the control may trigger one or more of the following measures in case of a high value of the nitrogen content measured in the argon-containing fraction.

- Reducing the pressurized gaseous nitrogen withdrawal from the high-pressure column, where the distillation system for oxygen-nitrogen separation additionally comprises a high-pressure column being in heat-exchange relationship with the low-pressure column and a pressurized gaseous nitrogen stream is withdrawn from the upper section of the high-pressure column and recovered as a pressurized gaseous nitrogen product.
- Reducing the oxygen product withdrawal from the low-pressure column, where an oxygen product is withdrawn from the lower section of the low-pressure column in gaseous and/or in liquid form, whereby the control comprises reducing the oxygen product withdrawal from the lower section of the low-pressure column.
- Reducing the recycle stream, where a working fluid of the air separation is used as recycle stream, the recycle stream being warmed, compressed, cooled and turbine-expanded.
- Reducing the turbine stream, where a working fluid of the air separation is used as turbine stream, the turbine stream being turbine-expanded.

- Increasing the amount of feed air into the distillation system for oxygen-nitrogen separation.

[0011] A "high value of the nitrogen content measured in the argon-containing fraction" means a value above a predefined threshold value. The threshold value may be the same for all above controlled parameters or different for at least two of them or for all. Those threshold values may be constant for an operational condition, vary with operating condition or depend on other parameters. In particular the nitrogen concentration threshold value may additionally depend on the load of the crude argon column, i.e. on the amount of argon-containing fraction withdrawn from the low-pressure column and introduced to the crude argon column; in case of reduced load, the nitrogen content in the crude argon condenser is allowed to be higher.

[0012] The "turbine stream" may or may not be identical to the "recycle stream". If it is not a recycle turbine, the turbine-expander may be an air turbine expanding into the high-pressure column or into the low-pressure column, or a nitrogen turbine expanding gaseous nitrogen from the high-pressure column or from the low-pressure column.

[0013] In the invention, the crude argon column may be used for recovering a final or intermediate product by withdrawing the argon-enriched fraction from the crude argon column as a crude argon product. Such crude argon product can be directly used or further purified in a pure argon column. Alternatively, the crude argon column may be used as argon rejection column for removing argon from process without using it as a final product. In this case, the argon-enriched fraction is either directly rejected or warmed in the main heat exchanger before, perhaps after being mixed with another waste gas.

[0014] In the process of the attached drawing of Figure 1, atmospheric air is sucked in via a filter 2 by an air compressor 3 and compressed therein to an absolute pressure of 5.0 to 7.0 bar, preferably about 5.5 bar and is then cooled in a direct contact cooler 4 in direct heat exchange with cooling water 5, 6, which comes on the one hand (5) from an evaporative cooler 7, on the other hand (6) is supplied from an external source. The compressed and cooled air 8 is purified in a purifying device 9, which has a pair of vessels filled with adsorption material, preferably molecular sieve. The purified air 10 is cooled in a main heat exchanger system 11a, 11b, 11c to about its dew point. The cold air 12 is introduced into the high-pressure column 13 of a distillation system for nitrogen-oxygen separation, which also has a low-pressure column 14. High-pressure column 13 and low-pressure column 14 are designed as classic Linde double columns and are connected via a main condenser 15 in heat-exchanging relationship. The operating pressures - each at the top - are 4.5 to 6.5 bar, preferably about 5.0 bar in the high-pressure column and 1.2 to 1.7 bar, preferably about 1.3 bar in the low-pressure column.

[0015] Liquid crude oxygen 16 is removed from the bot-

tom of the high-pressure column 13, cooled in a subcooler 17 and further cooled to a part 19 in a bottom evaporator 21 of the pure argon column 20. Another part 22 can be bypassed around the bottom evaporator 21. Subsequently, a part 23 flows into the evaporation chamber of a top condenser 24 of a raw argon column 25, another part into the evaporation chamber of a top condenser 27 of the pure argon column 20. The crude oxygen 28, 29 evaporated in the top condensers 24, 27 is supplied via line 30 to the low-pressure column 14 at a first intermediate point. The fraction 31 remaining in liquid form from the top condenser 24 of the crude argon column 25 is also led to the first intermediate point of the low-pressure column 14. The portion 32 remaining in liquid form from the top condenser 27 of the pure argon column 20 is fed at a second intermediate point of the low-pressure column 14, which lies above the first intermediate point.

[0016] Gaseous nitrogen 33 from the head of the high-pressure column 13 is fed to a first part 34 to the cold end of the main heat exchanger 11a, heated there to about ambient temperature and then divided into a pressure product flow 36 (GAN I) and a recycle stream 37. The recycle stream 37 is compressed in a recycle compressor 38 with aftercooler 39 to a pressure of 25 to 60 bar, preferably about 35 bar and cooled in the main heat exchanger 11a. Part 40 of the high-pressure nitrogen is removed from the main heat exchanger at an intermediate temperature and expanded in an expansion turbine 41 to about high-pressure column pressure. The expanded recycle stream 42 is again added to the cold pressure product flow 34. Any liquid present is separated beforehand (43) and sent to the top of the low-pressure column 14 via line 44. Another part 61 of the high-pressure nitrogen is guided to the cold end of the main heat exchanger 11a and then sent to the high-pressure column 13.

[0017] The remaining gaseous head nitrogen 45 of the high-pressure column 13 is at least partially condensed in the main condenser 15. The resulting liquid nitrogen 46 is fed in part 47 to the high-pressure column 13 as a reflux liquid. Another part 48, 49 is directed after subcooling in the subcooler 17 to the top of the low-pressure column 14. There, part 50 can be removed as a liquid nitrogen product (LIN).

[0018] Immediately above the bottom of the low-pressure column 14, gaseous oxygen 51 is taken, warmed in the main heat exchanger 11a and withdrawn via pipe 52 as a pressureless gaseous product (GOX III). A liquid oxygen stream 53 from the bottom of the low-pressure column 14 is subcooled in the subcooler 17 and fed via line 54 to a liquid tank (LOX). At least part of the liquid oxygen is removed from the tank via line 55, pressurized in a pump 56 to the required product pressure, for example 6 to 60 bar, preferably about 31 bar, and evaporated in the main heat exchanger 11a against high-pressure nitrogen (or pseudo-evaporated, if at supercritical pressure) and heated to ambient temperature and finally withdrawn via line 57 as a gaseous high-pressure product (GOX I). A part 58 of the high-pressure liquid is relaxed

via a throttle valve 59 to an intermediate pressure of, for example, 6 to 25 bar, preferably about 15 bar and evaporated under this lower pressure and withdrawn via line 60 as a gaseous medium pressure product (GOX II).

[0019] Gaseous nitrogen 62, 63, 64 from the top of the low-pressure column 14 and gaseous impurity nitrogen 65, 66, 67 from an intermediate point of the low-pressure column 14 are each warmed in the subcooler 17, heated in the main heat exchanger blocks 11c or 11b and via line 68 - optionally after heating 69 - used as a regenerating gas for the cleaning device 9, supplied via line 70 to the evaporative cooler 70 and/or via line 71 directly into the purifying device 9, supplied via line 70 to the evaporative cooler 70 and/or blown off via line 71 directly into the atmosphere.

[0020] At a third intermediate point, which is arranged below the first intermediate point, an argon-containing fraction 72 is taken from the low-pressure column 14 and fed to the crude argon column 25 directly above the bottom. (In this embodiment, the crude argon column 25 is placed in a single vessel; alternatively it could be split into two or more vessels arranged side by side.) Bottom liquid 73 of the crude argon column is fed back into the low-pressure column via pump 74 and line 75.

[0021] The top condenser 24 of the crude argon column 25 is designed as a reflux condenser. (Alternatively, it could be designed as conventional condenser, gas and liquid flow being in the same direction.) Gas from the top of the crude argon column 25 flows into the return passages at the bottom and is partially condensed there. The condensate generated in this way flows downwards in counterflow to the rising gas in the return passages and is used as a liquid return in the crude argon column 25. On the evaporation side, the top condenser 24 is designed as a bath condenser. The cooling fluid, which is formed here by liquid crude oxygen 23, flows into the evaporation passages at the bottom via one or more lateral openings and is partially evaporated there. Due to the thermosiphon effect, liquid is carried away, exits together with the evaporated portion at the upper end of the evaporation passages and is returned to the liquid bath. The top condenser is therefore designed on the evaporation side as a bath evaporator. (Alternatively, it could be a once-through evaporator.)

[0022] From the upper end of the reflux passages, a gaseous crude argon stream 76 is taken as the argon-enriched fraction via a lateral header and fed to the pure argon column 20 at an intermediate point. In the embodiment, the top condenser of the pure argon column 20 is conventionally designed on the liquefaction side, that is, the top gas 77 of the pure argon column 20 flows from top to bottom through the liquefaction passages. (Alternatively, the top condenser 27 of the pure argon column 20 and/or the main condenser 15 could also be formed as reflux condensers.) A residual gas stream 78 is extracted from the head condenser 27 and blown off into the atmosphere in the example. Alternatively, it can be returned via its own blower into the distillation column

system for nitrogen-oxygen separation or in front of the air compressor 3.

[0023] The bottom liquid 79 of the pure argon column 20 is evaporated to a part 80 in the bottom evaporator 21 and the vapor 81 generated is used as an ascending gas in the pure argon column 20. The remainder is taken as a liquid pure argon product stream 82.

[0024] According to the invention, a nitrogen analyzer 100 measuring the nitrogen content is arranged in line 72 carrying the argon-containing fraction from the low-pressure column 14 to the crude argon column 25. The analyzer 100 (or a separate oxygen analyzer) may additionally measure the oxygen content in the argon-containing fraction 72. The measurement data are sent via data connection 101 to a computer 110, which predicts the nitrogen content in the crude argon condenser on the basis of the measured nitrogen content and optionally the argon content there. A further data line controls at least one control device depending on the predicted nitrogen content.

Claims

1. Process for producing an argon-enriched fraction by cryogenic air separation comprising
 - introducing feed air into a distillation system for oxygen-nitrogen separation comprising a low-pressure column,
 - withdrawing an argon-containing fraction from the low-pressure column and introducing it into a crude argon column having a crude argon top condenser being indirectly cooled by a cryogenic working fluid,
 - withdrawing an argon-enriched fraction from an upper section of the crude argon column,
 - measuring the oxygen content in the argon-containing fraction,

characterized in

- measuring the nitrogen content in the argon-containing fraction,
 - predicting the nitrogen content in the crude argon condenser on the basis of the measured nitrogen content and
 - controlling the operation of the crude argon column depending on such predicted nitrogen content in the crude argon condenser.
2. Process according to claim 1, using a gas chromatograph for measuring the nitrogen content, in particular a fast gas chromatograph.
 3. Process according to claim 1 or 2, that one or more of the following control actions are performed depending on the predicted nitrogen content in the

crude argon condenser:

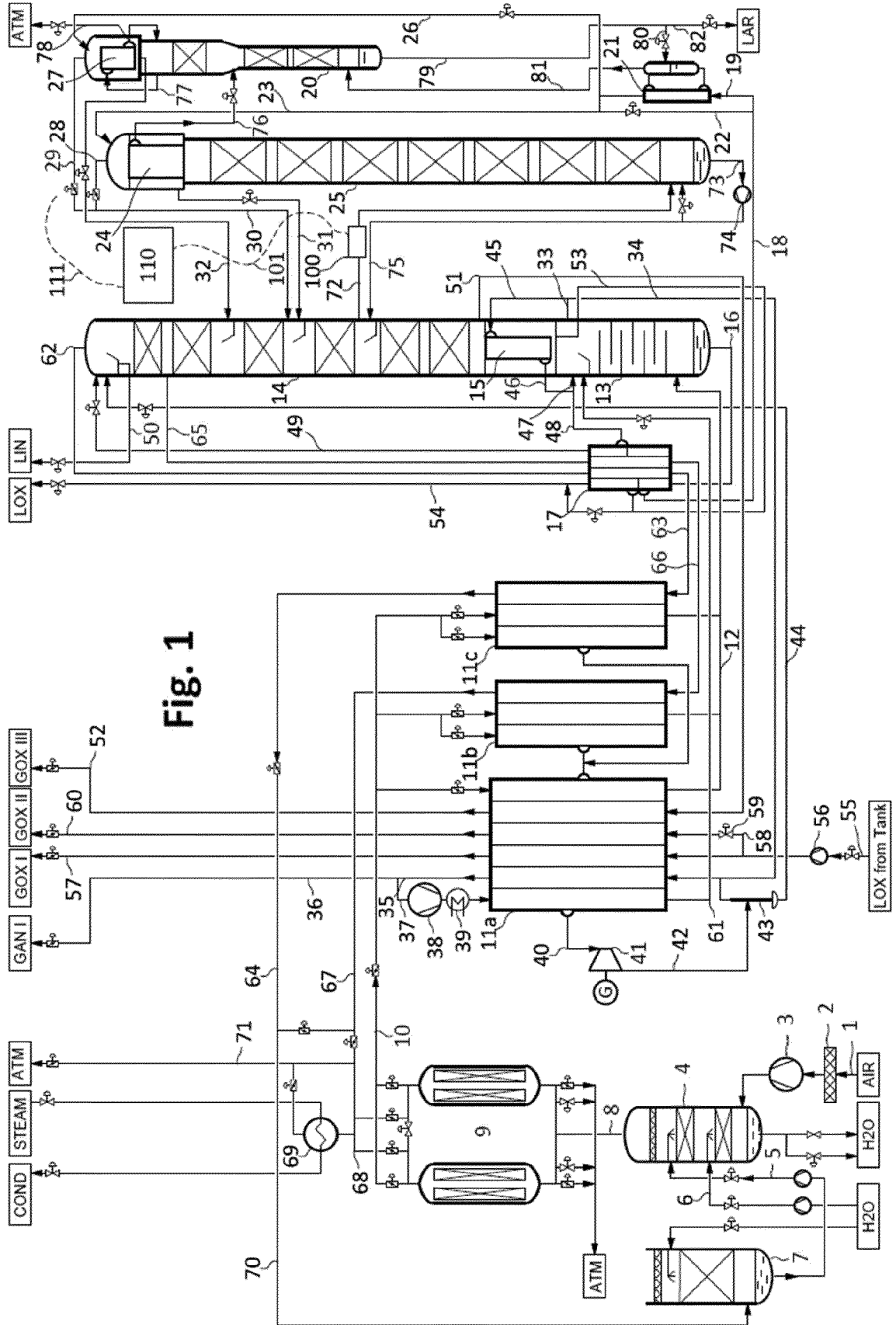
- correct of the setpoint of the controller for the oxygen content in the argon-containing fraction,
 - initiate a blow off of crude argon from the top of the crude argon column, from the crude argon top condenser and/or from the crude argon product line to avoid instability in the crude argon top condenser,
 - adapt the crude argon condenser duty to optimize the recovery, in particular by controlling the flow of argon-containing fraction from the low-pressure column to the crude argon column.
4. Process according to one of claims 1 to 3, the distillation system for oxygen-nitrogen separation additionally comprising a high-pressure column being in heat-exchange relationship with the low-pressure column, whereby a pressurized gaseous nitrogen stream is withdrawn from the upper section of the high-pressure column and recovered as a pressurized gaseous nitrogen product, and the control comprises reducing the pressurized gaseous nitrogen withdrawal in case of a high value of the nitrogen content measured in the argon-containing fraction.
5. Process according to one of claims 1 to 4, an oxygen product being withdrawn from the lower section of the low-pressure column, whereby the control comprises reducing the oxygen product withdrawal from the lower section of the low-pressure column in case of a high value of the nitrogen content measured in the argon-containing fraction.
6. Process according to one of claims 1 to 5, where a working fluid of the air separation is used as recycle stream, the recycle stream being warmed, compressed, cooled and turbine-expanded, in case of a high value of the nitrogen content measured in the argon-containing fraction.
7. Process according to one of claims 1 to 6, where a working fluid of the air separation is used as turbine stream, the turbine stream being turbine-expanded, whereby the turbine stream is reduced in case of a high value of the nitrogen content measured in the argon-containing fraction.
8. Process according to one of claims 1 to 7, whereby the amount of feed air into the distillation system for oxygen-nitrogen separation is increased in case of a high value of the nitrogen content measured in the argon-containing fraction.
9. Process according to any of the preceding claims, whereby the argon-enriched fraction is withdrawn from the crude argon column as a crude argon product.

10. Apparatus for producing an argon-enriched fraction by cryogenic air separation comprising

- an air feed line for introducing feed air into a distillation system for oxygen-nitrogen separation comprising a low-pressure column,
- an argon transition line for withdrawing an argon-containing fraction from the low-pressure column and introducing it into a crude argon column having a crude argon top condenser being indirectly cooled by a cryogenic working fluid,
- a crude argon product line for withdrawing an argon-enriched fraction from an upper section of the crude argon column,
- an oxygen analyzer for measuring the oxygen content in the argon-containing fraction,

being characterized by

- a nitrogen analyzer measuring the nitrogen content in the argon-containing fraction,
- computing means for predicting the nitrogen content in the crude argon condenser on the basis of the measured nitrogen content and
- control means for controlling the operation of the crude argon column depending on such predicted nitrogen content in the crude argon condenser.





EUROPEAN SEARCH REPORT

Application Number

EP 22 02 0618

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TECHNICAL FIELDS
SEARCHED (IPC)

F25J

The present search report has been drawn up for all claims

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Place of search

Munich

Date of completion of the search

14 June 2023

Examiner

Schopfer, Georg

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

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

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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 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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