RESOLVING GAS MIXTURES

Inventors: Gerhard Heinze, Schildgen; Reiner Sarnes, Nellingen, both of Germany

Assignees: Bayer Aktiengesellschaft, Leverkusen; J. F. Mahler, Apparate-Und Ofenbau Kommandite-Gesellschaft, Esslingen, Germany

Filed: Nov. 8, 1971
Appl. No.: 196,604

ABSTRACT

In the resolution of air containing water vapor by the pressure-variation technique wherein the air is passed successively through first and second separation zones, the water vapor being removed from the air in the first zone and the nitrogen being selectively removed from the balance of the air mixture in the second zone, the air leaving the second zone being enriched in oxygen and improvement which comprises intermittently discontinuing passage of the air the first and second zones, reducing the pressure in the first zone relative to the second zone by withdrawing air from said first zone, whereby the nitrogen adsorbed in said second zone is desorbed, passes into said first zone, replaces the water vapor therein and the now desorbed, previously adsorbed water vapor in the first zone is withdrawn from the first zone, discontinuing the reduction of pressure in said first zone, reinitiating passage of air to said first zone and from there into said second zone, and temporarily delaying the flow of air from said first zone into said second zone so that the pressure in said first zone builds up prior to buildup of pressure in said second zone. The delay of air flow can be due to a complete interruption of flow or a throttling of flow from the first to the second zone. Other gas mixtures may be similarly resolved.

10 Claims, 5 Drawing Figures
FIG. 5
RESOLVING GAS MIXTURES

The so-called pressure-variation process has recently been introduced into practice for resolving, i.e. drying and separating, gas mixtures. This adsorptive process can generally be used for separating gas mixtures whose components differ from one another in their affinity for adsorption. The pressure-variation process was proposed in particular for the production of inert gases and for dissociating air. In the following, reference is made essentially to the production of oxygen-enriched air because this process is of considerable commercial significance. However, the statements are also applicable to the separation of other gas mixtures containing water vapor.

Oxygen-enriched air is required for example for intensifying oxidation reactions in chemical processes, for use in metallurgy, for accelerating fermentative processes and for producing hot flames. The advantage of adsorptive methods for producing oxygen-enriched air is embodied in the simplicity of the processes, which are generally carried out at ambient temperature. Since no high-percentage oxygen or even liquid oxygen is formed in the plants, plants of this kind can be operated in the complete absence of danger and the safety precautions normally taken in liquid air plants are unnecessary. By virtue of the simplicity of the installations, it is also possible to build economically operating units, even down to extremely low capacities.

Installations for the adsorptive enrichment of constituents of a gas mixture on the pressure-variation principle function in the pressure range between the inlet or entry pressure \( p \) of the gas to be separated, which can be available either at atmospheric pressure or at excess pressure, and the desorption pressure \( p' \) which is produced by a vacuum pump. In the case of installations where the gases enter under excess pressure, the desorption pressure \( p' \) can also be atmospheric pressure, in other words the gas is allowed to expand to atmospheric pressure in the absence of a vacuum pump. Accordingly, pressure-variation installations can be operated in the excess pressure - normal pressure, normal pressure - vacuum or excess pressure - vacuum ranges. In installations for enriching the oxygen in air, it is preferred to operate by evacuation with a vacuum pump because the \( N_2 \)-desorption at atmospheric pressure is inadequate. Installations of this kind can consist of a single adsorption system communicating with a storage vessel, or of two or more parallel adsorption systems functioning in sequence so that a constant stream of oxygen-enriched air is obtained as the product gas. In the case of three units, the overflow, evacuation and pressure-buildup cycles follow one another in chronologic rotation.

Adsorptive enrichment processes for oxygen are based on the principle that different molecular sieve zeolites adsorb nitrogen to a greater extent than they adsorb oxygen. Since only a few percent by weight of nitrogen are adsorbed at ambient temperature, the charging cycles are so short that the nitrogen cannot be thermally desorbed. Accordingly, the zeolite is regenerated by pressure reduction, optionally combined with the application of a purge gas.

Molecular sieve zeolites only show an adequate charging capacity for nitrogen in anhydrous form. In cases where, as is normally the case, atmospheric air is used for separation, therefore, the adsorbent would gradually become saturated with water vapor so that it could not be used for separation. For this reason, one feature common to all conventional separating processes for adsorptive dissociation of air is that dried air is used. Stringent requirements are imposed on the completeness of drying because the molecular sieve zeolites used for separation are highly effective drying agents and would gradually become saturated with water even from air that has been dried by conventional techniques. For example, the equilibrium load of a calcium zeolite A with a pore width of 5 A in air with a dew point of minus 40°C still amounts to approximately 17 g of water per 100 g of anhydrous zeolite at room temperature. Accordingly, predrying of the air represents a difficult problem which hitherto has not been satisfactorily solved. More particularly, the economy of the enrichment process as a whole is largely determined by the predrying stage of the air.

The air can adequately be predried in adsorbers filled with molecular sieve zeolites which are thermally regenerated after saturation with water. Unfortunately, a drying installation of this kind with the associated regenerating apparatus is relatively complex and also has the disadvantage that a considerable, undesirable increase in the temperature of the air stream occurs during the adsorptive removal of water, especially when air at atmospheric pressure is being dried, on account of the heat of adsorption. Unfortunately, the separating efficiency of an adsorptive oxygen enrichment installation decreases with increasing temperature.

For this reason, it has already been proposed (DAS 1,259,857) to dry the air by passing it through low temperature recuperators until its water content amounts to less than 20 \( p \) mg/Nm\(^3\) (\( p \) is the pressure in kg/cm\(^2\)). However, a process of this kind can only be worked economically in cases where adsorptive oxygen enrichment is to be carried out at low temperatures of, for example, from -60°C to -100°C.

It has also been proposed (DAS 1,259,844) to have the actual oxygen enrichment installation for drying the air preceded by an independently operating, adsorption installation functioning on the pressure-variation principle which is filled with any drying agent suitable for this purpose, for example activated alumina, and which delivers the dried air to a storage vessel from which the actual separating plant is fed. Apart from the outlay it involves in terms of apparatus, a process of this kind has the disadvantage of high energy consumption because, to regenerate the drying towers, some of the previously compressed air has to be continuously vented to the atmosphere.

In an experiment which has also been described, air at a pressure of 5.3 kg/cm\(^2\) and with water content of from 3000 to 6000 ppm was processed in an oxygen-enrichment apparatus on the pressure-variation principle into an oxygen-rich product gas which only contained from 2 to 6 ppm of water. In this case, the adsorber was completely filled with molecular sieve zeolites and the entry zone acted as a drying zone, while the rest of the filling was available for the actual oxygen enrichment process. However, this basically simple arrangement gives only inadequate separation based on the energy consumed, because experience has
shown that the water-charging zone in pressure-variation systems has no sharp limitation, but runs along the adsorber in the form of a flat abatement zone and on the other hand zeolites precharged even with only a few percent of water are almost completely ineffective so far as oxygen enrichment is concerned.

Another serious disadvantage of this arrangement is that, in the event of prolonged inoperative periods, the H₂O-charge of the entry zone is distributed by diffusion throughout the entire filling of the adsorber, making it unsuitable for oxygen enrichment.

It is accordingly an object of the invention to provide a process and apparatus for resolving gas mixtures, which is economical in its energy requirements and simple to carry out.

These and other objects and advantages are realized in accordance with the present invention which relates to the resolution of a gas mixture containing water vapor and at least two additional gases by the pressure-variation technique wherein the gas mixture is passed successively through first and second separation zones, the water vapor being removed from the gas mixture in the first zone and a more readily adsorbable component being removed from the balance of the gas mixture in the second zone, the gas leaving the second zone being enriched in the non-adsorbed gaseous component relative to the initial gas mixture. In accordance with the invention the process also includes intermittently discontinuing passage of the gas mixture through the first and second zones, reducing the pressure in the first zone relative to the second zone by withdrawing gas from said first zone, whereby the gaseous component adsorbed in said second zone is desorbed, passes into said first zone, replaces the adsorbed gas therein and the now desorbed, previously adsorbed gas in the first zone is withdrawn from the first zone, discontinuing the reduction of pressure in said first zone, reinitiating passage of the gas mixture to said first zone and from there into said second zone, and temporarily delaying the flow of said gas mixture from said first zone into said second zone so that the pressure in said first zone builds up prior to build-up of pressure in said second zone.

The process according to the invention obviates the disadvantages of earlier processes and enables the oxygen content of moist air to be enriched without an appreciable energy requirement for drying. The process according to the invention can be carried out as follows for example using zeolites as adsorbents: a zeolite-filled adsorber and an adsorber filled with a drying agent are associated with one another and connected by a pipe provided with a throttle means. In the course of one complete adsorption and desorption cycle, a fairly high resistance is put up to the gas flowing through the connecting pipe in alternating directions as it flows from the drying agent to the zeolite (adsorption), at least during the period of pressure increase in the zeolite adsorber from the desorption pressure to at most the working pressure, with the throttle means more closed than open. When the gas flows in the opposite direction from the zeolite to the drying agent (desorption), a lower resistance is offered to the gas stream during the period of pressure decrease from the working pressure to the desorption pressure with the throttle means more open than closed.

In another advantageous embodiment, after regeneration of the adsorption system and resumption of the flow of gas to the first zone (zone I) the flow of gas from zone I to the second zone (zone II) is altogether interrupted, rather than being merely throttled, until the pressure in zone I approaches or reaches its normal working level.

In the process according to the invention, predrying of the air and the separation of nitrogen are carried out in a single process stage. Although the drying agent and the adsorbent for nitrogen are arranged in separate vessels, one dryer and one nitrogen adsorbent together form a unit through which the gases to be dried and enriched and, in the opposite direction, the regeneration gases flow chronologically in the same cycle. During adsorption, the moist gas enters the dryer, gives off its moisture to the drying agent and then flows through the separating column. During desorption, the gas flows through the dryer in the opposite direction from the separating column and carries the moisture previously stored there into the open.

When the moist air flows into the dryer/adsorber combination adjusted beforehand to a low desorption pressure, the throttle means arranged between the two zones I and II is substantially or completely closed so that the entry pressure p of the air is adjusted relatively quickly in the dryer, while the increase of pressure in the zeolite adsorber, by virtue of the throttle effect, only takes place after some delay. The advantage of this measure is that drying of the entry air, taken as an average over the inflow time, takes place at a higher pressure than in the absence of the throttle means. Since, at the same time as the pressure, the H₂O partial pressure is also increased accordingly, greater charging of the drying agent and hence a shorter adsorption zone are obtained. In addition, the effective rate of flow in the dryer is reduced which also improves the drying effect. During desorption, the pressure would fall more rapidly in the dryer than in the zeolite adsorber if the throttle means were substantially closed. Basically, this would promote the desorption of water from the drying agent because, in the event of a rapid drop in pressure, an effectively larger quantity of regenerating gas would flow through the drying agent. On the other hand, it is actually the desorption stage, providing it is carried out by evacuation with a vacuum pump, which is the principal energy-consuming stage in oxygen enrichment processes. In order to use a minimum of energy, therefore, the flow of gas between the zones II and I is kept as free as possible from interference in the process according to the invention during the desorption stage in order to reduce flow resistances, especially for as long as the vacuum pump is functioning effectively, i.e. during the fall in pressure from the working pressure to the desorption pressure, at least from that point in time at which atmospheric pressure is approximately reached in the drying agent adsorber.

The invention will be further described with reference to the accompanying drawings, wherein:

FIG. 1 is a schematic illustration of an apparatus in accordance with the invention having a time-controlled throttled valve between first and second zones;

FIG. 2 is a similar view of another embodiment with a one-way valve in a by-pass pipe extending between the first and second zones;
FIG. 3 is a similar view of still another embodiment of valving to delay pressure build-up in the second zone;

FIG. 4 is a schematic illustration of a system comprising two banks of adsorption zones arranged in parallel, one undergoing desorption while the other is undergoing adsorption; and

FIG. 5 is a schematic illustration of a system with three banks arranged in parallel, one undergoing adsorption, one desorption and the third pressure build-up after desorption and prior to renewed adsorption.

Referring now more particularly to the drawings, in the simplest case, the variable throttle means can consist of a non-return flap which is installed in a bypass pipe to the connecting pipe as shown in FIG. 2. In the Figure, the reference I denotes the adsorber filled with drying agent while the reference II denotes the zeolite adsorber for the adsorption of N₂. The two adsorbers are connected to the regulating valve 5 through the pipe 3. The regulating valve 5 is fixedly adjusted to the required through-flow cross section. A bypass pipe 4 with the non-return valve 6 leads around the valve 5. When the gas is flowing from I to II (adsorption), the non-return valve is closed, whereas when the gases are flowing in the opposite direction (desorption) it is automatically opened so that the total cross-sectional area of pipe for flow of gas is larger than during adsorption.

As shown in FIG. 1, however, the throttle means can also consist of an electrically or pneumatically controlled valve 5 which is accommodated in the connecting pipe 3 between the two zones. In this case, the valve is actuated, i.e. more or less widely opened, by a time-dependent regulating system. In a preferred embodiment, the throttle valve 5 is regulated directly as a function of the pressure difference between zones I and II, rather than by a time control system. When the air flow into the previously evacuated vessel in the direction from I to II, the throttle valve 5 remains less widely open until the pressure prevailing in the zeolite column II has approached the entry pressure of the air adjusted in the drying column I. This method of regulation has the advantage that any changes in the operating parameters of the installation, such as the through-

entry pressure, cycle time, pump efficiency, etc., do not necessitate readjustment of the setting of the throttle valve 5.

Another embodiment is shown in FIG. 3. A regulating valve 5 is arranged in the connecting pipe 3 between the two zones I and II, being completely closed during charging and completely open during desorption. An overflow valve is installed in the bypass pipe 4 parallel to this regulating valve, remaining initially closed during charging to produce a particularly rapid build up of pressure in the dryer I. Only after a certain pre-adjusted pressure has been reached does the overflow valve open, allowing the adsorber II to fill up while maintaining the pressure in the dryer I.

The combination of one dryer with one nitrogen adsorber according to the invention into a unit which functions in time in the adsorption cycle, and the principle of regulating the flow resistance in the connecting line between both vessels by a throttle means in the manner described above, can be applied to oxygen enrichment plants with 2, 3 or more nitrogen adsorbers. The principle of the invention is not confined to a cer-
After atmospheric pressure has been reached in the adsorber \( \text{IIa} \), the non-return flap \( \text{7a} \) opens and oxygen-rich dry product gas flows through pipe 14 to a gasometer 15. During the same switching cycle, the adsorbers \( \text{Ib} \) and \( \text{IIb} \), with the non-return flap \( \text{7b} \) closed, are evacuated through the magnetic valve \( \text{9b} \) and the pipe 17 by the vacuum pump 18 which gives off nitrogen-rich moist gas to the atmosphere. In the second switching cycle, the same operations take place with the magnetic valves \( \text{8b} \) and \( \text{9a} \) opened and the magnetic valves \( \text{8a} \) and \( \text{9b} \) closed, only the adsorption systems \( a \) and \( b \) exchanging their functions. For an average rate of flow of the entry air of 420 N-1/hour, 150 N-1/hour of dry product gas with an oxygen content of 43 percent by volume are obtained.

The vacuum reached at the end of each switching cycle in the nitrogen adsorber amounts to 105 Torr.

Despite complete saturation of the entry air with water, the indicator color of the silica gel in the dryers \( \text{Ia} \) and \( \text{lb} \) showed that, after a few hours' operation, the charging front did not move any further forwards, but remained stationary. When the non-return valves \( \text{6a} \) and \( \text{6b} \) were forcefully prevented from closing through jamming of the cones, the \( \text{H}_2\text{O} \)-charging zone moved through the dryers which were not adequate for this operational state. When the function of the non-return flaps \( \text{6a} \) and \( \text{6b} \) was restored, the water-charging zone returned again and settled at the original stationary value.

**EXAMPLE 2**

In an industrial installation comprising three adsorber units of the kind shown in Fig. 5, 113 liters (90 kg) of silica gel in bead form with so-called Blaugel as the moisture indicator were accommodated in each of the containers \( \text{Ia}, \text{b} \) and \( \text{c} \), while 190 liters (125 kg) of calcium zeolite A in bead form were accommodated in each of the containers \( \text{Ila}, \text{b} \) and \( \text{c} \). The containers \( \text{Ia}, \text{b} \) and \( \text{c} \) were used to dry the incoming atmospheric air, while the containers \( \text{IIa}, \text{b} \) and \( \text{c} \) were used for nitrogen adsorption and oxygen enrichment. As in Fig. 3, one regulating valve \( \text{5a}, \text{b} \) and \( \text{c} \) and one overflow valve \( \text{6a}, \text{b} \) and \( \text{c} \) was arranged between each drying-agent container and the associated zeolite container. The valves \( \text{7a}, \text{7b} \) and \( \text{7c} \) at the head of the zeolite containers were non-return valves. At the beginning of the cycle, the pair of containers \( \text{Ia} \) and \( \text{Ila} \) were simultaneously evacuated through the opened valves \( \text{5a} \) and \( \text{9a} \), the pipe 17 and the vacuum pump 18. Accordingly, the reduction in pressure in the containers \( \text{Ia} \) and \( \text{Ila} \) took place in the same way. The vacuum pump had a delivery of approximately 500 m³h⁻¹.

During the same period, the containers \( \text{Ib} \) and \( \text{IIb} \) which had been previously evacuated were adjusted with atmospheric air flowing in through pipe 16 and the opened valve \( \text{8b} \) from an absolute pressure of approximately 50 to 100 Torr to atmospheric pressure. The valves \( \text{5b} \) and \( \text{9b} \) were closed during this operation. The overflow valve \( \text{6b} \) was also initially closed and, as a result, caused the rapid build up of atmospheric pressure in container \( \text{Ib} \). After this pressure had been reached valve \( \text{6b} \) permitted gas to escape into container \( \text{IIb} \) so that its pressure also rose to atmospheric whereas upon valve \( \text{5b} \) could be opened for resumption of normal flow during adsorption.

Again during the same period, atmospheric air flowed through pipe 16 and the opened valve \( \text{8c} \) into the container \( \text{Ic} \) and further through the opened overflow valve \( \text{6c} \) into the zeolite container \( \text{IIc} \) and further through the opened non-return valve \( \text{7c} \) and the pipe 14 into the collecting vessel 15.

The operations described above were then repeated with the difference that the group of containers \( a \) were evacuated, the group of containers \( b \) adjusted to atmospheric pressure by the admission of air and the group of containers \( b \) traversed by air in order to give off oxygen-enriched gas to the collecting vessel 15, etc.

Approximately 22 Nm³/hr of product gas with an average oxygen content of 60 percent by volume flowed constantly through the pipe 14 into the collecting vessel 15.

In order to monitor drying, the containers \( \text{Ia}, \text{b} \) and \( \text{c} \) were provided with one transparent wall. Even after continuous operation for several weeks, it was impossible to detect any local change in the mass-transfer zone, i.e. the zone in which the Blaugel undergoes a change in color to pink, remained stationary.

It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. In the resolution of a gas mixture containing water vapor and at least two additional gases by the pressure-variation technique wherein the gas mixture is passed successively through first and second separation zones, the water vapor being removed from the gas mixture in the first zone and a more readily adsorbable component being removed from the balance of the gas mixture in the second zone, the gas leaving the second zone being enriched in the non-adsorbed gaseous component relative to the initial gas mixture, the improvement which comprises intermittently discontinuing passage of the gas mixture through the first and second zones, reducing the pressure in the first zone relative to the second zone by withdrawing gas from said first zone, whereby the gaseous component adsorbed in said second zone is desorbed, passes into said first zone, replaces the adsorbed gas therein and the now desorbed, previously adsorbed gas in the first zone is withdrawn from the first zone, discontinuing the reduction of pressure in said first zone, reinitiating passage of the gas mixture to said first zone and from there into said second zone, and temporarily delaying the flow of said gas mixture from said first zone into said second zone so that the pressure in said first zone builds up prior to build-up of pressure in said second zone.

2. The process according to claim 1, wherein the temporary delay of flow of said gas mixture from said first zone to said second zone is effected by sealing off said zones from one another until the pressure in said first zone approaches its normal working level.

3. The process according to claim 1, wherein the temporary delay of flow of said gas mixture from said first zone to said second zone is effected by throttling the flow of gas from said first zone to said second zone until the pressure in said first zone approaches its normal working level.
4. The process according to claim 1, wherein the gas mixture is supplied to said first zone during adsorption at a positive pressure up to about 15 atmospheres, the gas desorbed in said first zone being withdrawn therefrom at about atmospheric pressure.

5. The process according to claim 1, wherein the gas mixture is supplied to said first zone during adsorption at about atmospheric pressure, the gas desorbed in said first zone being withdrawn therefrom by a vacuum.

6. The process according to claim 1, wherein the gas mixture is supplied to said first zone during adsorption at a positive pressure up to about 15 atmospheres, the gas desorbed in said first zone being withdrawn therefrom by a vacuum.

7. The process according to claim 1, wherein the temporary delay of flow of said gas mixture from said first zone to said second zone is discontinued when the pressure in said first zone reaches a predetermined level.

8. The process according to claim 1, wherein the temporary delay of flow of said gas mixture from said first zone to said second zone is discontinued after a predetermined time interval.

9. The process according to claim 1, wherein said gas mixture is air.

10. The process according to claim 1, wherein said gas mixture contains carbon dioxide and a selective adsorbent therefor is located in said second zone for its removal.

11. The process according to claim 1, wherein said gas mixture is air and a selective adsorbent therefor is located in said second zone for its removal.

12. The process according to claim 1, wherein said gas mixture contains carbon dioxide and a selective adsorbent therefor is located in said second zone for its removal.

13. The process according to claim 1, wherein said gas mixture contains carbon dioxide and a selective adsorbent therefor is located in said second zone for its removal.

14. The process according to claim 1, wherein said gas mixture contains carbon dioxide and a selective adsorbent therefor is located in said second zone for its removal.

15. The process according to claim 1, wherein said gas mixture contains carbon dioxide and a selective adsorbent therefor is located in said second zone for its removal.

16. The process according to claim 1, wherein said gas mixture contains carbon dioxide and a selective adsorbent therefor is located in said second zone for its removal.