Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 2976341 C 2023/07/11

(11)(21) **2 976 341**

(12) BREVET CANADIEN
CANADIAN PATENT

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date**: 2016/01/26
(87) **Date publication PCT/PCT Publication Date**: 2016/08/18
(45) **Date de délivrance/Issue Date**: 2023/07/11
(85) **Entrée phase nationale/National Entry**: 2017/08/10
(86) **N° demande PCT/PCT Application No.**: EP 2016/000131
(87) **N° publication PCT/PCT Publication No.**: 2016/128111
(30) **Priorité/Priority**: 2015/02/10 (DE10 2015 001 664.4)

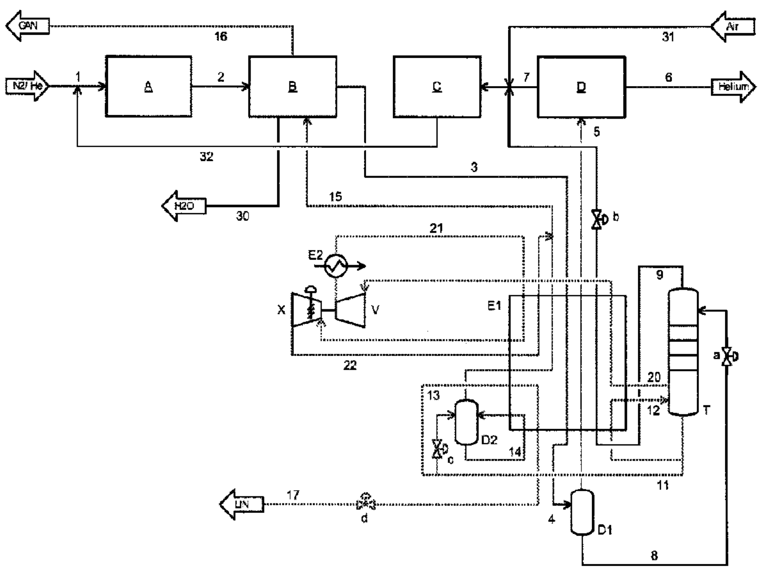
(51) **Cl.Int./Int.Cl.** *F25J 3/02* (2006.01), *F25J 1/02* (2006.01)

(72) **Inventeurs/Inventors**:
BAUER, HEINZ, DE;
GWINNER, MARTIN, DE;
BUB, ANDREAS, DE;
HERTEL, CHRISTOPH, DE

(73) **Propriétaire/Owner**:
LINDE AKTIENGESELLSCHAFT, DE

(74) **Agent**: AIRD & MCBURNEY LP

(54) Titre : PROCEDE D'EXTRACTION D'HELIUM
(54) Title: METHOD FOR RECOVERING HELIUM



(57) **Abrégé/Abstract**:
A method for recovering a helium product fraction (6) from a nitrogen- and helium-containing feed fraction (3) is described, wherein the nitrogen- and helium-containing feed fraction (3) is partially condensed (El), separated into a first helium-enriched fraction (5) and a first nitrogen-enriched fraction (8) and the former is cleaned again in an adsorptive manner.

According to the invention, the separation is carried out in a separation column (T), which is supplied with the first nitrogen-enriched fraction (8) as return flow and with a sub-flow of the second nitrogen-enriched fraction as stripping gas (12), wherein the stripping gas quantity (12) is set such that a third nitrogen-enriched fraction (20), which contains at least 30 % of the nitrogen contained in the first nitrogen-enriched fraction (8), can be recovered in the separation column (T).

Abstract

Method for recovering helium

A method for recovering a helium product fraction (6) from a nitrogen- and helium-containing feed fraction (3) is described, wherein the nitrogen- and helium-containing feed fraction (3) is partially condensed (E1), separated into a first helium-enriched fraction (5) and a first nitrogen-enriched fraction (8) and the former is cleaned again in an adsorptive manner.

According to the invention, the separation is carried out in a separation column (T), which is supplied with the first nitrogen-enriched fraction (8) as return flow and with a sub-flow of the second nitrogen-enriched fraction as stripping gas (12), wherein the stripping gas quantity (12) is set such that a third nitrogen-enriched fraction (20), which contains at least 30 % of the nitrogen contained in the first nitrogen-enriched fraction (8), can be recovered in the separation column (T).

(Included is Figure 1.)

Specification

Method for recovering helium

The invention relates to a method for recovering a helium product fraction from a nitrogen- and helium-containing feed fraction, wherein

- the nitrogen- and helium-containing feed fraction is partially condensed and separated into a first helium-enriched fraction and a first nitrogen-enriched fraction,
- the first helium-enriched fraction is subjected to an adsorptive cleaning process and the helium-enriched fraction recovered therefrom represents the helium product fraction,
- the first nitrogen-enriched fraction is separated into a second helium-enriched fraction and a second nitrogen-enriched fraction, and
- the second helium-enriched fraction is preheated against the nitrogen- and helium-containing feed fraction to be partially condensed, condensed and admixed to the nitrogen- and helium-containing feed fraction to be partially condensed.

The term “helium product fraction” be comprised of highly purified helium, the concentration and contamination of which do not exceed a value of 100 vppm, preferably of 10 vppm.

The term “nitrogen- and helium-containing feed fraction” be understood as a fraction, which contains 1 to 20 mol-% helium and 80 to 99 mol-% nitrogen. Further, this feed fraction can contain 0,1 to 2 mol-% methane and traces of hydrogen, argon and/or other noble gases.

Currently, helium is obtained almost exclusively from a mixture of volatile natural gas components, which typically contains methane and nitrogen as well as traces of hydrogen, argon and other noble gases besides helium. To avoid separation by freezing of undesired decontamination during helium liquification, the concentration of this decontamination in helium cannot exceed a value of 100 vppm, preferably of 10 vppm.

The helium purification prior to the actual helium liquefaction generally consists of a combination of cryogenic – based on partial condensation – and adsorptive methods with regeneration through pressure and/or temperature changes. Based on the comparatively high product value, a helium yield as high as possible, preferably > 99 %, is desirable. In consequence, the helium-enriched fraction is often transferred from the liquid into the gaseous phase by pressure release and/or stripping from the liquid to the gaseous phase during the cryogenic step to remain available for further processing.

A method implication is known from US patent 5,167,125, wherein a nitrogen-enriched flow, which has elevated pressure and contains helium, is separated by using a pressure drop in a helium-containing flow of average pressure and a nitrogen-enriched flow of lower pressure. Such separation is implemented in a rectification column, which has a reboiler and a condenser.

Figure 1 illustrates a method for recovering a helium product fraction in accordance with the present invention.

It is the object of the present invention to specify a generic method for recovering a helium product fraction, which facilitates generation of at least a partial quantity of the nitrogen-enriched flow accruing during separation at the same pressure as the helium-containing flow, to be able to subsequently supply the nitrogen-enriched flow to a work-performing expansion.

For the solution of said object, a generic method for recovering a helium product fraction is suggested, which is characterized in that

- the separation of the first nitrogen-enriched fraction into a second helium-enriched fraction and a second nitrogen-enriched fraction is implemented in a separation column, to which the first nitrogen-enriched fraction is supplied as return flow,
- a sub-flow of the second nitrogen-enriched fraction evaporates and the separation column is supplied as stripping gas,
- at least a sub-flow of the second nitrogen-enriched fraction is evaporated against the nitrogen- and helium-containing feed fraction to be partially condensed under a pressure of less than 5 bar,
- a third nitrogen-enriched fraction is removed from the separation column,
- wherein the stripping gas quantity is set such that the third nitrogen-enriched fraction contains at least 30 % of the nitrogen contained in the first nitrogen-enriched fraction, and
- the third nitrogen-enriched fraction serves at least partially to cool the nitrogen- and helium-containing feed fraction to be partially condensed.

Further advantageous embodiments of the method according to the invention for recovering a helium product fraction, which represent subject matters of the dependent claims are characterized in that

- the third nitrogen-enriched fraction is at least partially work-performing expanded (X),

Date Reçue/Date Received 2022-06-29

- the separation column is operated with a pressure of 7 to 20 bar, preferably of 10 to 15 bar,
- the third nitrogen-enriched fraction contains at least 50 % of the nitrogen contained in the first nitrogen-enriched fraction,
- at least a sub-flow of the second nitrogen-enriched fraction is evaporated against the nitrogen- and helium-containing feed fraction to be partially condensed under a pressure of less than 3 bar, and/or
- the adsorptive cleaning process is a (V)PSA and/or TSA process.

The method according to the invention for recovering a helium product fraction as well as further advantageous embodiments thereof are explained in further detail by means of the embodiment example represented in **Figure 1**.

Via line 1, a nitrogen- and helium-containing feed fraction, which originates, for example, from a separation process of natural gas, is first supplied to catalytic methane oxidation A and subsequently via line 2 to a drying unit B. The water separated in the drying unit B is removed via line 30. The feed fraction conventionally pretreated in such way, which typically has a pressure of between 10 and 40 bar, preferably between15 and 25 bar, is supplied to the heat exchanger El via line 3 and partially condensed therein against method flows yet to be explained. Via line 4, the partially condensed feed fraction is supplied to a separator D1 and separated therein into a first helium-enriched fraction 5 as well as a first nitrogen-enriched fraction 8.

The helium-enriched fraction 5 is supplied to an adsorptive cleaning process D after preheating in the heat exchanger El. Such process is designed as (V)PSA and/or TSA process. The helium-enriched fraction recovered therein and removed via line 6, represents the helium product fraction, the concentration of decontamination of which does not exceed a value of 100 vppm, preferably of 100 vppm. As a rule, this helium product fraction is supplied to a liquefaction process not illustrated in Figure 1.

The helium-containing residue gas removed from the adsorptive cleaning process D is supplied to a return compressor C via line 7, is compressed therein to the pressure of the feed fraction 1 to be supplied to the catalytic methane oxidation A and admixed thereto via line 32.

Date Reçue/Date Received 2022-06-29

The above mentioned first nitrogen-enriched fraction 8 is expanded in valve a and supplied to the separation column T in its upper section as return flow. The separation column T is preferably operated at a pressure between 7 and 20 bar, in particular between 10 and 15 bar. A separation into a second helium-enriched gas fraction 9 and a second nitrogen-enriched liquid fraction 11 is implemented therein. The second helium-enriched fraction 9 is preheated in heat exchanger El against the feed fraction 3 to be partially condensed, and supplied to the mentioned return compressor C via control valve b, as well. Additional air is supplied thereto via line 31. The oxygen contained in the air serves as oxidation means for the catalytic methane oxidation A.

A sub-flow of the second nitrogen-enriched liquid fraction 11 is evaporated in heat exchanger El and supplied to the separation column T as stripping gas 12. Such stripping gas supply causes the separation process taking place in separation column T and determines the helium content of the second helium-enriched fraction 9.

At least a sub-flow of the second nitrogen-enriched fraction 11 is evaporated in heat exchanger El against the feed fraction to be partially condensed 3 under a pressure of less than 5 bar, preferably of less than 3 bar. This method serves to set a temperature as low as possible in separator Dl. In the embodiment example illustrated in Figure 1, a sub-flow of the second nitrogen-enriched fraction 11 is supplied to a circulation container D2 via control valve c. The liquid fraction removed therefrom via line 14 is supplied to heat exchanger El under the above mentioned low pressure, at least partially evaporated therein, and resupplied to the circulation container D2.

A nitrogen-enriched gas fraction 15 is removed from the top of circulation container D2, preheated in heat exchanger El against the feed fraction to be partially condensed 3, and subsequently resupplied as regeneration gas to the above mentioned drying unit B, which is an adsorptive drying process, as a rule. This loaded regeneration gas is removed from the process via line 16.

The sub-flow 13 of the second nitrogen-enriched fraction 11, which is not supplied to the circulation container D2, can be supercooled in heat exchanger El and can be generated as supercooled liquid via control valve d and line 17. By means of this configuration of the method according to the invention, an otherwise required generation or provision of liquefied nitrogen (LIN), as the case may be, can be refrained from.

Date Reçue/Date Received 2022-06-29

Alternative or supplemental to the method implementation illustrated in Figure 1, a sub-flow of liquid fraction 14 removed from the circulation container D2 can be removed in the above described manner via control valve d and line 17.

The coldness required for the partial condensation of the feed fraction 3 can principally be provided by preheating cold, gaseous decomposition products as well as the above described evaporation of liquid fraction 14, which was removed from the circulation container D2. Generally, the following is true: the larger the stripping gas quantity 12 evaporated in heat exchanger El, the lower can be the quantity of liquid fraction 14 removed from the circulation container D2. It must, however, be ensured that heat exchange and temperature of flow 12 are suitable for cooling and partially condensing feed fraction 3. If the content of flow 12 in the heat turnover in heat exchanger El becomes too large, the temperature in separator D1 increases undesirably.

The quantity of the stripping gas 12 supplied to separation column T is selected according to the invention to such amount that a third nitrogen-enriched fraction 20 can be removed from separation column T in the section of its bottom, wherein such fraction contains at least 30 %, preferably at least 50 % of the nitrogen contained in the first nitrogen-enriched fraction 8. These nitrogen contents are achieved in that a larger stripping gas quantity 12 is boiled up in the bottom of separation column T than would be required for the actual stripping process in separation column T.

Opposed to the method mentioned and described in US patent 5,167,125, a further nitrogen-enriched fraction can be recovered in separation column T under increased pressure. This further or third nitrogen-enriched fraction can be condensed to a pressure after preheating in heat exchanger El, which is above the pressure of column T by 4 to 20 bar, preferably by 5 to 15 bar. After removing the condensation heat in heat exchanger E2, the nitrogen-enriched fraction 21 is cooled in heat exchanger El and subsequently work-performing expanded in expansion device X. The expanded nitrogen-enriched fraction 22 is subsequently preheated against the feed fraction to be partially condensed 3 in heat exchanger El and admixed to the above described nitrogen-enriched fraction 15. Such work-performing expansion X, which increases thermo-dynamic efficiency of the process, is optional, facilitates or increases the quantity of the cooled liquid (UN) removed via line 17, however.

Date Reçue/Date Received 2022-06-29

Patent Claims

1. A method for recovering a helium product fraction from a nitrogen-and helium-containing feed fraction, wherein
   - the nitrogen- and helium-containing feed fraction is partially condensed and separated into a first helium-enriched fraction and a first nitrogen-enriched fraction,
   - the first helium-enriched fraction is subjected to an adsorptive cleaning process and the helium-enriched fraction recovered therefrom represents the helium product fraction,
   - the first nitrogen-enriched fraction is separated into a second helium-enriched fraction and a second nitrogen-enriched fraction, and
   - the second helium-enriched fraction is preheated against the nitrogen- and helium-containing feed fraction to be partially condensed, condensed and admixed to the nitrogen- and helium-containing feed fraction to be partially condensed,

   wherein
   - the separation of the first nitrogen-enriched fraction into the second helium-enriched fraction and the second nitrogen-enriched fraction is implemented in a separation column, to which the first nitrogen-enriched fraction is supplied as return flow,
   - a first sub-flow of the second nitrogen-enriched fraction evaporates and the separation column is supplied as stripping gas,
   - at least a second sub-flow of the second nitrogen-enriched fraction is evaporated against the nitrogen- and helium-containing feed fraction to be partially condensed under a pressure of less than 5 bar,
   - a third nitrogen-enriched fraction is removed from the separation column,
   - wherein the stripping gas quantity is set such that the third nitrogen-enriched fraction contains at least 30 % of the nitrogen contained in the first nitrogen-enriched fraction, and
   - the third nitrogen-enriched fraction serves at least partially to cool the nitrogen- and helium-containing feed fraction to be partially condensed.

2. The method according to claim 1, wherein the third nitrogen-enriched fraction is at least partially work-performing expanded.

Date Reçue/Date Received 2022-06-29

3. The method according to claim 1 or 2, wherein the separation column is operated under a pressure of 7 to 20 bar.

4. The method according to claim 1 or 2, wherein the separation column is operated under a pressure of 10 to 15 bar.5. The method according to any one of claims 1 to 4, wherein the third nitrogen-enriched fraction contains at least 50 % of the nitrogen contained in the first nitrogen-enriched fraction.

6. The method according to any one of claims 1 to 5, wherein at least the second sub-flow of the second nitrogen-enriched fraction is evaporated against the nitrogen- and helium-containing feed fraction to be partially condensed under a pressure of less than 3 bar.

7. The method according to any one of claims 1 to 6, wherein the adsorptive cleaning process is a (V)PSA and/or TSA process.

Date Reçue/Date Received 2022-06-29

FIGURE

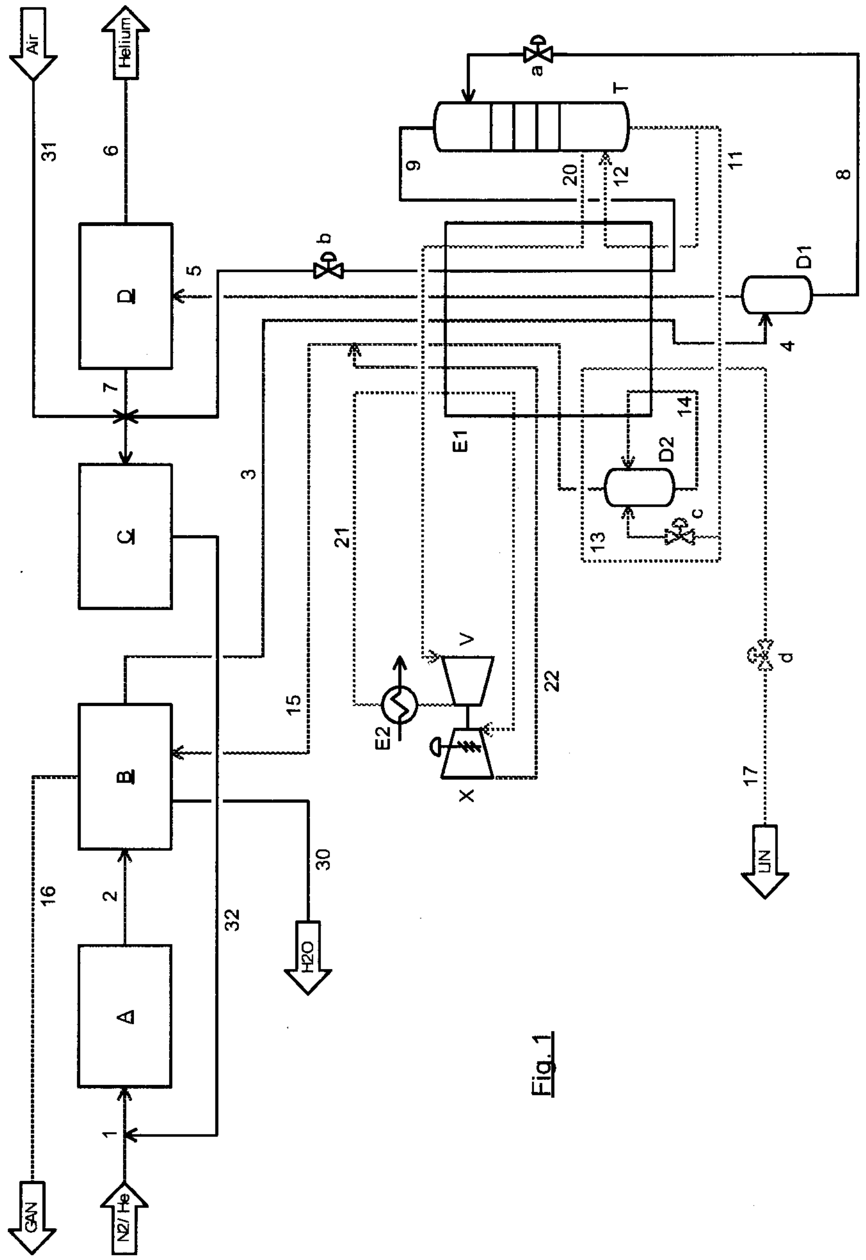
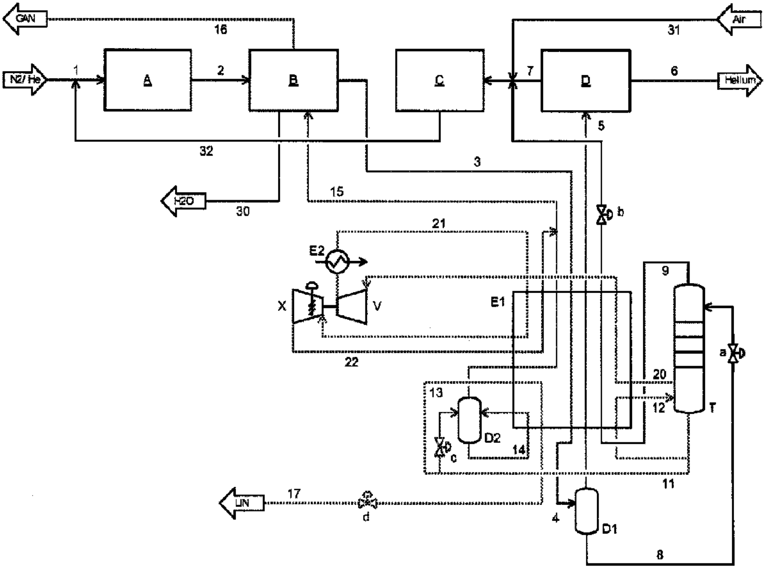

Air
Helium
N2/ He
GAN
H2O
LIN
A
B
C
D
E1
E2
D1
D2
T
V
X
a
b
c
d
1
2
3
4
5
6
7
8
9
11
12
13
14
15
16
17
20
21
22
30
31
32

Fig. 1



GAN
16
Air
31
N2/ He
1
A
2
B
C
7
D
6
Helium
5
32
3
H2O
30
15
b
21
E2
X
V
E1
9
22
a
20
13
12
T
D2
14
c
11
17
LIN
d
4
D1
8