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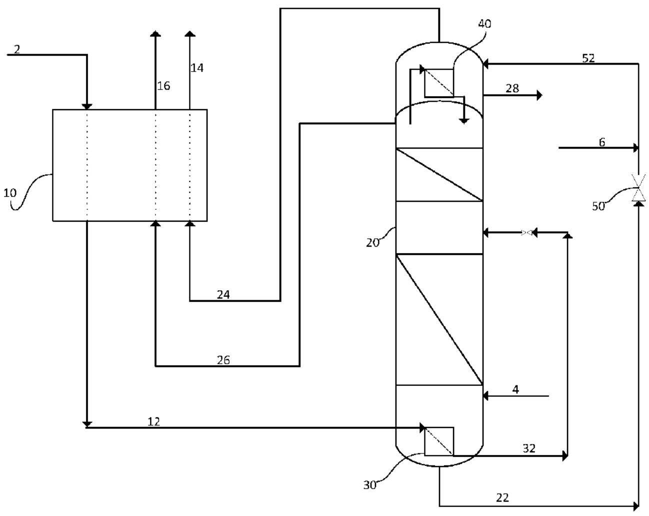
(54) Title: PURIFICATION OF INERT GASES TO REMOVE TRACE IMPURITIES

FIG. 1



(57) Abstract: A method for purifying an argon stream is provided. The method includes pretreating an argon waste stream to remove impurities to provide a pre-treated argon waste stream having argon, nitrogen, and hydrogen; cooling the argon waste stream to create a cold feed stream; and condensing the cold feed stream to create a liquid feed stream. The liquid feed stream is fed to the cryogenic distillation column to create a bottoms argon product stream and a gas waste stream. The bottoms argon product stream travels to an expansion device to provide a cooled bottoms argon product stream, which can optionally be combined with an argon lift stream downstream of the expansion device. The combined argon lift stream and cooled bottoms argon product stream are fed to the overhead condenser and vaporized to create a purified vapor phase argon stream.

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PURIFICATION OF INERT GASES TO REMOVE TRACE IMPURITIES

Technical Field of Invention

[0001] The present invention relates to a method for the purification of inert gases. More specifically, the present disclosure relates to a method for the onsite removal of trace impurities, such as nitrogen and methane, from an argon stream using cryogenic distillation separation.

Background of the Invention

[0002] The use of argon as an inert gas is important to a number of industries including the production of monocrystalline and polycrystalline silicon, steel making (e.g., using the hot isotatic pressing (HIP) process to make steel, aluminum and nonmetallic castings from powders), heat treating, and semiconductor, wafer, and electronics manufacturing. Given the rising costs of argon gas, onsite purification of waste argon streams to recycle back to the manufacturing process is increasingly common.

[0003] One manufacturing process suitable for argon purification and recycle is the production of monocrystalline silicon using the Czochralski Process. High purity argon, i.e., having a purity of 99.999% or greater, is used in the process to control the atmosphere and to purge contaminants and volatilized materials from the process as a waste stream. Purity of the argon stream is critical because it affects the both the purity and the quality of the silicon ingot grown in the Czochralski Process.

[0004] The waste stream from the process, which may include between about 95 to about 99% argon (Ar), may contain any number of contaminants including: oxygen (O_2), hydrogen (H_2), volatilized silicon oxide (SiO), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), water (H_2O), methane (CH_4), other hydrocarbons, and other impurities. Although commercial technologies currently address the removal of contaminants such as O_2, H_2, CO_2,

CO, H_2O, and hydrocarbons, cryogenic distillation is still the preferred route for the removal of N_2 and CH_4.

[0005] Current methods for the purification of argon typically utilize a cryogenic distillation process used in conjunction with a pre-treatment process. Current pre-treatment process systems begin by compressing the waste stream. The compressed gas is fed, along with excess O_2 and H_2 if necessary, to a series of commercially available catalyst beds that oxidize CO and CH_4 to CO_2 and H_2O. The CO_2 and H_2O can be removed by adsorption, either by using molecular-sieve or a combination of silica gel and molecular-sieve. The waste stream now contains primarily argon, N_2, and H_2, and may also contain minute quantities of CH_4 (methane slippage), which must be removed prior to recycle to the manufacturing process. With the CO_2 and H_2O removed, the argon waste stream may be fed to a cryogenic distillation system capable of removing the N_2, any remaining H_2.

[0006] Argon purification systems, as described above, are available in packaged skids typically sold to companies for housing on their property for use in their manufacturing process. However, current systems do not address methane slippage and are incapable of removing impurities below part per million (ppm) levels.

[0007] Therefore, it would be beneficial to have a simpler cryogenic distillation method with fewer mechanical parts. Additional benefits could be gained if a simpler method was capable of removing more impurities and addressing methane slippage from the pre-treatment process.

Summary of the Invention

[0008] The present invention relates to a method for the purification of inert gases. More specifically, the present disclosure relates to a method for the onsite removal of trace impurities, such as nitrogen and methane, from an argon stream using cryogenic distillation separation.

[0009] In one embodiment, a method for purifying an argon stream including argon, nitrogen, hydrogen carbon monoxide, carbon dioxide, water, and methane is provided. The method includes pretreating an argon waste stream to remove carbon monoxide, carbon dioxide, water, and methane to provide a pre-treated argon waste stream having argon, nitrogen, hydrogen, cooling the argon waste stream with a cryogenic heat exchanger to create a cold feed stream, and condensing the cold feed stream in a reboiler to create a liquid feed stream. The cold feed stream is in a heat exchange relationship with liquid in the bottom of a cryogenic distillation column, which includes a reboiler in the lower portion of the distillation column and an overhead condenser in the upper portion of the distillation column. Then the liquid feed stream is fed to the cryogenic distillation column and the components of the liquid feed stream are separated in the cryogenic distillation column into a bottoms argon product stream and a gas waste stream. The bottoms argon product stream is supplied from the cryogenic distillation column to an expansion device to provide a cooled bottoms argon product stream, which is combined with an argon lift stream downstream of the expansion device. The combined argon lift stream and cooled bottoms argon product stream are fed to the overhead condenser attached to the cryogenic distillation column and the combined argon lift stream and cooled bottoms argon product stream are vaporized in the overhead condenser to create a purified vapor phase argon stream. The purified vapor phase argon stream is fed to the cryogenic heat exchanger, wherein it is used to cool the pre-treated argon waste stream. The gas waste stream is removed from the distillation column.

[0010] In certain embodiments the method for purifying an argon stream includes feeding the gas waste stream to the cryogenic heat exchanger, wherein the gas waste stream is used to cool the pre-treated argon waste stream. In certain embodiments the heat added in the process of vaporizing the combined argon lift stream and cooled bottoms argon product stream is removed from condensing vapors in the top of the cryogenic distillation column. In certain embodiments the step of supplying the bottoms argon product stream to the expansion device is performed by pumping bottoms argon product stream from the bottom of the cryogenic distillation column to the expansion device. In certain embodiments the method for purifying an argon stream includes feeding the bottoms argon product stream and argon lift stream to separation stages in the cryogenic distillation column positioned above the overhead condenser. In certain embodiments the method for purifying an argon stream includes separating a portion of a product stream downstream of the cryogenic heat exchanger to create a recycle stream, compressing the recycle stream, cooling a compressed recycle stream in the cryogenic heat exchanger, and feeding a cooled recycle stream to the cryogenic distillation column. In certain embodiments the method for purifying an argon stream includes pumping the bottoms argon product stream to a sorbent bed system, feeding the bottoms argon product stream through the sorbent bed system, wherein the sorbent bed system further removes trace impurities in the bottoms argon product stream, and feeding a sorbent bed outlet stream to the overhead condenser. In certain embodiments the sorbent bed system includes regenerable adsorbents. In certain embodiments the sorbent bed system includes getter material. In certain embodiments the method for purifying an argon stream does not include the step of compressing the purified argon stream for refrigeration purposes.

Brief Description of the Drawings

[0011] These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, claims, and accompanying drawings. It is to be noted, however, that the drawings illustrate only several embodiments of the invention and are therefore not to be considered limiting of the invention's scope as it can admit to other equally effective embodiments.

[0012] FIG. 1 shows one preferred embodiment of the invention.

[0013] FIG. 2 shows another preferred embodiment of the invention.

[0014] FIG. 3 shows an alternative preferred embodiment of the invention.

[0015] FIG. 4 shows another preferred embodiment of the invention.

Detailed Description

[0016] While the invention will be described with several embodiments, it is understood that one of ordinary skill in the relevant art will appreciate that many examples variations, and alterations to the following details are within the scope and spirit of the invention. Accordingly, the exemplary embodiments of the invention described herein are set forth without any loss of generality, and without imposing limitations, relating to the claimed invention.

[0017] In one embodiment, the present invention describes a cryogenic distillation method capable of removing trace impurities from an argon stream.

[0018] FIG. 1 provides an illustration of an embodiment of the present invention. Pre-treated argon waste stream 2 is the outlet of the pre-treatment process. The waste gas stream from the manufacturing process will include argon, H_2, O_2, CO_2, CO, CH_4, and H_2O, along with other trace impurities. The pre-treatment process begins by compressing the waste gas stream. The compressed gas is then fed, along with excess O_2 and H_2, or air, if necessary, to a series of commercially available catalyst beds that oxidize CO, CH_4, and O_2 to CO_2 and H_2O. The CO_2 and H_2O are removed by adsorption, either by using molecular-sieve or a combination of silica gel and molecular-sieve, resulting in pre-treated argon waste gas stream 2.

[0019] Pre-treated argon waste stream 2 contains greater than about 95% argon, less than about 4% N_2, less than about 1% H_2, less than about 1 ppm H_2, O_2, CO, and CH_4, and no CO_2 or H_2O. The exact temperature, pressure and composition of pre-treated argon waste stream 2 will depend on the specific manufacturing and pre-treatment processes that are employed. In certain embodiments, the pre-treatment process removes as much O_2, CO, and CH_4 as possible, to achieve concentrations from about 1 ppm to 10 ppm, alternatively to below 1 ppm.

[0020] Pre-treated argon waste stream 2 is fed into cryogenic heat exchanger 10, where it is cooled to a temperature between about -150°C and -160°C, alternatively between about -152°C and -157°C, alternatively between about -153°C and -155°C, alternatively about -153.6°C. Cryogenic heat exchanger 10 may be any heat exchanger of the type and materials commonly employed in a cryogenic air separation process. In certain embodiments, the heat exchanger is constructed of brazed aluminum.

[0021] Cold feed stream 12 exits cryogenic heat exchanger 10 and enters reboiler 30. Additional energy is removed from cold feed stream 12 in reboiler 30, and the heat from cold feed stream 12 is used to provide reboil liquid at the bottom of column 20. This results in condensing of cold feed stream 12. Liquid feed stream 32 exits reboiler 30 at a temperature between about -150°C to about -160°C, preferably about -156.9°C. Liquid feed stream 32 is then fed to cryogenic distillation column 20 at a point above the bottom section and below the upper section, preferably in the packing section.

[0022] Argon stream 4 is fed to cryogenic distillation column 20 to make up for argon lost as waste in gaseous waste stream 26 and the liquid purge 28. Any refrigeration requirements for the process such as heat leakage, temperature differences in heat exchanger 10, liquid purge or other losses can be compensated by the addition of argon stream 4. In one embodiment, Argon stream 4 is a high purity source of liquid argon containing at least about 99.999% argon, less than about 0.001% O_2, and less than about 0.001% N_2. Advantageously, argon feed stream 4 can also provide additional cooling for cryogenic distillation column 20. The temperature of argon feed stream 4 is preferably close to its dew point.

[0023] Bottoms argon product stream 22 exits cryogenic distillation column 20. Bottoms argon product stream 22 has a purity of at least about 99.999% argon. After exiting cryogenic distillation column 20, bottoms argon product stream 22 is cooled by expansion in expansion device 50. Expansion device 50 may be any device capable of reducing the pressure and temperature of bottoms argon product stream 50.

[0024] Bottoms argon product stream 22 can be supplied to overhead condenser 40. In one embodiment, argon lift stream 6 (a small stream of argon gas, less than about 1% by mass of bottoms argon product stream 22) can be added to bottoms argon product stream 22 after expansion valve 50 as a lift gas to drive the stream to overhead condenser 40. This feature can be useful to ease the liquid transfer when distillation column 20 is tall, particularly due to the relatively high density of liquid argon and the low differential pressure between the bottom of distillation column 20 and overhead condenser 40. A partial vapor stream that includes argon lift stream 6 and bottoms argon product stream 22 (i.e., bottoms lift stream 52) operates by virtue of the buoyancy of a gas-liquid slug.

[0025] Bottoms lift stream 52 provides cooling to overhead condenser 40, which vaporizes bottoms lift stream 52 to create purified vapor phase argon stream 24. Vapor from the top of cryogenic distillation column 20 partially condenses in overhead condenser 40 due to the cooling provided by bottoms lift stream 52. A small liquid purge stream 28 containing some heavy impurities such as hydrocarbons, carbon dioxide, etc… can be removed from overhead condenser 40.

[0026] Purified vapor phase argon stream 24 can be fed to cryogenic heat exchanger 10 to provide cooling for pre-treated argon waste stream 2. Product stream 14, having a temperature of about ambient temperature, may be returned to the manufacturing process requiring pure argon, may be stored, may be diverted for other processes, or may be distributed off-site. The purity of product stream 14 is greater than about 99.999% argon.

[0027] Nitrogen and H_2, being more volatile than argon, collect near the top of cryogenic distillation column 20 and are removed from the distillation column as gaseous waste stream 26. Gaseous waste stream 26 can be supplied to cryogenic heat exchanger 10 to provide cooling of pre-treated argon waste stream 2. Warm gas waste stream 16 may then be recycled to the manufacturing process, disposed of, or used to regenerate the mole-sieve beds of the pre-treatment process.

[0028] In a second embodiment of the system in FIG. 1, a pump (not shown) can be used to supply the driving force to drive bottoms argon product stream 22 to overhead condenser 40. The pump may be of any type and materials commonly used in a cryogenic distillation system. In one embodiment, argon lift stream 6 is not used when the pump is used.

[0029] FIG. 2 demonstrates an additional embodiment of the invention. In this embodiment, in addition to the features shown in FIG. 1 and described above, additional separation stages can been included in cryogenic distillation column 20 above overhead condenser 40. The additional separation stages allow for further purification of the argon stream by removing CH_4 not removed during the pre-treatment process, thus addressing methane slippage. Methane, which is less volatile than argon, will be carried out the bottom of cryogenic distillation column 20 in bottoms argon product stream 22. The additional stages in cryogenic distillation column 20 allow for the separation and removal of this CH_4 prior to purified vapor phase argon stream 24 exiting cryogenic distillation column 20. Methane waste stream 28 may be bled from the column below the additional stages and disposed of or redirected as necessary. The flowrate of argon stream 4 can be adjusted to account for additional argon losses in methane waste stream 28. It is understood that the additional separation stages shown in Figure 2 can also be added to the additional embodiments described herein, for example FIG. 3 and FIG. 4.

[0030] FIG. 3 illustrates an alternative embodiment of the invention. In this embodiment, in addition to the features shown in FIG. 1 and described above, a portion of product stream 14 can be diverted to compressor 60 through recycle stream 15. Compressor 60 compresses recycle stream 15 to the pressure of cryogenic distillation column 20, creating compressed argon recycle stream 68. Compressed stream 68 can be fed to cryogenic heat exchanger 10 to be cooled. The cooled and compressed argon recycle stream 18 is cooled to a temperature at or about its dew point, and is fed to cryogenic distillation column 20.Between about 5 and 25% of product stream 14 by volume can be recycled to cryogenic distillation column 20 to improve the overall recovery of argon. In alternate embodiments, between about 5 and 10% by volume is recycled, alternatively between about 10 and 15% by volume, alternatively between about 15 and 20% by volume, alternatively between about 20 and 25%. In certain embodiments, by recycling approximately 10% of product stream 14 to cryogenic distillation column 20 can increase overall argon recovery from about 83% to greater than 90%, alternatively greater than 95%, alternatively to about 99%.

[0031] FIG. 4 illustrates yet another embodiment of the invention. In this embodiment, in addition to the features shown in FIG. 1 and FIG. 3 and described above, bottoms argon product stream 22 can be supplied to sorbent bed system 80 to reduce contaminants in bottoms argon product stream 22. Pump 70 can provide the drive necessary so sorbent bed feed stream 72 can pass through sorbent bed system 80 and can enter overhead condenser 40.

[0032] Sorbent bed system 80 can include two or more beds in parallel, or alternatively can include two or more beds such that at least one is a back-up for use when another bed is being serviced. Sorbent bed system 80 may be filled with regenerable adsorbents or nonregenerable getter materials. Getter materials can include finely divided metals (such as, for example, zirconium, tantalum, copper, nickel, etc.) on a substrate, such as alumina, ceria or kieselguhr. In certain embodiments, sorbent bed system 80 will remove contaminants such that the concentration of CO, CH_4, H_2, O_2, N_2, and H_2O is reduced to between about 1 ppm to about 10 ppm, alternatively to between about 1 ppb to 10 ppb. Outlet stream 82 from sorbent bed system 80 may be returned to overhead condenser 40, or alternatively may be diverted for other processes.

Example 1:

[0033] The present invention is further demonstrated by the following illustrative embodiment, which does not limit the claims of the present invention.

[0034] Table 1 provides data for a representative process, utilizing the embodiment illustrated in FIG. 1. The manufacturing process pre-treated argon gas waste stream is provided from a monocrystalline silicon production process. A molar gas flowrate of 500 m^3/h was chosen for simulation purposes. The process conditions of pre-treated argon waste stream 2 are based on the outlet of a pre-treatment process, which typically takes place at an ambient temperature, but with a compressed gas stream, thus for simulation purposes an inlet temperature of 20°C and 147 psig were chosen. Finally, the composition of pre-treated argon waste stream 2 assumes some CH_4 leakage and impurities of CO and O_2 on the part per million scale.

Table 1: Representative Data

Stream Name	2	12	32	22	52	24	14	26	16
Vapor Fraction	1	1	0	0	0.0303	1	1	1	1
Temperature (C)	20	-153.6	-156.9	-159	-161.9	-162	16.3	-159.5	16.3
Pressure (psig)	147	144.1	143.5	111.5	90.31	90.02	87.12	110.5	107.6
Molar Flow (Nm3/h)(gas))	500	500	500	436.7	438.7	438.7	438.7	89.85	89.85
Comp Mole Frac (Ar)	0.995042	0.995042	0.995042	0.999992	0.999992	0.999992	0.999992	0.972445	0.972445
Comp Mole Frac (N2)	0.003960	0.003960	0.003960	0.000005	0.000005	0.000005	0.000005	0.022014	0.022014
Comp Mole Frac (H2)	0.000995	0.000995	0.000995	0	0	0	0	0.00537	0.00537
Comp Mole Frac (CH4)	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001	0	0
Comp Mole Frac (CO)	0.000001	0.000001	0.000001	0	0	0	0	0.000003	0.000003
Comp Mole Frac (O2)	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001
Comp Mole Frac (CO2)	0	0	0	0	0	0	0	0	0
Comp Mole Frac (H2O)	0	0	0	0	0	0	0	0	0

[0035] As shown in Table 1, the present invention is capable of removing trace impurities to produce an argon stream (product stream 14), having an argon purity of greater than 99.999%. Cold feed stream 12 leaving cryogenic heat exchanger 10 was cooled to a temperature of -153.6°C by using the cold from purified vapor phase argon stream 24 and gaseous waste stream 26.

[0036] While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims. The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. Furthermore, if there is language referring to order, such as first and second, it should be understood in an exemplary sense and not in a limiting sense. For example, it can be recognized by those skilled in the art that certain steps can be combined into a single step.

[0037] The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

[0038] "Comprising" in a claim is an open transitional term which means the subsequently identified claim elements are a nonexclusive listing (i.e., anything else may be additionally included and remain within the scope of "comprising"). "Comprising" as used herein may be replaced by the more limited transitional terms "consisting essentially of" and "consisting of" unless otherwise indicated herein.

[0039] "Providing" in a claim is defined to mean furnishing, supplying, making available, or preparing something. The step may be performed by any actor in the absence of express language in the claim to the contrary a range is expressed, it is to be understood that another embodiment is from the one.

[0040] Optional or optionally means that the subsequently described event or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

[0041] Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such particular value and/or to the other particular value, along with all combinations within said range.

[0042] All references identified herein are each hereby incorporated by reference into this application in their entireties, as well as for the specific information for which each is cited.

CLAIMS

What is claimed is:

1. A method for purifying an argon stream comprising argon, nitrogen, hydrogen, carbon monoxide, carbon dioxide, water, and methane, the method comprising the steps of:

cooling an argon waste stream with a cryogenic heat exchanger to create a cold feed stream;

condensing the cold feed stream in a reboiler to create a liquid feed stream, wherein the cold feed stream is in a heat exchange relationship with bottoms liquid of a cryogenic distillation column, said distillation column comprising packing, the reboiler disposed in a lower portion of the cryogenic distillation column, and an overhead condenser in an upper portion of the cryogenic distillation column;

withdrawing the liquid feed stream from the reboiler and introducing the liquid feed stream to the cryogenic distillation column;

separating components of the liquid feed stream in the cryogenic distillation column into a bottoms argon product stream and a gas waste stream, the bottoms argon product stream having an increased purity of argon as compared to the cold feed stream;

withdrawing the bottoms argon product stream from the cryogenic distillation column and expanding the bottoms argon product stream using an expansion device to provide a cooled bottoms argon product stream;

feeding the cooled bottoms argon product stream to the overhead condenser and vaporizing the cooled bottoms argon product stream in the overhead condenser to create a purified vapor phase argon stream;

feeding the purified vapor phase argon stream to the cryogenic heat exchanger, wherein the purified vapor phase argon stream is used to cool the pre-treated argon waste stream, thereby producing a warm product stream; and removing the gas waste stream from the cryogenic distillation column.

2. The method as claimed in Claim 1, further comprising the step of feeding the gas waste stream to the cryogenic heat exchanger, wherein the gas waste stream is used to cool the pre-treated argon waste stream.

3. The method as claimed in any of the preceding claims, further comprising the step of pretreating the argon waste stream to remove impurities to provide a pre-treated argon waste stream having argon, nitrogen, hydrogen prior to the cooling step, wherein the impurities removed are selected from the group consisting of oxygen, carbon monoxide, carbon dioxide, water, methane, and combinations thereof.

4. The method as claimed in any of the preceding claims, further comprising the step of combining the cooled bottoms argon product stream and an argon lift stream downstream of the expansion device to provide lift to the cooled bottoms argon product stream.

5. The method as claimed in any of the preceding claims, wherein the step of withdrawing the bottoms argon product stream from the cryogenic distillation column further comprises pumping the bottoms argon product stream from the bottom of the cryogenic distillation column to the overhead condenser.

6. The method as claimed in any of the preceding claims, further comprising the step of feeding the bottoms argon product stream to separation stages in the cryogenic distillation column positioned above the overhead condenser.

7. The method as claimed in any of the preceding claims, further comprising the steps of:

separating a portion of the warm product stream downstream of the cryogenic heat exchanger to create a recycle stream;

compressing the recycle stream;

cooling a compressed recycle stream in the cryogenic heat exchanger to produce a cooled recycle stream; and

feeding the cooled recycle stream to the cryogenic distillation column such that the recovery of the warm product stream is increased as compared to when the cooled recycle stream is not fed to the cryogen distillation column.

8. The method as claimed in any of the preceding claims, further comprising the steps of:

sending the bottoms argon product stream to a sorbent bed system;

removing trace impurities in the bottoms argon product stream using the sorbent bed system to produce a sorbent bed outlet stream;

feeding the sorbent bed outlet stream to the overhead condenser.

9. The method as claimed in Claim 8, wherein the sorbent bed system comprises regenerable adsorbents.

10. The method as claimed in Claim 8, wherein the sorbent bed system comprises getter material.

11. The method as claimed in any of the preceding claims, wherein the method does not include the step of compressing the warm product stream for refrigeration purposes.

FIG. 1

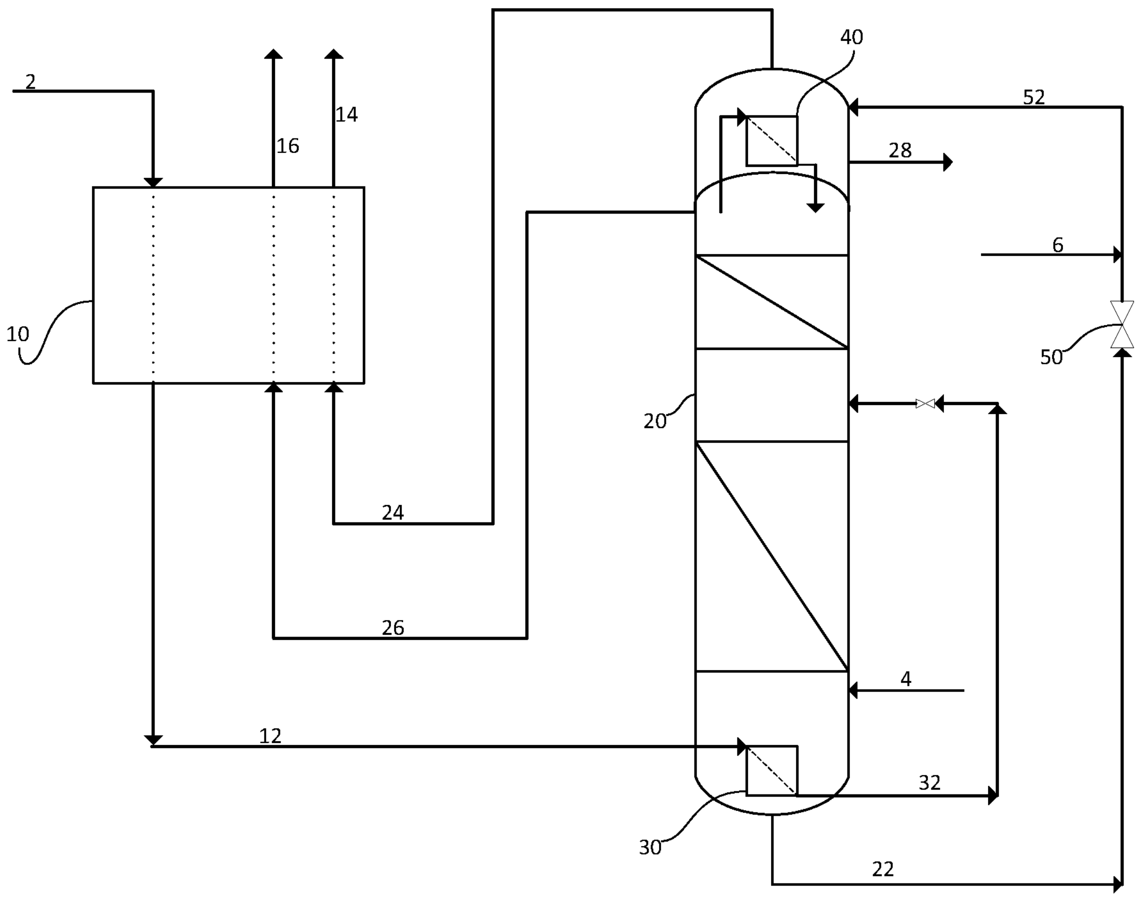

FIG. 2

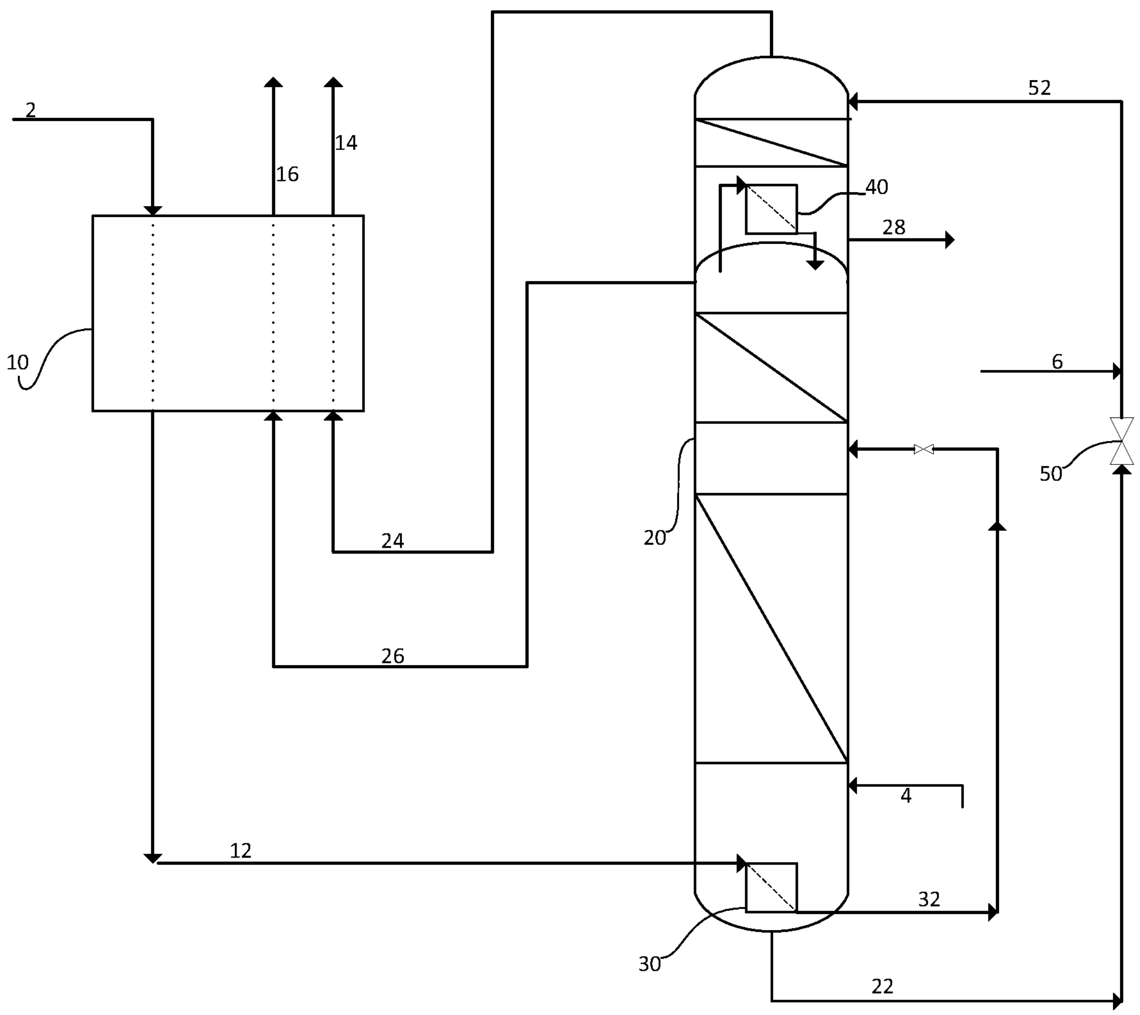

FIG. 3

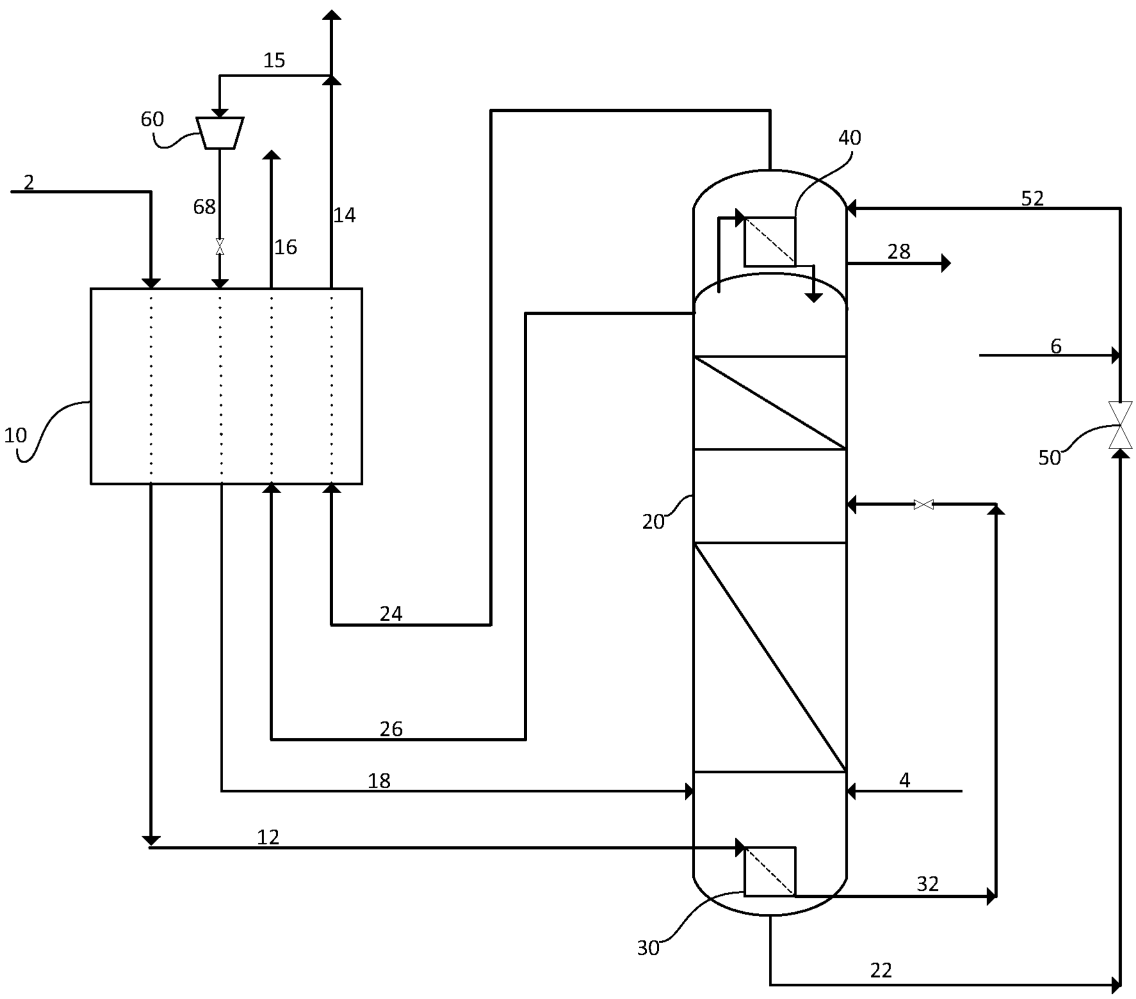

FIG. 4