

Description

The present invention relates to a method of and an apparatus for separating a gaseous mixture to produce an enriched gas. More particularly, the present invention is directed to an improved pressure swing adsorption method of and apparatus for separating gaseous mixtures which comprises an adsorption step, a pressure equalisation step, a back fill step, and an evacuation and purge step.

Pressure swing adsorption (PSA) is a well known method for separating gaseous mixtures. Pressure swing adsorption involves passing a gaseous mixture at an elevated pressure through a bed of an adsorbent material which selectively adsorbs one or more of the components of the gaseous mixture. Product gas, enriched in the unadsorbed gaseous component(s), is then withdrawn from the bed. The adsorption bed may be regenerated by reducing the pressure of the bed.

The term "gaseous mixture", as used herein, refers to a gaseous mixture, such as air, primarily comprised of two components having different molecular size. The term "enriched gas" refers to a gas comprised of the component(s) of the gaseous mixture relatively unadsorbed after passage of the gaseous mixture through the adsorbent bed. The enriched gas generally must meet a predetermined purity level, for example, from about 90% to about 99.9%, in the unadsorbed component(s). The term "lean gas" refers to a gas exiting from the adsorption bed that fails to meet the predetermined purity level set for the enriched gas.

The selectivity of the adsorbent material may depend on a difference in either adsorption kinetics or adsorption equilibrium. The selectivity of carbon molecular sieves is generally governed by the volume of the pore size and the distribution of that pore size in the adsorbent. Gaseous molecules with a kinetic diameter less than, or equal to, the pore size of the adsorbent are adsorbed and retained in the adsorbent while gaseous molecules with a diameter larger than the pore size of the adsorbent pass through the adsorbent. The adsorbent thus sieves the gaseous molecules according to their molecular size. The adsorbent may also separate molecules according to their different rates of diffusion in the pores of the adsorbent.

Zeolite molecular sieves adsorb gaseous molecules with some dependence upon crystalline size. In general, adsorption into zeolite is fast and equilibrium is reached typically in a few seconds. The sieving action of zeolite is generally dependent upon the difference in the equilibrium adsorption of the different components of the gaseous mixture. When air is separated by a zeolite adsorbent, nitrogen is preferentially adsorbed over oxygen and the pressure swing adsorption method may be em-

ployed to produce an oxygen enriched product.

The sieving action of carbon molecular sieves is generally not dependent upon differences in equilibrium adsorption but rather by differences in the rate of adsorption of the different components of the gaseous mixture. When air is separated by carbon molecular sieves, oxygen is preferentially adsorbed over nitrogen and the pressure swing adsorption method may be employed to produce a nitrogen enriched product.

As a gaseous mixture travels through a bed of adsorbent, the adsorbable gaseous components of the mixture enter and fill the pores of the adsorbent. After a period of time, the composition of the gas exiting the bed of adsorbent is essentially the same as the composition entering the bed. This is known as the break-through point. At some time prior to this breakthrough point, the adsorbent bed must be regenerated. Regeneration involves stopping the flow of gaseous mixture through the bed and purging the bed of the adsorbent components generally by venting the bed to the atmosphere.

A pressure swing adsorption system generally employs two adsorbent beds operated on cycles which are sequenced to be out of phase with one another by 180° so that when one bed is in the adsorption step, the other bed is in the regeneration step. The two adsorption beds may be connected in series or in parallel. In a serial arrangement, the gas exiting the outlet end of the first bed enters the inlet end of the second bed. In a parallel arrangement, the gaseous mixture enters the inlet end of all beds comprising the system. Generally, a serial arrangement of beds is preferred for obtaining a high purity gas product and a parallel arrangement of beds is preferred for purifying a large quantity of a gaseous mixture in a short time cycle.

As used herein, the term "adsorption bed" refers either to a single bed or serial arrangement of two beds. The inlet end of a single bed system is the inlet end of the single bed while the inlet end of the two bed system (arranged in series) is the inlet end of the first bed in the system. The outlet end of a single bed system is the outlet end of the single bed and the outlet end of the two bed system (arranged in series) is the outlet end of the second bed in the system. By using two adsorption beds in parallel in a system and by cycling (alternating) between the adsorption beds, product gas can be obtained continuously.

Between the adsorption step and the regeneration step, the pressure in the two adsorption beds is generally equalized by connecting the inlet ends of the two beds together and the outlet ends of the two beds together. During pressure equalization, the gas within the void spaces of the adsorption bed which has just completed its adsorption step

(under high pressure) flows into the adsorption bed which has just completed its regeneration step (under low pressure) because of the pressure differential which exists between the two beds. This pressure equalization step improves the yield of the product gas because the gas within the void spaces of the bed which has just completed its adsorption step has already been enriched.

Gas separation by the pressure swing adsorption method is more fully described in "Gas Separation by Adsorption Processes", Ralph T. Yang, Ed., Chapter 7, "Pressure Swing Adsorption: Principles and Processes" Butterworth 1987, which reference is incorporated herein by reference.

US-A-4,376,640, issued to Vo, discloses a pressure swing adsorption method for separating a gaseous mixture which comprises separating a gaseous mixture in a first adsorption bed, pressurising a second vented and evacuated adsorption bed with lean gas from the first adsorption bed at higher pressure, isolating the second bed to allow the pressurised vessel to decrease in pressure through the adsorption of the gas contained therein, separating the gaseous mixture in a second adsorption bed, and regenerating the first adsorption bed.

GB-A-2,195,097A, to Garrett, discloses a pressure swing adsorption method for separating a gaseous mixture which comprises the improvement of flowing gas from the product reservoir to an adsorption bed whenever the pressure in the product reservoir exceeds that of the adsorption bed.

JP-A-63079714, to Hareuma, discloses a pressure swing adsorption method for separating a gaseous mixture which comprises the improvement of cycling three adsorption beds in cycle fashion under very specific pressure swing adsorption conditions.

GB-A-2, 154,465, to Matsui, discloses a PSA process employing at least three adsorption beds and columns for separating a gas mixture including hydrogen involving performing seven operating steps namely: passing feed gas through a first bed and collecting product gas; equalising the pressure in the first bed with that in a second bed; further reducing the pressure in the first bed by passing gas to a third bed; evaluating the first bed; purging the first bed with gas from the second bed while evacuation is continued; repressurising the first bed with product gas; and equalising the pressure in the first bed with that in the third bed. Corresponding steps are performed in appropriate sequence by the second and third beds. The process may be performed at a relatively low adsorption pressure.

US-A-4,925,461 to Gamba, discloses a process for separation of nitrogen from a gas mixture predominantly composed of nitrogen and oxygen. The process is characterised by the manner of commu-

nicating an adsorber after adsorption step with an adsorber after regeneration step for gas transfer from the former to the latter, the operation of discontinuing the gas transfer before establishment of pressure equalization, and the regeneration promotion by causing back flow of product gas.

While the above pressure swing adsorption methods provide improvements in the separation of gaseous mixtures, these methods are not entirely satisfactory. Common problems with pressure swing adsorption methods include low product yield, low product purity, the need for large amounts of adsorbent, and energy inefficient regeneration methods. Hence there is a need for improved pressure swing adsorption methods.

It is an aim of the present invention to provide an improved pressure swing adsorption method and apparatus for the separation of gaseous mixtures in high yield and high purity.

According to one aspect of the present invention an adsorption method for separating a gaseous mixture in a plurality of adsorption beds operated out of phase with one another to produce an enriched gas having a predetermined purity comprises the steps of:

- a) passing the gaseous mixture into an inlet end of one adsorption bed at an adsorption pressure in the range of about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig) while withdrawing enriched gas from the outlet end of said one adsorption bed and collecting the enriched gas as product;
- b) when the purity of the enriched gas from the outlet end of said one adsorption bed drops to about 0.1% to about 10% below said predetermined purity thereby becoming lean gas, stopping the flow of gaseous mixture into said one adsorption bed and passing the lean gas from the outlet end of said one adsorption bed into the inlet end of another adsorption bed which has just completed step c) until the pressure of said other adsorption bed is in the range of about 25% to about 50% of the adsorption pressure;
- c) stopping the flow of lean gas from the outlet end of said one adsorption bed and evacuating said one adsorption bed from the inlet end to a desorption pressure of about $3.33 \times 10^3 \text{ Pa}$ (25 torr) to about $465.1 \times 10^3 \text{ Pa}$ (350 torr) while purging said one adsorption bed by passing enriched gas product into the outlet end of said one adsorption bed;
- d) partially pressurising said one adsorption bed by passing lean gas from the outlet end of another adsorption bed which has just completed step a) to the inlet end of said one adsorption bed until the pressure in said one adsorption bed is in the range of about 25% to

about 50% of the adsorption pressure;

e) further pressurising said one adsorption bed by passing enriched gas into the outlet end of said one adsorption bed to back fill said one adsorption bed until the pressure of the back filled adsorption bed is in the range of about 50% to about 100% of the adsorption pressure;

f) further pressurising said one adsorption bed by passing the gaseous mixture into the inlet end of said one adsorption bed at an adsorption pressure in the range of about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig); and

g) repeating the above steps in a continuous cycle treating each other adsorption bed in said plurality of adsorption beds like said one adsorption bed.

In a modification of the above procedure, step c) is carried out by passing the lean gas from the outlet end of the first adsorption bed into both the inlet end and the outlet end of the second bed simultaneously to equalize substantially the pressure of the first adsorption bed and the second adsorption bed.

Embodiments of the invention will now be described by way of example, reference being made to the Figures of the accompanying diagrammatic drawings in which:-

Figure 1 is a schematic drawing of a two bed pressure swing adsorption apparatus suitable for separating gaseous mixtures according to the present invention;

Figure 2 illustrates in graphic format the specific product of nitrogen obtained versus oxygen concentration when air is separated using various pressure swing adsorption methods (Examples 1-5);

Figure 3 illustrates in graphic format the product yield of nitrogen obtained versus oxygen concentration when air is separated using various pressure swing adsorption methods (Examples 1-5);

Figure 4 illustrates in graphic format the specific product of nitrogen obtained versus oxygen concentration when air is separated employing the pressure swing adsorption method of the present invention at cycle times of 180 seconds and 240 seconds (Example 1); and

Figure 5 illustrates in graphic format the product yield of nitrogen obtained versus oxygen concentration when air is separated employing the pressure swing adsorption method of the present invention at cycle times of 180 seconds and 240 seconds (Example 1).

Applicant has found that the combination of a specific pressure equalisation step, an evacuation and product gas purge step, and a product gas back fill step provides a pressure swing adsorption method which yields enriched gases in high yield

and in high purity. The combination of the pressure equalisation step, the evacuation and purge step, and the back fill step enhances the purity of the product gas and more efficiently regenerates the adsorption bed. Specifically, evacuating and purging the adsorption bed to be regenerated with enriched gas from the product reservoir desorbs more adsorbed gas permitting the bed to adsorb more gas in the next cycle. Equalising the pressure of the adsorption beds by passing lean gas from the outlet end of the first adsorption bed into the inlet end of the second adsorption bed or into both the inlet end and the outlet end of the second adsorption bed simultaneously utilises already enriched gas thereby improving the purity and yield of product. Back filling the adsorption bed to be regenerated with product gas after the pressure equalisation step from the outlet end displaces the lean gas deeper into the bed and provides highly enriched gas at the top of the bed so that the first gas to be withdrawn from the bed is of highest purity and does not contaminate the gas in the product reservoir with impurities.

In accord with the present invention, the pressure swing adsorption method for separating a gaseous mixture to produce an enriched gas having a predetermined purity comprises the steps of a) passing the gaseous mixture into an inlet end of a first adsorption bed at an adsorption pressure in the range from about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig), b) withdrawing enriched gas from an outlet end of the first adsorption bed and passing the enriched gas into a product reservoir, c) when the purity of the enriched gas from the outlet end of the first adsorption bed drops from about 0.1% to about 10% below the predetermined purity thereby becoming lean gas, passing the lean gas from the outlet end of the first adsorption bed into an inlet end of a second adsorption bed or simultaneously into an inlet and an outlet of a second bed to substantially equalise the pressure of the first adsorption bed and the second adsorption bed, wherein the pressure of the second adsorption bed is in the range from about 25% to about 50% of the adsorption pressure, d) stopping the flow of lean gas from the outlet end of the first adsorption bed and evacuating the first adsorption bed from the inlet end to a desorption pressure from about $3.33 \times 10^3 \text{ Pa}$ (25 torr) to about $465.1 \times 10^3 \text{ Pa}$ (350 torr) while purging the first adsorption bed by passing enriched gas from the product reservoir into the outlet end of the first adsorption bed, e) further pressurising the second adsorption bed by passing enriched gas from the product reservoir into the outlet end of the second adsorption bed to back fill the second adsorption bed, wherein the pressure of the back filled second adsorption bed is in the range from about 50% to

about 100% of the adsorption pressure, f) further pressurising the second adsorption bed by passing the gaseous mixture into the inlet end of the second adsorption bed at an adsorption pressure in the range from about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig), and g) repeating the above steps in a continuous cycle treating the second adsorption bed like the first adsorption bed and the first adsorption bed like the second adsorption bed.

The pressure swing adsorption method of the present invention employing the novel combination of a pressure equalisation step, an evacuation and purge step, and a back fill step can be better understood by reference to the apparatus in Figure 1. Any gaseous mixture including, but not limited to air (nitrogen and oxygen), methane and carbon dioxide, and hydrogen and carbon monoxide, may be separated by the method of the present invention. For simplicity, the present method will be described in connection with the separation of air although the method may be used to separate other gaseous mixtures normally separated by the pressure swing adsorption method.

Referring to Figure 1, two pressure resistant columns, 1 and 2, are filled with beds of adsorbents 3 and 4, respectively. The beds may be filled, for example, with carbon molecular sieve adsorbents suitable for the fractionation of a gaseous mixture, such as nitrogen from air. Column 1 contains the first adsorption bed and column 2 contains the second adsorption bed. Columns 1 and 2 are essentially identical to each other as are beds of adsorbents 3 and 4. While Figure 1 shows columns 1 and 2 in a vertical position, the columns may also be employed in a horizontal position.

Ambient air is fed through air feed conduit 5 to compressor 6. Compressor 6 compresses the air to the adsorption pressure which is then introduced into the inlet end of column 1 or column 2 via air inlet conduit 7 and stop valve (on-off stop valve) 8 or 9, respectively. Stop valve 8 introduces feed air into the inlet end at the bottom of column 1 and stop valve 9 introduces feed air into inlet end at the bottom of column 2.

The feed air may be modified prior to passage into adsorption column 1 or 2 by passing the air through a condenser to remove excess humidity (a relative humidity of 40% or less is preferred). A filter or scrubber may also be employed to remove gases such as carbon dioxide, sulphur dioxide, or nitrogen oxides from the feed air. These purification steps are optional and improve the purity of the product gas and also prolong the useful life of the adsorption beds.

Feed air admitted to column 1 or column 2 is adsorbed into bed of adsorbent 3 or 4, respectively, to selectively sieve oxygen. Product gas,

enriched in nitrogen, is withdrawn from column 1 or column 2 via stop valve 12 or stop valve 13, respectively, and outlet conduit 10 into product reservoir 11. Product gas from reservoir 11 may similarly be back filled into column 1 or column 2 via conduit 10 and stop valve 12 or stop valve 13, respectively.

The product reservoir 11 has an outlet conduit 14 and stop valve 15 for venting product gas. The instantaneous nitrogen flow rate is measured by a mass flow meter and the enriched gas oxygen content is analyzed upstream from the product reservoir.

For evacuation of column 1 or 2, the inlet end of column 1 and the inlet end of column 2 are first vented to the atmosphere and then connected to vacuum pump 17 via outlet conduit 16 and stop valve 18 and stop valve 19, respectively. For pressure equalisation, the outlet end of column 1 is connected to the inlet end of column 2 via conduit 20 and stop valves 21 and 24 or to both the inlet end and the outlet end of column 2 via stop valves 21, 23 and 24 and the corresponding conduits. Similarly, the outlet end of column 2 is connected to the inlet end of column 1 via conduit 20 and stop valves 23 and 22 or to both the inlet end and the outlet end of column 1 via stop valves 21, 22 and 23 and the corresponding conduits.

At the start of the pressure swing adsorption cycle, feed air from conduit 5 is compressed in compressor 6 to the adsorption pressure and then passed to the inlet end of column 1 and adsorption bed 3 via conduit 7 and open stop valve 8. The adsorption pressure is in the range from about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig), preferably from about $346 \times 10^3 \text{ Pa}$ (50 psig) to about $1.38 \times 10^6 \text{ Pa}$ (200 psig). Adsorption bed 4 in column 2 is evacuated simultaneously. The feed air is adsorbed in adsorption bed 3 to sieve selectively oxygen. Product gas, enriched in nitrogen and having a predetermined purity, is withdrawn from the outlet end of column 1 via open stop valve 12 and outlet conduit 10 and passed into product reservoir 11. The predetermined purity of the product gas is generally from about 90% to about 99.9%.

When the purity of the enriched gas from the outlet end of column 1 drops from about 0.1% to about 10% below the predetermined purity thereby becoming lean gas, stop valves 8 and 12 are closed stopping the production of product gas. Stop valves 21 and 24 are then opened and, according to a first embodiment of the invention, lean air is then passed from the outlet end of column 1 to the inlet end of column 2 via conduit 20 to substantially equalise the pressure of column 1 and column 2. The pressure of column 2 is in the range from about 25% to about 50%, preferably from

about 35% to about 45%, of the adsorption pressure.

When the pressure equalisation step is complete, stop valves 21 and 24 are then closed and stop valve 13 is opened. Product gas from reservoir 11 is then passed into the outlet end of column 2 to back fill column 2. The pressure of back filled column 2 is generally in the range from about 50% to about 100%, preferably from about 60% to about 80%, of the adsorption pressure.

When the back fill step is complete, stop valve 9 is opened to admit feed gas from compressor 6 to the inlet end of column 2 and the cycle is repeated.

Column 1 is regenerated by opening stop valves 12 and 18 and venting column 1 to the atmosphere. Column 1 is then evacuated from the inlet end via stop valve 18 to the desorption pressure while enriched gas from product reservoir 11, or alternatively from producing column 2, is passed at the product gas purge rate into the outlet end of column 1 via stop valve 12. In general, the desorption pressure is from about $3.33 \times 10^3 \text{ Pa}$ (25 torr) to about $465 \times 10^3 \text{ Pa}$ (350 torr), preferably from about $6.67 \times 10^3 \text{ Pa}$ (50 torr) to about $33.3 \times 10^3 \text{ Pa}$ (250 torr). In general, the product gas purge rate is from about 0.01 1/1/cycle to about 2 1/1/cycle, preferably from about 0.1 1/1/cycle to about 0.8 1/1/cycle.

Hence, when one adsorption bed is producing gas, the other adsorption bed is being regenerated. In general, the time to complete a cycle (cycle time) is in the range from about 30 seconds to about 600 seconds, preferably from about 45 seconds to about 300 seconds.

In the embodiment of the process of the invention described above, equalisation of the pressure in columns 1 and 2 following the completion of the nitrogen production step is effected by transferring gas out of the column which has just completed production, via its outlet, and into the column which has just completed regeneration, via its inlet (outlet to inlet pressure equalisation). For example, when column 1 has completed its production cycle, and column 2, its regeneration cycle, equalisation of columns 1 and 2 is carried out by transferring gas from column 1 to column 2 through valve 21, line 20 and valve 24.

It sometimes happens that the flow of equalisation gas into the column which has just completed its evacuation step significantly disturbs the adsorption bed in this column. This results because the sudden rush of high pressure gas into the evacuated bed causes violent levitation of the bed. This is particularly the case when the ratio of the column's diameter to its height is small. The following alternative embodiment of the invention minimizes the disturbance of the beds in columns

having such a configuration. In this embodiment, pressure equalisation between the two columns following the pressure swing adsorption step is carried out by a variation of the above-described procedure.

According to the procedure of this embodiment, pressure equalisation of vessels 1 and 2 is accomplished by transferring gas from the column that has just completed its production step to the column that has just completed its evacuation step by causing the gas to exit out of the former column through its outlet end and enter the latter column by flowing through both its inlet end and its outlet end (outlet to inlet and outlet pressure equalisation). The simultaneous flow of pressurising gas into both the outlet end and the inlet end of the column receiving the gas may take place for the entire duration of the pressure equalisation period or for only a part of this period. For example, the gas may continuously flow into the second column through both its inlet end and its outlet end for the entire pressure equalisation period or it may flow into the column through both its inlet end and its outlet end for a part of the pressure equalisation period and through either its inlet end or the outlet end for the remainder of the equalisation period. Any combination of flows is permissible as long as flow to both the column's inlet end and outlet end occurs during some part of the pressure equalisation period.

With reference to Figure 1, the modified pressure equalisation of this embodiment may proceed as follows. After column 1 has completed its production step and column 2 has completed its evacuation step, pressure equalisation of vessels 1 and 2 can be accomplished by closing stop valve 8 and 12 and opening stop valves 21, 23 and 24. Lean gas then flows out of vessel 1 through its outlet end, through open valve 21 and into vessel 2 through both open valves 23 and 24 simultaneously. In the alternate cycle, when vessel 2 has just completed its production step and vessel 1 its evacuation step, stop valves 9 and 13 are closed and stop valves 21, 22 and 23 are opened. This permits gas to flow out of vessel 2 through its outlet end, through open valve 23, and into vessel 1 through both open valves 21 and 22 simultaneously. The modified procedure of this embodiment has the advantage that it permits rapid equalisation of vessels 1 and 2 with very little or no disturbance of the bed receiving the pressurising gas.

The present invention is further illustrated by the following examples which are presented for the purpose of demonstrating, but not limiting, the method of this invention.

EXAMPLES 1-7

These Examples illustrate the separation of a gaseous mixture to form enriched gas via conventional pressure swing adsorption methods and the pressure swing adsorption method according to the present invention.

Air was separated to form enriched nitrogen via the pressure swing adsorption method at an adsorption pressure of $698 \times 10^3 \text{ Pa}$ (100 psig), a desorption pressure of $18 \times 10^3 \text{ Pa}$ (135 torr), a cycle time of 240 seconds, and a specific product gas purge rate of 0.25 l/cycle (liters of gas/liters of adsorbent/cycle).

When air was separated according to the method of the present invention (outlet end-inlet end pressure equalisation step, back fill step, and evacuation and purge step) at 99% nitrogen purity, the specific product obtained was 129.2 l/h and the yield of product was 66.5%, Example 1, see Figures 2-3. When air was separated in the manner set out above except that the purge step was carried out without evacuation but with only vent to atmosphere pressure, the specific product obtained was 72.2 l/h and the yield of product was 52%, Example 2, see Figures 2-3. When air was separated in the manner set out above except that the pressure equalisation step was carried out by connecting top-top (outlet end-outlet end) and bottom-bottom (inlet end-inlet end), the specific product was 117.6 l/h and the yield of product was 63.7%, Example 3, see Figures 2-3. When air was separated in the manner set out above except that the pressure equalisation step was carried out by connecting top-top (outlet end-outlet end) and bottom-bottom (inlet end-inlet end) and the purge step was carried out without evacuation but with only vent to atmosphere pressure, the specific product obtained was 81.7 l/h and the yield of product was 55.5%, Example 4, see Figures 2-3. When air was separated in the manner set out above except that the pressure equalisation step was carried out by connecting top-top (outlet end-outlet end) and bottom-bottom (inlet end-inlet end), the purge step was carried out without evacuation but with only vent to atmosphere pressure, and the pressurisation step was carried out using only lean air and not with a back fill step, the specific product obtained was 77.1 l/h and the yield of product was 54.4%, Example 5, see Figures 2-3.

When the pressurisation step was carried out using only lean gas, as described in US-A-4,376,640, and the ultrapressurised vessel was isolated, then vented and evacuated, the specific product obtained was 125.2 l/h and the yield of product was 62.6%.

When the cycle time for the method of Example 1 was decreased from 240 seconds to 180

seconds, the specific product obtained at 99% nitrogen purity increased to 150.2 l/h and the product yield decreased to 65.3%, see Figures 4-5.

Example 6 illustrates the separation of air by the embodiment of the invention in which the equalisation step is conducted by transferring gas from the column completing its product step through its outlet and into the column completing its evacuation step through both its inlet and its outlet.

Air was separated to form enriched nitrogen via pressure swing adsorption, at an adsorption pressure of $698 \times 10^3 \text{ Pa}$ (100 psig), a cycle time of 240 seconds, a specific product gas purge rate of 0.5 l/cycle and with desorption at atmospheric pressure. The specific product and product yield were respectively 26.5% and 12.3% greater than the specific product and product yield obtained when the experiment was conducted under identical conditions except that the equalisation of the columns was carried out by transferring gas from the outlet end of the column that has just completed its production step and into only the inlet end of the column that has just completed its evacuation step.

In Example 7, the procedure of Example 6 was repeated except that the desorption was carried out at a pressure of $40 \times 10^3 \text{ Pa}$ (300 torr). The increase in the specific product and the product yield compared to the specific product and product yield obtained by outlet end to inlet end only pressure equalisation was 4.4% and 5.2%, respectively.

Accordingly, the improved pressure swing adsorption method for separating gaseous mixtures according to both embodiments of the present invention provides enriched gases in high yield and high purity.

Claims

1. An adsorption method for separating a gaseous mixture in a plurality of adsorption beds operated out of phase with one another to produce an enriched gas having a predetermined purity which comprises the steps of:
 - a) passing the gaseous mixture into an inlet end of one adsorption bed at an adsorption pressure in the range of about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig) while withdrawing enriched gas from the outlet end of said one adsorption bed and collecting the enriched gas as product;
 - b) when the purity of the enriched gas from the outlet end of said one adsorption bed drops to about 0.1% to about 10% below said predetermined purity thereby becoming lean gas, stopping the flow of gaseous mixture into said one adsorption bed and passing the lean gas from the outlet end of

EXAMPLES 1-7

These Examples illustrate the separation of a gaseous mixture to form enriched gas via conventional pressure swing adsorption methods and the pressure swing adsorption method according to the present invention.

Air was separated to form enriched nitrogen via the pressure swing adsorption method at an adsorption pressure of $698 \times 10^3 \text{ Pa}$ (100 psig), a desorption pressure of $18 \times 10^3 \text{ Pa}$ (135 torr), a cycle time of 240 seconds, and a specific product gas purge rate of 0.25 l/cycle (liters of gas/liters of adsorbent/cycle).

When air was separated according to the method of the present invention (outlet end-inlet end pressure equalisation step, back fill step, and evacuation and purge step) at 99% nitrogen purity, the specific product obtained was 129.2 l/h and the yield of product was 66.5%, Example 1, see Figures 2-3. When air was separated in the manner set out above except that the purge step was carried out without evacuation but with only vent to atmosphere pressure, the specific product obtained was 72.2 l/h and the yield of product was 52%, Example 2, see Figures 2-3. When air was separated in the manner set out above except that the pressure equalisation step was carried out by connecting top-top (outlet end-outlet end) and bottom-bottom (inlet end-inlet end), the specific product was 117.6 l/h and the yield of product was 63.7%, Example 3, see Figures 2-3. When air was separated in the manner set out above except that the pressure equalisation step was carried out by connecting top-top (outlet end-outlet end) and bottom-bottom (inlet end-inlet end) and the purge step was carried out without evacuation but with only vent to atmosphere pressure, the specific product obtained was 81.7 l/h and the yield of product was 55.5%, Example 4, see Figures 2-3. When air was separated in the manner set out above except that the pressure equalisation step was carried out by connecting top-top (outlet end-outlet end) and bottom-bottom (inlet end-inlet end), the purge step was carried out without evacuation but with only vent to atmosphere pressure, and the pressurisation step was carried out using only lean air and not with a back fill step, the specific product obtained was 77.1 l/h and the yield of product was 54.4%, Example 5, see Figures 2-3.

When the pressurisation step was carried out using only lean gas, as described in US-A-4,376,640, and the ultrapressurised vessel was isolated, then vented and evacuated, the specific product obtained was 125.2 l/h and the yield of product was 62.6%.

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Example 6 illustrates the separation of air by the embodiment of the invention in which the equalisation step is conducted by transferring gas from the column completing its product step through its outlet and into the column completing its evacuation step through both its inlet and its outlet.

Air was separated to form enriched nitrogen via pressure swing adsorption, at an adsorption pressure of $698 \times 10^3 \text{ Pa}$ (100 psig), a cycle time of 240 seconds, a specific product gas purge rate of 0.5 l/cycle and with desorption at atmospheric pressure. The specific product and product yield were respectively 26.5% and 12.3% greater than the specific product and product yield obtained when the experiment was conducted under identical conditions except that the equalisation of the columns was carried out by transferring gas from the outlet end of the column that has just completed its production step and into only the inlet end of the column that has just completed its evacuation step.

In Example 7, the procedure of Example 6 was repeated except that the desorption was carried out at a pressure of $40 \times 10^3 \text{ Pa}$ (300 torr). The increase in the specific product and the product yield compared to the specific product and product yield obtained by outlet end to inlet end only pressure equalisation was 4.4% and 5.2%, respectively.

Accordingly, the improved pressure swing adsorption method for separating gaseous mixtures according to both embodiments of the present invention provides enriched gases in high yield and high purity.

Claims

1. An adsorption method for separating a gaseous mixture in a plurality of adsorption beds operated out of phase with one another to produce an enriched gas having a predetermined purity which comprises the steps of:
 - a) passing the gaseous mixture into an inlet end of one adsorption bed at an adsorption pressure in the range of about $104 \times 10^3 \text{ Pa}$ (15 psig) to about $3.448 \times 10^6 \text{ Pa}$ (500 psig) while withdrawing enriched gas from the outlet end of said one adsorption bed and collecting the enriched gas as product;
 - b) when the purity of the enriched gas from the outlet end of said one adsorption bed drops to about 0.1% to about 10% below said predetermined purity thereby becoming lean gas, stopping the flow of gaseous mixture into said one adsorption bed and passing the lean gas from the outlet end of



said one adsorption bed into the inlet end of another adsorption bed which has just completed step c) until the pressure of said other adsorption bed is in the range of about 25% to about 50% of the adsorption pressure;

c) stopping the flow of lean gas from the outlet end of said one adsorption bed and evacuating said one adsorption bed from the inlet end to a desorption pressure of about 3.33×10^3 Pa (25 torr) to about 465×10^3 Pa (350 torr) while purging said one adsorption bed by passing enriched gas product into the outlet end of said one adsorption bed;

d) partially pressurising said one adsorption bed by passing lean gas from the outlet end of another adsorption bed which has just completed step a) to the inlet end of said one adsorption bed until the pressure in said one adsorption bed is in the range of about 25% to about 50% of the adsorption pressure;

e) further pressurising said one adsorption bed by passing enriched gas into the outlet end of said one adsorption bed to back fill said one adsorption bed until the pressure of the back filled adsorption bed is in the range of about 50% to about 100% of the adsorption pressure;

f) further pressurising said one adsorption bed by passing the gaseous mixture into the inlet end of said one adsorption bed at an adsorption pressure in the range of about 104×10^3 Pa (15 psig) to about 3.448×10^6 Pa (500 psig); and

g) repeating the above steps in a continuous cycle treating each other adsorption bed in said plurality of adsorption beds like said one adsorption bed.

2. A method as claimed in Claim 1, in which at step d) the partial pressurisation of said one adsorption bed is achieved by passing lean gas from the outlet end of another adsorption bed which has just completed step a) to both the inlet end and the outlet end of said one adsorption bed until the pressure in said one adsorption bed is in the range of about 25% to about 50% of the adsorption pressure.
3. A method as claimed in Claim 1 or 2, in which the adsorption beds comprise carbon molecular sieves, the gaseous mixture is air and the enriched gas is nitrogen.
4. A method as claimed in any one of Claims 1, 2 or 3, in which the predetermined purity is from

about 90% to about 99.9%.

5. A method as claimed in any one of claims 1 to 4, in which in step a) the adsorption pressure is in the range of about 346×10^3 Pa (50 psig) to about 3.448×10^6 Pa (500 psig).
6. A method as claimed in any preceding claim, in which in step b) the pressure of said other adsorption bed after the pressure equalisation step is in the range of about 35% to about 45% of the adsorption pressure.
7. A method as claimed in any preceding claim, in which in step c) said one adsorption bed is evacuated from the inlet end to a desorption pressure of about 6.67×10^3 Pa (50 torr) to about 33.3×10^3 Pa (250 torr).
8. A method as claimed in any preceding claim, in which in step c) said one adsorption bed is purged by passing enriched gas product into the outlet end of said one adsorption bed at a purge rate of about 0.01 1/1/cycle to about 2 1/1/cycle.
9. A method as claimed in any preceding claim, in which the pressure of said one adsorption bed at the end of step e) is in the range of about 60% to about 80% of the adsorption pressure.
10. A method according to any preceding claim, in which the pressure of said one adsorption bed at the end of step f) is in the range of about 6.67×10^3 Pa (50 psig) to about 1.38×10^6 Pa (200 psig).

Patentansprüche

1. Ein Adsorptionsverfahren zum Trennen einer gasförmigen Mischung in einer Vielzahl von Adsorptionsbetten, die außer Phase miteinander betrieben werden, um ein angereichertes Gas mit einer vorbestimmten Reinheit zu erzeugen, welches die Schritte umfaßt, daß:
 - a) die gasförmige Mischung in ein Einlaßende eines Adsorptionsbettes bei einem Adsorptionsdruck in dem Bereich von 104×10^3 Pa (15 psig) bis ungefähr 3.448×10^6 Pa (500 psig) geführt wird, während angereichertes Gas aus dem Auslaßende des einen Adsorptionsbettes entzogen wird und das angereicherte Gas als Produkt gesammelt wird;
 - b) wenn die Reinheit des angereicherten Gases aus dem Auslaßende des einen Adsorptionsbettes zu ungefähr 0,1 % bis un-



gefähr 10 % unter die vorbestimmte Reinheit fällt, wodurch es Magergas wird, der Fluß der gasförmigen Mischung in das eine Adsorptionsbett gestoppt wird und das Magergas aus dem Auslaßende des einen Adsorptionsbettes in das Einlaßende eines anderen Adsorptionsbettes geführt wird, welches gerade Schritt c) abgeschlossen hat, bis der Druck des anderen Adsorptionsbettes in dem Bereich von ungefähr 25 % bis ungefähr 50 % des Adsorptionsdruckes liegt;

c) der Fluß von Magergas aus dem Auslaßende des einen Adsorptionsbettes beendet wird und das eine Adsorptionsbett von dem Einlaßende zu einem Desorptionsdruck von ungefähr $3,33 \times 10^3$ Pa (25 Torr) bis ungefähr 465×10^3 Pa (350 Torr) evakuiert wird, während das eine Adsorptionsbett gereinigt wird, indem angereichertes Gasprodukt in das Auslaßende des einen Adsorptionsbettes hineingeführt wird;

d) das eine Adsorptionsbett partiell unter Druck gesetzt wird, indem Magergas aus dem Auslaßende eines anderen Adsorptionsbettes, welches gerade Schritt a) abgeschlossen hat, zu dem Einlaßende des einen Adsorptionsbettes geführt wird, bis der Druck in dem einen Adsorptionsbett in dem Bereich von ungefähr 25 % bis ungefähr 50 % des Adsorptionsdruckes liegt;

e) weiter das eine Adsorptionsbett unter Druck gesetzt wird, indem angereichertes Gas in das Auslaßende des einen Adsorptionsbettes geführt wird, um das eine Adsorptionsbett zurückzufüllen, bis der Druck des zurückgefüllten Adsorptionsbettes in dem Bereich von ungefähr 50 % bis ungefähr 100 % des Adsorptionsdruckes liegt;

f) das eine Adsorptionsbett unter Druck gesetzt wird, indem die gasförmige Mischung in das Einlaßende des einen Adsorptionsbettes bei einem Adsorptionsdruck in dem Bereich von ungefähr 104×10^3 Pa (15 psig) bis ungefähr $3,448 \times 10^6$ Pa (500 psig) geführt wird; und

g) die obigen Schritte in einem kontinuierlichen Zyklus wiederholt werden, der ein anderes Adsorptionsbett in der Vielzahl von Adsorptionsbetten wie das eine Adsorptionsbett behandelt.

2. Ein Verfahren nach Anspruch 1, in welchem bei Schritt d) das partielle Unter-Druck-Setzen des einen Adsorptionsbettes erreicht wird, indem Magergas aus dem Auslaßende eines anderen Adsorptionsbettes geführt wird, welches gerade Schritt a) abgeschlossen hat, und zwar

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sowohl zu dem Einlaßende als auch dem Auslaßende des einen Adsorptionsbettes, bis der Druck in dem einen Adsorptionsbett in dem Bereich von ungefähr 25 % bis ungefähr 50 % des Adsorptionsdruckes liegt.

3. Ein Verfahren nach Anspruch 1 oder 2, in welchem die Adsorptionsbetten Kohlenstoffmolekularsiebe umfassen, die gasförmige Mischung Luft ist und das angereicherte Gas Stickstoff ist.

4. Ein Verfahren nach einem der Ansprüche 1, 2 oder 3, in welchem die vorbestimmte Reinheit zwischen ungefähr 90 % bis ungefähr 99,9 % liegt.

5. Ein Verfahren nach einem der Ansprüche 1 bis 4, in welchem in Schritt a) der Adsorptionsdruck in dem Bereich von ungefähr 346×10^3 Pa (50 psig) bis ungefähr $3,448 \times 10^6$ Pa (500 psig) liegt.

6. Ein Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem in Schritt b) der Druck des anderen Adsorptionsbettes nach dem Druckausgleichsschritt in dem Bereich von ungefähr 35 % bis ungefähr 45 % des Adsorptionsdruckes liegt.

7. Ein Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem in Schritt c) das eine Adsorptionsbett von dem Einlaßende zu einem Desorptionsdruck von ungefähr $6,67 \times 10^3$ Pa (50 Torr) zu ungefähr $33,3 \times 10^3$ Pa (250 Torr) evakuiert wird.

8. Ein Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem in Schritt c) das eine Adsorptionsbett gereinigt wird, indem angereichertes Gasprodukt in das Auslaßende des einen Adsorptionsbettes bei einer Reinigungsrate von ungefähr 0,01 1/1 Zyklus bis ungefähr 2 1/1 Zyklus geführt wird.

9. Ein Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem der Druck des einen Adsorptionsbettes beim Ende von Schritt e) in dem Bereich von ungefähr 60 % bis ungefähr 80 % des Adsorptionsdruckes liegt.

10. Ein Verfahren nach irgendeinem vorhergehenden Anspruch, in welchem der Druck des einen Adsorptionsbettes beim Ende von Schritt f) in dem Bereich von ungefähr $6,67 \times 10^3$ Pa (50 psig) bis ungefähr $1,38 \times 10^6$ Pa (200 psig) liegt.



Revendications

1. Procédé d'adsorption destiné à la séparation d'un mélange gazeux dans plusieurs lits d'adsorption qui sont utilisés sous forme déphasée mutuellement, pour la création d'un gaz enrichi ayant une pureté prédéterminée, comprenant les étapes suivantes :

a) la circulation du mélange gazeux à une extrémité d'entrée d'un lit d'adsorption à une pression d'adsorption comprise entre environ 104.10^3 Pa (15 psig) et environ $3,448.10^6$ Pa (500 psig) avec extraction du gaz enrichi à l'extrémité de sortie d'un premier lit d'adsorption et collecte du gaz enrichi comme produit,

b) lorsque la pureté du gaz enrichi provenant de l'extrémité de sortie du premier lit d'adsorption tombe au-dessous de la pureté prédéterminée d'une valeur comprise entre environ 0,1 et 10 %, et forme ainsi un gaz appauvri, l'arrêt de la circulation du mélange gazeux dans le premier lit d'adsorption et la circulation du gaz appauvri de l'extrémité de sortie du premier lit d'adsorption vers l'extrémité d'entrée d'un autre lit d'adsorption qui vient juste de terminer l'étape

c) jusqu'à ce que l'autre lit d'adsorption ait une pression comprise entre environ 25 et 50 % de la pression d'adsorption,

c) l'arrêt de la circulation du gaz appauvri provenant de l'extrémité de sortie du premier lit d'adsorption et l'évacuation de ce premier lit d'adsorption par l'extrémité d'entrée jusqu'à une pression de désorption comprise entre environ $3,33.10^3$ Pa (25 torr) et environ 465.10^3 Pa (350 torr), avec purge du premier lit d'adsorption par passage du produit gazeux enrichi vers l'extrémité de sortie du premier lit d'adsorption,

d) la mise sous pression partielle du premier lit d'adsorption par circulation du gaz appauvri provenant de l'extrémité de sortie du premier lit d'adsorption qui a juste terminé l'étape a) vers l'extrémité d'entrée du premier lit d'adsorption jusqu'à ce que la pression dans le premier lit d'adsorption soit comprise entre environ 25 et 50 % de la pression d'adsorption,

e) la mise sous pression supplémentaire du premier lit d'adsorption par circulation du gaz enrichi à l'extrémité de sortie du premier lit d'adsorption de manière que le premier lit d'adsorption subisse un remplissage par circulation en sens inverse jusqu'à ce que la pression du lit d'adsorption rempli par circulation en sens inverse soit comprise entre environ 50 et 100 % de la pression

d'adsorption,

f) la mise supplémentaire sous pression du premier lit d'adsorption par circulation du mélange gazeux à l'extrémité d'entrée du premier lit d'adsorption à une pression d'adsorption comprise entre environ 104.10^3 Pa (15 psig) et environ $3,448.10^6$ Pa (500 psig), et

g) la répétition des étapes précédentes, sous forme d'un cycle continu, avec traitement de chaque autre lit d'adsorption des divers lits d'adsorption de la même manière que le premier lit d'adsorption.

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2. Procédé selon la revendication 1, dans lequel, dans l'étape d), la mise sous pression partielle du premier lit d'adsorption est réalisée par circulation du gaz appauvri de l'extrémité de sortie d'un autre lit d'adsorption qui a juste terminé l'étape (a) à la fois vers l'extrémité d'entrée et l'extrémité de sortie du premier lit d'adsorption jusqu'à ce que la pression dans le premier lit d'adsorption soit comprise entre environ 25 et 50 % de la pression d'adsorption.

3. Procédé selon la revendication 1 ou 2, dans lequel les lits d'adsorption comprennent des tamis moléculaires à base de carbone, le mélange gazeux est l'air, et le gaz enrichi est l'azote.

4. Procédé selon l'une quelconque des revendications 1, 2 ou 3, dans lequel la pureté prédéterminée est comprise entre environ 90 et 99,9 %.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel, au cours de l'étape a), la pression d'adsorption est comprise entre environ 346.10^3 Pa (50 psig) et $3,448.10^6$ Pa (500 psig).

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel, au cours de l'étape b), la pression de l'autre lit d'adsorption, après l'étape d'égalisation de pression, est comprise entre environ 35 et 45 % de la pression d'adsorption.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel, au cours de l'étape c), le premier lit d'adsorption est évacué par l'extrémité d'entrée à une pression de désorption d'environ $6,67.10^3$ Pa (50 torr) et d'environ $33,3.10^3$ Pa (250 torr).



8. Procédé selon l'une quelconque des revendications précédentes, dans lequel, au cours de l'étape c), le premier lit d'adsorption est purgé par circulation du produit gazeux enrichi à l'extrémité de sortie du premier lit d'adsorption avec un débit de purge compris entre environ 0,01 et 2 l/cycle. 5
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la pression du premier lit d'adsorption à la fin de l'étape (e) est comprise entre environ 60 et 80 % de la pression d'adsorption. 10
10. Procédé selon l'une quelconque des revendications précédentes, dans lequel la pression du premier lit d'adsorption à la fin de l'étape f) est comprise entre environ $6,67 \cdot 10^3$ Pa (50 psig) et environ $1,38 \cdot 10^6$ Pa (200 psig). 15

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