

Method and Apparatus for Producing Nitrogen by Cryogenic
Distillation of Air

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The present invention relates to a method and an apparatus for producing nitrogen by cryogenic distillation. The pharmaceuticals industry is a potential market for the sale of nitrogen.

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In order to be fit for such an application, however, the nitrogen must satisfy the following specifications:

$\text{CO}_2 < 300 \text{ ppm}$

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$\text{CO} < 5 \text{ ppm}$

$\text{O}_2 < 5 \text{ ppm}$

$\text{H}_2\text{O} < 67 \text{ ppm}$

$\text{N}_2 > 99.5\%$

20 All the purities in this document are molar purities.

Only the CO content may raise concern. This is because in a single-column nitrogen generator, with addition of liquid nitrogen in order to maintain refrigeration, the CO content in the nitrogen produced is about 80% of the CO content in the air supplying the single column.

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It can therefore be seen that the critical CO content in the air, beyond which the constraint for the CO content in the nitrogen is no longer satisfied, is of the order of 6 ppm.

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Although the normal content of CO in the air (0.6 ppm) is generally much less than this critical value, it is possible that it may significantly exceed the limit value, either continuously or more generally as a peak.

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It will then be necessary to shut down the production by cryogenic distillation of air and supply the customer by vaporizing liquid nitrogen from a storage unit whose content has been controlled.

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This is more expensive, and this operating mode has no autonomy other than the stored capacity of liquid.

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It is known to reduce the carbon monoxide content of a nitrogen-rich product when the air has a constant carbon monoxide content. In this case, cryogenic distillation (EP-A-0376465, Gas Aktuell 39, 1990, pp 4-8) or catalysis (US-A-5441719) may be used in order to purify the air or the nitrogen.

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US-A-4617040 and JP-A-05001882 describe a method according to the preamble of claim 1.

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It is an object of the invention to permit the production of nitrogen with a very low carbon monoxide content by cryogenic distillation of air, even if the air supplying the column is occasionally highly polluted with carbon monoxide.

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One aspect of the invention provides a method for producing nitrogen by cryogenic distillation of air, in which air containing carbon monoxide is sent to a cryogenic distillation column, a flow D of nitrogen is taken from the top of the distillation column, with a CO content less than a fixed value S1, and a flow of nitrogen-rich cryogenic liquid coming from an external source is sent to the top of the column, the flow rate of cryogenic liquid sent to the column being less than a value V if the CO content in the air does not exceed a previously defined threshold (S0), characterized in that: the flow rate of cryogenic liquid sent to the column is greater than a value V if the carbon monoxide content of the air exceeds this previously defined threshold (S0).

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According to other optional aspects:

- 5 - the flow rate of air sent to the distillation column is reduced if the carbon monoxide content of the air exceeds the previously defined threshold;
- 10 - if the carbon monoxide content of the air is below the given threshold, the molar flow rate of cryogenic liquid sent to the column is at most equal to 5% of the molar flow rate of nitrogen gas D taken from the column;
- 15 - a flow of oxygen-enriched purging liquid is produced, characterized in that the flow rate of oxygen-rich cryogenic liquid produced is substantially constant when the flow rate of cryogenic liquid sent to the column is less than a value V and increased relative to the constant flow rate if the flow rate of cryogenic liquid sent to the column is greater than a value V;
- 20 - the increase in the oxygen-enriched molar flow rate taken off is substantially equal to the increase in the molar flow rate of cryogenic liquid sent to the column;
- 25 - the ratio between the flow rate of cryogenic liquid sent to the column and the carbon monoxide content of the air is constant;
- 30 - the flow rate of cryogenic liquid sent to the column has one or more given values if the carbon monoxide content of the air lies in one or more predefined ranges;
- 35 - the flow rate of cryogenic liquid is regulated according to the carbon monoxide content of the air;
- 35 - the flow rate of cryogenic liquid is regulated according to the carbon monoxide content of the nitrogen produced.

One aspect of the invention provides an apparatus for producing nitrogen by cryogenic distillation, comprising a

cryogenic distillation column, a conduit for sending air containing carbon monoxide to the column, a conduit for taking a nitrogen-rich product from the column and a conduit for sending liquid nitrogen to the column from an external source, for example a storage unit, characterized in that it comprises means for regulating the flow rate of liquid nitrogen sent to the column as a function of the carbon monoxide content of the air.

10 The apparatus optionally comprises means for measuring the carbon monoxide content of the air or of the nitrogen-rich product and means for increasing the flow rate of liquid nitrogen sent to the column if the content exceeds a threshold.

15 The proposed invention makes it possible to increase significantly the limiting CO content in the air, beyond which sufficiently pure nitrogen gas can no longer be produced using the air separation apparatus.

20 The invention will be described in more detail with reference to the figure, which represents an air separation apparatus according to the invention.

25 A flow of air 1, purified with respect to CO₂ and humidity but containing carbon monoxide, is cooled in a heat exchanger 2. Its carbon monoxide content is measured by an analyzer 3 upstream of the distillation column 5.

30 The air is separated into a nitrogen-rich top gas and an oxygen-enriched bottom liquid. The bottom liquid 17 is expanded through a valve 18 and sent to the top condenser 9 in a known way. The vaporized liquid 21 is heated in the exchanger 2. A nitrogen-rich gas product 29 is taken from the top of the column, heated in the exchanger 2 and sent to a customer. Its carbon monoxide content is measured by an analyzer 23 and must not exceed a threshold S1, for example 5 ppm.

Refrigeration of the apparatus is maintained by sending liquid nitrogen coming from a storage unit 7, which constitutes a source external to the air separation apparatus. The flow rate V of this liquid is substantially constant so long as the carbon monoxide content of the air does not exceed a threshold S_0 . The liquid nitrogen conduit 19 is connected to the top of the column 5 through a valve 11. A nitrogen-rich liquid can be taken from the column 5 through a conduit 13.

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If the air 1 has a carbon monoxide content less than the given threshold S_0 , for example 5.9 ppm, the molar quantity V of liquid nitrogen sent to the column 5 through the conduit 19 corresponds to at most about 5% of the molar flow rate of nitrogen produced, optionally at most 3% of the molar flow rate of nitrogen produced, that is to say the quantity which is necessary in order to maintain refrigeration of the apparatus in the absence of an expansion turbine or other means for refrigeration. The quantity V is therefore substantially constant. The CO content of this nitrogen flow rate V is less than 5 ppm, since the liquid stored in this external storage unit 7 can if necessary serve as a backup after vaporization in the event of a shutdown, untimely or not, of the nitrogen production unit. All the liquid taken from the bottom is sent through the conduit 17 to the condenser 9.

If the carbon monoxide content exceeds the given threshold of S_0 for the air, the analyzer 3 sends a signal to the FIC 12 in order to modify the flow rate sent through the conduit 19 in order to increase the quantity of liquid nitrogen arriving in the column, so that the flow rate exceeds the value V . The more impure the air is, the greater the increase must be. Owing to this method, by sending 10% of the nitrogen production flow rate as a liquid nitrogen flow, the limiting content of CO in the air can increase to 6.5 ppm without the carbon monoxide content of the nitrogen 19 produced exceeding 5 ppm, which is required by the standards. By sending liquid nitrogen

corresponding to 40% of the nitrogen production flow rate, the limiting content of CO in the air 1 is 9.5 ppm without the carbon monoxide content of the nitrogen 19 produced exceeding 5 ppm, which is required by the standards.

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When increasing the flow rate of liquid nitrogen, it is necessary to reduce the flow rate of supply air and therefore reduce the quantity of CO introduced into the nitrogen production unit; this also reduces the electricity
10 consumption of the apparatus.

At the same time, an additional flow of oxygen-enriched liquid 13 is taken from the bottom of the column 5 by means of a valve 15 and a conduit when the carbon monoxide
15 content of the air exceeds the threshold S0 and when the liquid nitrogen arrives through the conduit 19. This purging flow rate is substantially the same, on a molar basis, as the extra flow rate sent into the column through the conduit 19, and is extracted from the production unit.
20 It may optionally be stored in a dedicated reservoir, or discharged to the atmosphere after vaporization.

The ratio between the flow rate of cryogenic liquid sent to the column and the carbon monoxide content of the air may
25 be constant. If not, the flow rate of cryogenic liquid sent to the column may be fixed at one or more given values, the value being a function of the fact that the carbon monoxide content of the air lies in one or more predetermined ranges. For instance, the flow rate may be 10% if the
30 content is between 5 and 6.5 ppm, and 40% if the content is between 6.5 and 9.5 ppm.

CLAIMS

1. Method for producing nitrogen by cryogenic distillation of air, in which air containing carbon
5 monoxide is sent to a cryogenic distillation column, a flow
D of nitrogen is taken from the top of the distillation
column (5), with a CO content less than a fixed value S1,
and a flow of nitrogen-rich cryogenic liquid coming from an
external source (7) is sent to the top of the column, the
10 flow rate of cryogenic liquid sent to the column being less
than a value V if the CO content in the air does not exceed
a previously defined threshold (S0), characterized in that:
the flow rate of cryogenic liquid sent to the column is
greater than a value V if the carbon monoxide content of
15 the air exceeds this previously defined threshold (S0).

2. Method according to Claim 1, wherein the flow rate
of air sent to the distillation column (5) is reduced if
the carbon monoxide content of the air exceeds the
20 previously defined threshold.

3. Method according to one of the preceding claims,
wherein if the carbon monoxide content of the air is below
the given threshold, the molar flow rate of cryogenic
25 liquid sent to the column (5) is at most equal to 5% of the
molar flow rate of nitrogen gas D taken from the column.

4. Method according to one of the preceding claims,
wherein a flow of oxygen-enriched purging liquid is
30 produced, characterized in that the flow rate of oxygen-
rich cryogenic liquid produced is substantially constant
when the flow rate of cryogenic liquid sent to the column
(5) is less than a value V and increased if the flow rate
of cryogenic liquid sent to the column is greater than a
35 value V.

5. Method according to Claim 4, wherein the increase
in the oxygen-enriched molar flow rate taken off is

substantially equal to the increase in the molar flow rate of cryogenic liquid sent to the column (5).

6. Method according to one of the preceding claims, wherein the ratio between the flow rate of cryogenic liquid sent to the column (5) and the carbon monoxide content of the air is constant.

7. Method according to one of Claims 1 to 6, wherein the flow rate of cryogenic liquid sent to the column (5) has one or more given values if the carbon monoxide content of the air lies in one or more predefined ranges.

8. Method according to one of the preceding claims, wherein the flow rate of cryogenic liquid is regulated according to the carbon monoxide content of the air.

9. Method according to one of the preceding claims, wherein the flow rate of cryogenic liquid is regulated according to the carbon monoxide content of the nitrogen produced.

10. Apparatus for producing nitrogen by cryogenic distillation, comprising a cryogenic distillation column (5), a conduit for sending air containing carbon monoxide to the column, a conduit for taking a nitrogen-rich product from the column and a conduit for sending liquid nitrogen to the column from an external source (7), for example a storage unit, characterized in that it comprises means for regulating the flow rate of liquid nitrogen sent to the column as a function of the carbon monoxide content of the air, and optionally means for measuring the carbon monoxide content of the air or of the nitrogen-rich product and means for increasing the flow rate of liquid nitrogen sent to the column if the content exceeds a threshold.