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REVIEW

Pressure Swing Adsorption: A Review of UK Patent Literature

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Abstract

This paper contains a review of the United Kingdom (UK) patent literature concerned with pressure swing adsorption (PSA) processes published between 1972 and 1984. The process variables that influence the design and operation of a PSA plant are discussed, and typical PSA processes are described. The ideas contained in several new patent applications are also discussed. A comprehensive reference source is included.

INTRODUCTION

A review of separation and purification methods using zeolite molecular sieves (ZMS) was presented by Landolt and Kerr (*1*). This paper contained a comprehensive listing of United States patents published between 1957 and 1972, under the separate headings of Separation, Purification, and Treating. Also presented was a bibliography of published literature between 1953 and 1972. A more recent review of published adsorption data has been presented by Ray (*2*).

A large number of patents are granted annually in both the United States and the UK. For adsorption processes, these patents contain a vast amount of scientific and process data. However, the usefulness of published patents is often not fully exploited by academic researchers (although this is generally not true of company research engineers). This situation probably arises because of the way in which information is

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presented in patents and the time required to locate relevant patents (there is no annual patent index equivalent to the *Engineering Index*).

This author has performed a survey and evaluation of the UK patent literature published between 1972 and 1984, details of which are presented in this paper. This survey has been confined mainly to pressure swing adsorption (PSA) processes, excluding patents for the manufacture or "tailoring" of special zeolites and related materials.

The patents that are included and reviewed later in this paper are categorized according to the number of adsorbent beds required in the process, i.e., 2, 3, 4, or more beds. The number of beds is chosen as the main distinguishing feature because it usually determines the complexity of the process and, hence, the construction and operating costs. Many process cycles can be used to perform different gas separations after appropriate modifications or by using relevant operating procedures, although the patent may contain specific examples or be described in terms of one particular or common application, e.g., air separation.

In the UK, the majority of PSA patents are held by BOC Ltd. (formerly BOC International Ltd., and previously the British Oxygen Co. Ltd.). In the United States, several large companies are active in this field, e.g., Union Carbide Corporation and W R Grace & Co. Several of the UK patents reviewed here are held by companies operating in the United States, Europe, and Japan, in order to provide patent protection in other countries. Surveying the list of UK patents presented in the Reference section, it is clear that few UK companies are active in this field. Only two UK-based companies have obtained patents relating to the design of "at-home" medical oxygen generators (*18, 84*), even though this represents a large potential market in the UK and is a growth sales area in the United States.

A review of the United States patent literature for the last 10 years would be a useful reference source for academic researchers and design engineers.

PSA PROCESS VARIABLES

Pressure swing adsorption is a process used for the separation of the gases in a mixture, or the purification of a gas mixture by removal of gaseous impurities. Processes using solid adsorbents are well known; the feed gas is passed through a bed of adsorbent contained inside a vessel and one or more components of the mixture are preferentially adsorbed. Unadsorbed gases flow out of the adsorbent vessel. Eventually the

adsorbent bed becomes saturated with one or more of the adsorbed gases and the flow of the gas mixture is stopped.

The adsorbent bed must then be regenerated, typically either by evacuation, controlled pressure release, or by passing a gas which is not adsorbed through the bed so that adsorbed gases are desorbed. If the desorption (regeneration) pressure is substantially different from the adsorption (operating) pressure, then this is known as a PSA process. If substantial temperature differences occur between the adsorption and desorption stages, then the process is known as a temperature swing adsorption process.

The successful design and operation of PSA separation equipment requires a full specification of the condition of the gas mixture to be treated, as well as consideration of the operating variables which are possible. The condition of the feed gas and any requirements for the product (and waste) gas provide constraints on the design of a suitable plant.

Subsequent discussion will be concerned with the process variables to be considered in the design of a PSA plant, and the alternatives available to the design engineer.

(1) Separation or Purification?

The distinction between separation and purification is arbitrary, but the following can be taken as a guide.

Bulk separations are those where the gas to be obtained as a product has a concentration between 20 and 80% in the feed mixture, e.g., air separation for either an oxygen- or nitrogen-rich product.

Gas purification involves the removal of a second gaseous component of between 5 and 20% concentration. Some purification processes remove much lower levels of impurities, e.g., air drying.

Adsorbent beds for purification applications typically operate for several hours (or even days) before regeneration is required. However, bulk separations usually have shorter adsorption cycle times, e.g., 30 s to 5 min, before the adsorbent becomes saturated and breakthrough of "impurity" occurs. Bed regeneration is then effected.

(2) Which Component Is Adsorbed?

The choice and availability of an adsorbent determines which of the components in a gas mixture will be adsorbed. The use of a zeolite molecular sieve (ZMS) adsorbent for air separation results in either a

nonadsorbed oxygen product which passes through the adsorbent bed or an adsorbed nitrogen product which is obtained during subsequent bed regeneration. Because argon is not adsorbed by ZMS 5A, the maximum purity that can be obtained is approximately 95% oxygen, although 98 to 99% nitrogen can be achieved. It would be preferable to use a sieving material that preferentially adsorbs the minor component in the feed gas; in the above example, oxygen from air. A carbon molecular sieve (CMS) has been developed with this ability (*24, 58*) but it is not widely available. Processes utilizing both ZMS and CMS to produce very high purity oxygen or nitrogen from air have been developed (*20, 27*), and details are given later in this paper.

The gases adsorbed by a particular adsorbent and the effectiveness of the sieving property depend upon the pore diameter, the chemical nature of the adsorbent, and the types of gases to be separated. Although oxygen and nitrogen molecules have a similar atomic diameter, a good separation can be achieved using either 5A sieve or similar adsorbent materials (*2, 3*).

(3) Impurities

The presence of impurities in a gas mixture, e.g., water vapor or carbon dioxide, can seriously reduce the adsorption capacity of a sieve. This is especially true if the impurities cannot be readily desorbed. The presence of nonadsorbed components can act to reduce the purity of a nonadsorbed product gas obtained from a PSA process (e.g., argon in air, previously quoted). Not all impurities are adsorbed to the same degree; a process where selectively desorbed species act as a purge for components lower down in a bed has been developed (*57*).

(4) Type of Adsorbent

Various materials are available that have been used as adsorbents. Some of these are naturally occurring minerals, e.g., mordenite, others are manufactured for special purposes, e.g., Zeolon, activated carbon. The selection of a particular adsorbent depends upon the following factors.

(a) The separating or sieving capability for the species comprising the gas mixture.
(b) The adsorption capacity of the sieve (volume of gas per mass of adsorbent).

(c) The rate of adsorption, e.g., the conditions required in the PSA plant and the degree of equilibrium achieved.
(d) The degree of saturation to be achieved by the adsorbent before regeneration. For gas purification this is usually low, but for bulk separations the entire bed may need to become saturated.

Materials that are commonly used and their typical applications are:

Silica gel and alumina for air drying.
Activated carbon and ZMS 3A for odor removal, e.g., H_2S, NH_3, NO_x.
ZMS 4A, 5A, and CMS for air separation.
ZMS 3A and 4A for hydrogen purification.
ZMS 5A, 10X, and 13X for separation of higher paraffins.

(5) Number of Adsorbent Vessels

The number of beds required in an adsorption plant depends mainly upon the product gas specification. The more beds that are required, the higher the capital cost of the plant, i.e., extra valves, pipework and vessels, the operating cost, i.e., more sophisticated control features, and the cost of start-up and construction. It is preferable to keep the adsorbent beds to the minimum size required for satisfactory plant operation, especially for applications where space requirements are restricted, e.g., oxygen-production units for medical use in the home (*18, 63, 84*).

In general, the more beds that are incorporated into a plant, the better utilization of low purity gas fractions that can be achieved and the more versatile the operation. An optimum balance should be achieved between reducing costs and the efficiency of operating procedures.

The number of beds required will depend upon the specification for the product gas to be produced by the plant. This specification is often for either a constant product purity (within narrow limits) or a constant flow rate of gas (at constant pressure), perhaps with some purity fluctuations being acceptable. In some cases the use of the product gas may require that it is supplied at a flow rate and purity which are both essentially free of major fluctuations. Most of the patents which comply with this latter specification require at least three adsorbent beds, a typical cycle of operations being:

Bed 1: Feed gas and adsorption.
Bed 2: Regeneration of saturated bed (desorption).
Bed 3: Repressurization of regenerated bed.

Many patents have been published that describe this type of cyclical operation. Most 2-bed processes have one or more of the following features of operation:

(a) A period of reduced product purity at the start and end of adsorption.
(b) A period of reduced product flow rate, usually at the start of adsorption when the bed is not fully repressurized.
(c) A period of zero product flow rate when the two beds are interconnected, allowing gas in the bed at the end of adsorption to enter and repressurize a regenerated bed.
(d) The incorporation in the plant of a gas storage vessel for either low purity product gas (LPPG) or waste gas, to be used to repressurize a regenerated bed. This storage vessel is effectively a third "empty" bed, i.e., a storage bed containing no adsorbent. Although the cost of adsorbent is saved in this 2-bed plus storage tank process, the associated valves, pipework, and control features make it otherwise comparable in costs with a 3-bed process. Later in this paper a 2-bed process without storage tanks is described. It will produce a product gas of essentially constant flow rate and constant purity. This process also has some disadvantages (full details are given in Ref. *4*).

(6) Operating Variables

The following operating variables must be specified or taken into account when selecting a PSA process.

(a) High pressure or low pressure process. The choice will depend upon the condition (pressure) of the feed gas and the specification for the product gas, also whether the product is an adsorbed or nonadsorbed species. If the feed gas is available at a low pressure and a nonadsorbed product is required at high pressure, it will be preferable to operate a low pressure process and subsequently compress only the product gas. If the product is an adsorbed species, then it will usually be obtained at a lower pressure than the feed gas and may need to be compressed. In such a situation, the release of feed pressure can be used during a depressurization stage to desorb product gas from the bed.
(b) Regeneration. This may be achieved by either venting, usually

countercurrent (to the flow of feed gas) depressurization, and/or evacuation, and/or the use of a purge gas.
(c) Use of product gas for purging (sometimes referred to as backflushing).
(d) Use of an inert (nonfeed) gas for purging.
(e) Use of low product purity gas (LPPG) fractions for purging or repressurizing (sometimes referred to as backfilling).
(f) Use of product gas for repressurization.
(g) Recycling of some vent gas to the feedline or to be used for repressurization.

(7) Bed Design

Traditional adsorbent bed design has been for vertical beds with feed gas entering and evacuated gas leaving the bed from the base, and nonadsorbed gas leaving from the top of the bed. The use of horizontal beds has been rejected mainly because of the problems associated with filling and emptying beds in this position, and because of adsorbent settling allowing some feed gas to flow through empty channels in the beds. However, the height of vertical beds is restricted (typically 2 m) by the crushing strength of the adsorbent, unless additional bed supports are included at intermediate points within the vessel. With this limitation upon the height of a bed, large diameter vessels may be required. It may be necessary to install devices at the bed inlet which ensure satisfactory feed gas distribution through the adsorbent material.

Patents have been published relating to beds containing partitions or annular regions (*37, 44, 49, 63, 86*); descriptions of these types of features are included later in this paper. It is possible for a reversing-flow annular bed (*5, 63*) to be operated in a horizontal position; the effects of channeling then become less significant. In some cases horizontal beds offer advantages of space and installation, as well as easier maintenance and modification.

(8) Heat Effects

For many gases the temperature determines the quantity of gas adsorbed (*6, 44*). For air separation using ZMS, more nitrogen is adsorbed at lower temperatures and desorption becomes easier as the temperature rises. Heat may be released during adsorption and taken up

during desorption. In this situation it may be advantageous to utilize this heat and also arrange heat exchange between the gas streams to improve the efficiency of the adsorption process.

Some processes have been described (*37, 44, 65, 96*) which utilize heat effects for PSA; however, they are usually economic only where the feed material is at a temperature significantly above or below ambient. In general, a process comprising several separate beds cannot efficiently incorporate heat transfer between the beds and the gas streams. An annular bed design (*7*), as described in this paper, would enable better utilization of any heat effects.

(9) Miscellaneous

A wide variety of novel ideas has been reported in the patent literature. Details of some of these are included here, e.g., reciprocating piston process (*80*), fluidized bed applications (*97*), regeneration of a sieve using a pneumatic transport system (*28*).

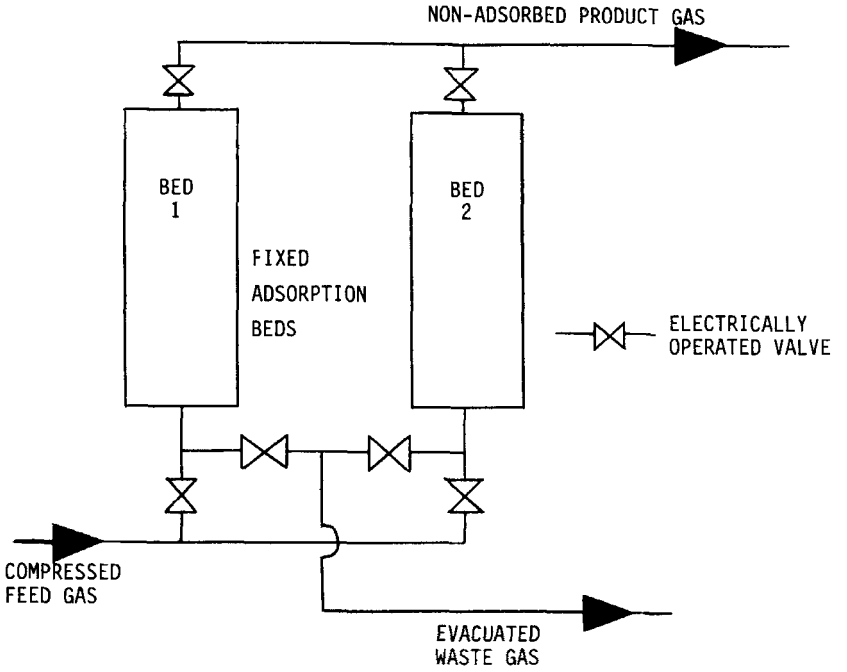
TYPICAL PSA CYCLES

The following descriptions of PSA processes relate to the separation of a gas mixture for production of a nonadsorbed product gas. With appropriate modification, most of these processes could be adapted to provide a product comprising the adsorbed species.

Simple 2-Bed Process

A typical process diagram and operating cycle are shown in Fig. 1. This would be an inefficient process in that there would be reduced product flow rate at the changeover from evacuation to adsorption (until the operating pressure is achieved). The product gas produced at the end of the adsorption cycle would be of declining purity and could be used to repressurize the regenerated bed.

The process in Fig. 1 could be improved by the addition of a product gas tank to smooth out the fluctuations in product purity and flow rate. An LPPG tank could also be incorporated, and this gas used to repressurize or purge an adsorbent bed.



SIMPLE ADSORPTION PLANT

PROCESS CYCLE

BED	CYCLE OF OPERATIONS					
1	FEED AND SELECTIVE ADSORPTION			DESORPTION (WASTE)		
	LPPG	PRODUCT	LPPG			
2	DESORPTION (WASTE)			FEED AND SELECTIVE ADSORPTION		
				LPPG	PRODUCT	LPPG

FIGURE 1.

Improved 2-Bed Process

A more efficient process providing a higher yield of product gas is shown in Fig. 2. The basis of this process is the utilization of LPPG fractions within the operating cycle, rather than allowing this gas to be either ejected as waste or diluting the product purity. Product gas produced at the beginning of the adsorption cycle (improving purity) is used to purge a bed prior to evacuation, and LPPG at the end of adsorption (declining purity) is used to repressurize an evacuated bed. In addition, a portion of the product gas is used to purge and/or repressurize (backfill) an evacuated bed.

This process will produce a high purity product but will still suffer from product flow rate fluctuations.

3-Bed Process (constant purity and flow rate)

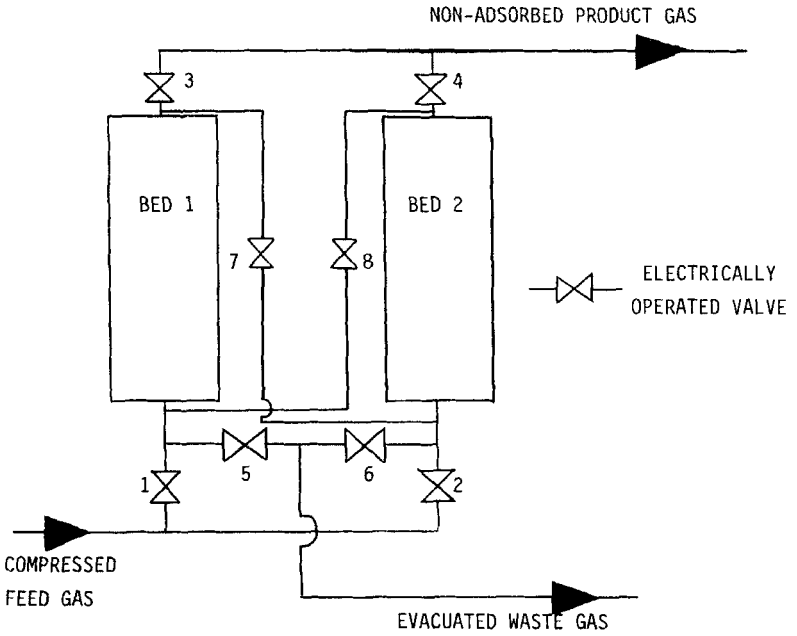
The 3-bed process shown in Fig. 3 will produce a product gas with only minor fluctuations in the product purity and flow rate. A flow regulating valve will be required on the repressurization (backfill) line to ensure a constant product flow rate from the plant. At the end of the adsorption stage, LPPG is fed to the repressurized bed and product gas is produced from this bed. Again, a flow regulating valve will be required (on the product line) because gas is fed through two beds in series with a resulting increased pressure drop. However, this part of the cycle is usually short, occupying typically less than 20% of the adsorption period.

4-Bed Process

Processes comprising 4 or more beds (*36, 40, 72*) are generally more versatile and allow better utilization of various gas fractions produced during adsorption and regeneration. However, they require higher capital cost and are more difficult and expensive to operate and control.

Combined Processes

Various processes have been developed that use a combination of adsorbents for removal of different species, e.g., high purity oxygen or nitrogen using ZMS and CMS (*20, 24, 27*), low temperature annular beds (*44*).

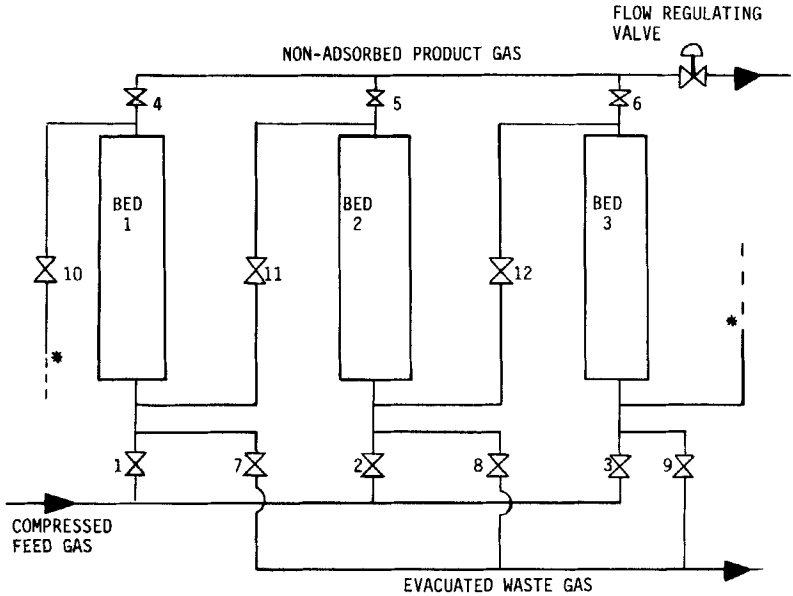


2-BED ADSORPTION PLANT

PROCESS CYCLE

BED	CYCLE OF OPERATIONS AND VALVES OPEN					
1	FEED(1) AND SELECTIVE ADSORPTION			PURGE	DESORB (5)	REPRESSURISE
	LPPG TO BED 2(3,4)	PRODUCT (3)	LPPG TO BED 2 (7)			
2	PURGE	DESORPTION (6)	REPRESSURISE	FEED(2) AND SELECTIVE ADSORPTION		
				LPPG TO BED 1(4,3)	PRODUCT (4)	LPPG TO BED 1 (8)

FIGURE 2.



3-BED ADSORPTION PLANT

PROCESS CYCLE:

BED	CYCLE OF OPERATIONS AND VALVES OPEN			
1	FEED (1) PRODUCT (4) AND REPRESSURISE BED 3 (6)	LPPG TO BED 3 (10)	DESORPTION(WASTE) (7)	GAS FROM BED 2 PRODUCT (4)
2	DESORPTION(WASTE) (8)	GAS FROM BED 3 PRODUCT (5)	FEED (2) PRODUCT (5) AND REPRESSURISE BED 1 (4)	LPPG TO BED 1 (11)
3	GAS FROM BED 1 PRODUCT (6)	FEED (3) PRODUCT (6) AND REPRESSURISE BED 2 (5)	LPPG TO BED 2 (12)	DESORPTION(WASTE) (9)

FIGURE 3.

ALTERNATIVE PSA SYSTEMS

Many new patents describing PSA processes and methods of separation are published annually. The next section provides a review of the more important UK patents over the last decade. This section summarizes the ideas presented in four new patent applications (*4, 5, 7, 8*). Two of these patent applications are concerned with PSA processes (*4, 8*), and the other two with adsorbent bed design (*5, 7*).

2-Bed PSA Processes

The first patent application (*4*) describes a 2-bed process that can provide a nonadsorbed product gas which is essentially of constant purity and constant flow rate. This is achieved without the use of any gas storage tanks. Alternative processes are illustrated in Figs. 4 and 5, and the operating cycles are given in Figs. 6 and 7. To produce a product gas without fluctuations in either its purity or flow rate, and only requiring 2 adsorbent beds, certain criteria must be fulfilled. These are:

A regenerated bed must be repressurized to the operating pressure before receiving feed gas.

LPPG fractions must be utilized within the process.

If product gas is to be used to repressurize (backfill) a regenerated bed, then some product gas must be utilized in the previous part of the cycle.

The process and its cycle of operations shown in Figs. 4 and 6 satisfy these criteria by recycling some product gas (via a compressor) to the feed line prior to the repressurization stage. Following repressurization, the LPPG fraction from the adsorbing bed is fed to the repressurized bed and product gas is then taken from this second bed. The repressurization and LPPG stages are short compared to the total adsorption period, typically between 10 and 20%.

An alternative process is shown in Fig. 5 and a cycle description is given in Fig. 7. In this situation, product is withdrawn from the adsorbing bed until LPPG is passed to the other bed. Following desorption, a bed is repressurized using feed gas. This requires that the feed gas supply can be increased for this short period, as would be possible for air separation using a flow regulating valve on the feed compressor inlet line.

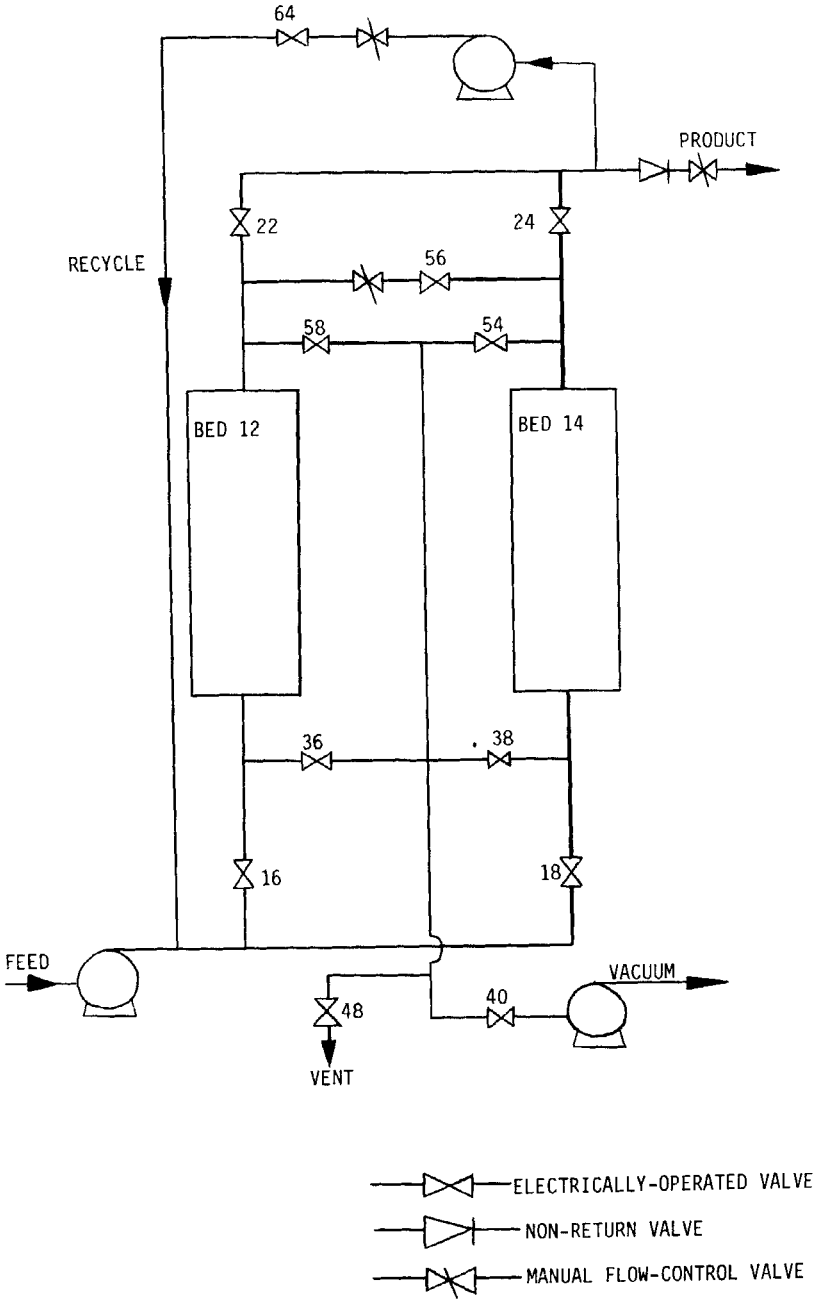


FIGURE 4.

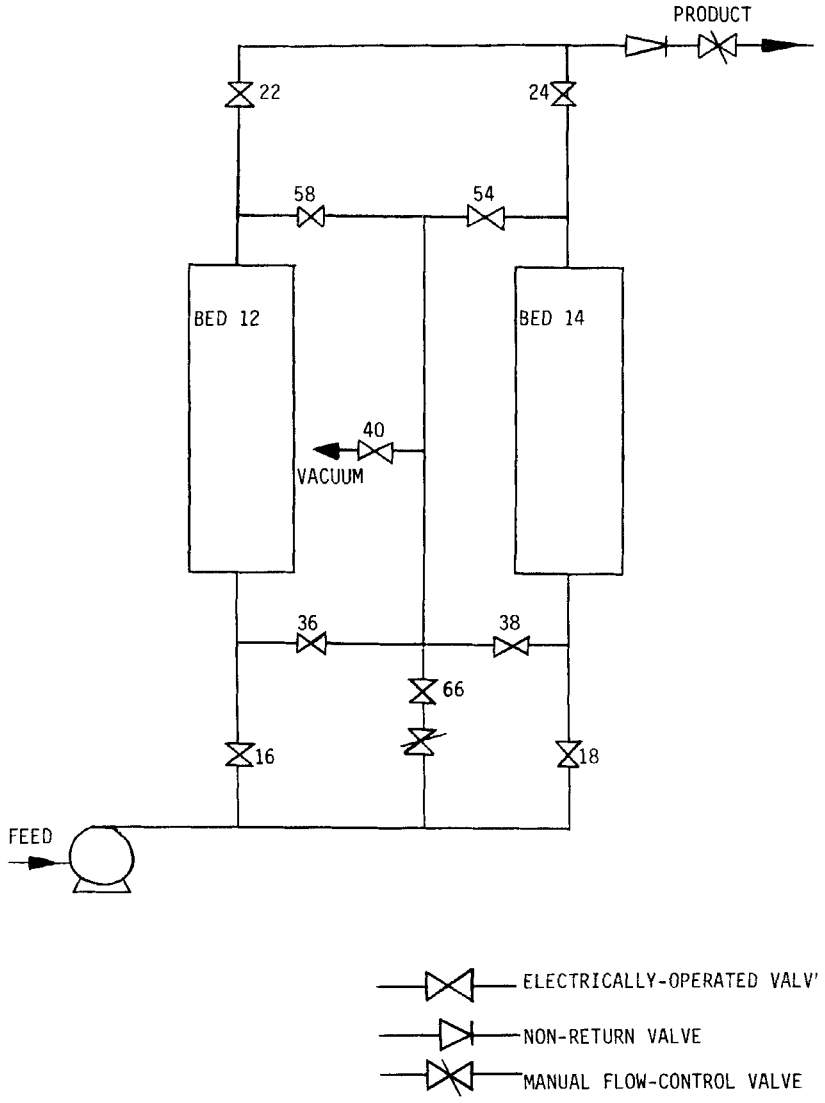


FIGURE 5.

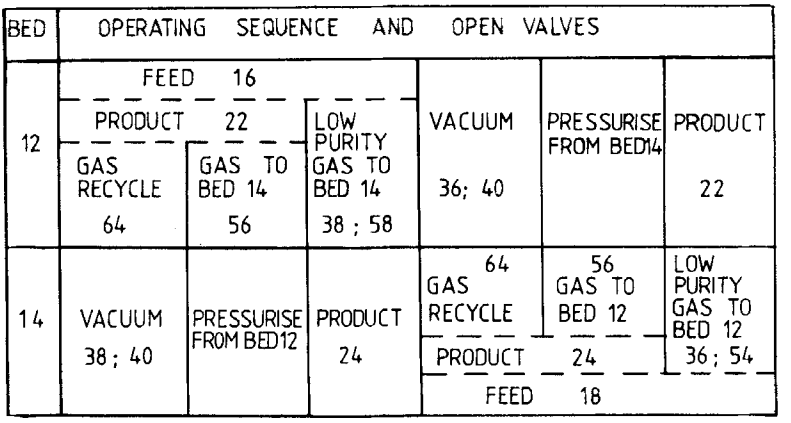


FIGURE 6.

2 Beds in Series (3 or 4-bed process)

PSA processes have been developed where two beds are operated in series during the adsorption stage (*8, 46, 71*). Feed gas enters the first bed and the first product gas (intermediate purity) leaving this bed is fed to the bottom of the second bed. Final separation occurs in the second bed and the second product gas (final purity) leaves this bed. The third adsorbent bed is being regenerated and repressurized during this sequence of operations. A typical 3-bed plant arrangement is shown in Fig. 8.

The advantage of operating two beds in series is that part of the first product gas can also be used to purge (regenerate) and/or repressurize a saturated bed, i.e., final product purity gas is not required. This cycle of operations is shown in Fig. 9.

An alternative operating cycle is shown in Fig. 10 where LPPG is used to repressurize a regenerated bed. When the product purity in the first adsorbing bed begins to decline, the exit gas is used to repressurize the regenerated bed. Feed gas and final product are taken from one bed, hence a flow regulating valve may be required because of the increase in flow rate (this part of the cycle should be very short).

A more flexible (and costly) operating procedure can be used with a 4-bed plant as shown in Fig. 11. Two possible operating cycles are shown in Figs. 12 and 13. Some operating efficiency is lost because of the periods of bed isolation, although these periods should be short compared to the adsorption cycle time. The period of bed isolation between the first and

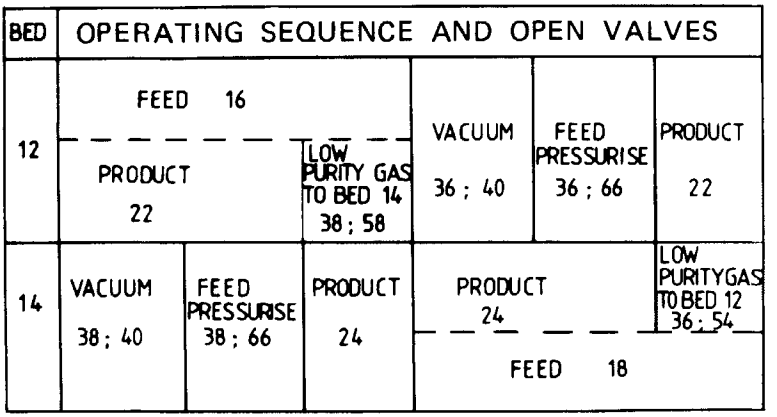


FIGURE 7.

second repressurization stages (Fig. 13) will be a period of adsorption and separation. The periods of isolation prior to evacuation can be more effectively utilized if gas fractions from a regenerating bed are recycled and used as a purge. Details of such an operation have been presented elsewhere (*8, 47, 90*).

Bed Design

Details have been published of adsorbent bed designs which provide for a more flexible operating arrangement, reduced space requirements, and/or utilization of heat effects (*5, 7, 37, 44, 49, 63, 86*).

The use of an annular partition within a bed, fixed at one end of the vessel, provides a reduced bed height as shown in Fig. 14. This also allows the use of a piping arrangement that is more easily assembled and maintained, i.e., feed, evacuation, and product lines are all connected to the same end of the bed (Fig. 14). Other advantages are that less space is required, which would be useful for "at-home" medical oxygen concentrators (*18, 84*), and both sections of a bed can be evacuated simultaneously with the addition of an extra pipeline to the outer annulus (shown dotted in Fig. 14). Channeling should be less of a problem with this type of reversing-flow bed if it is required to operate in a horizontal position. A bed could be evacuated from the nonfixed partition end, evacuating both regions of the bed simultaneously. The advantage would be more effective evacuation; however, low levels of

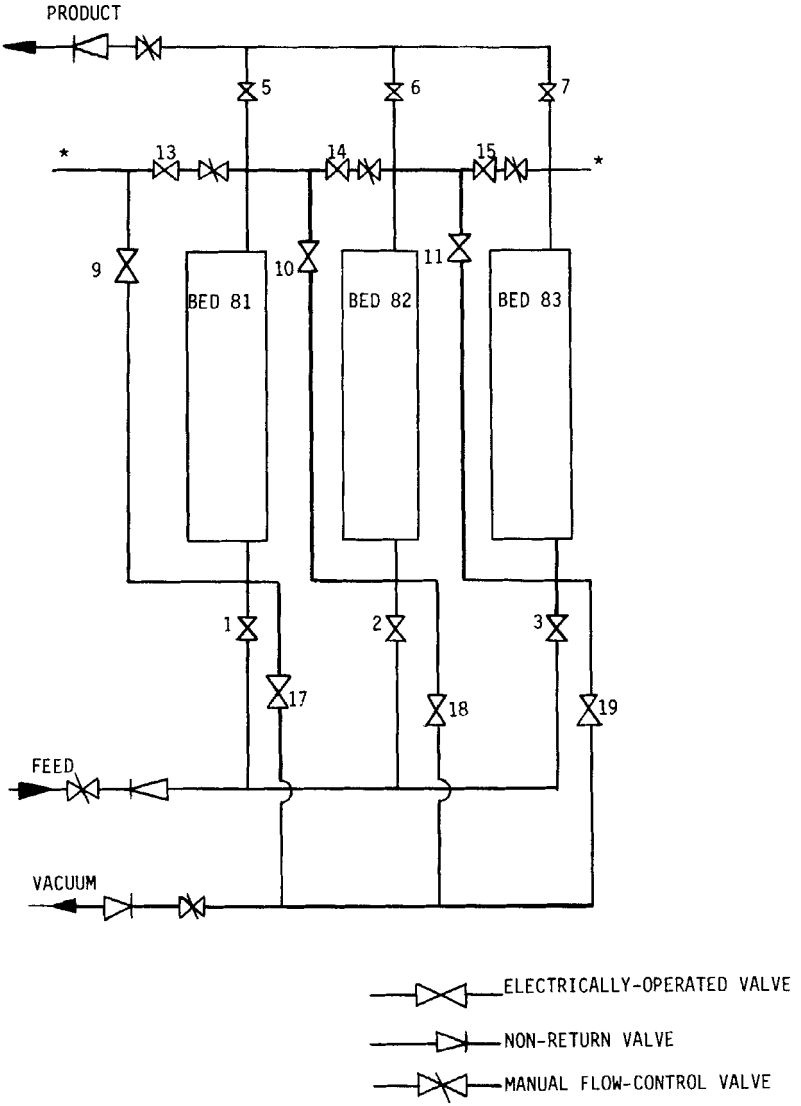


FIGURE 8.

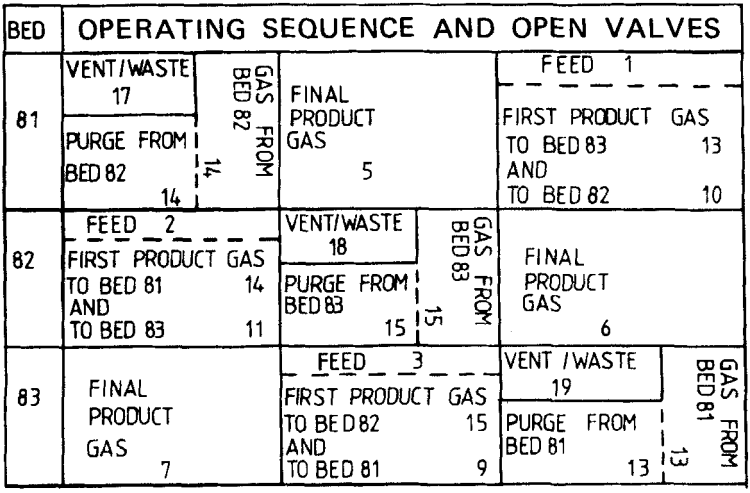


FIGURE 9.

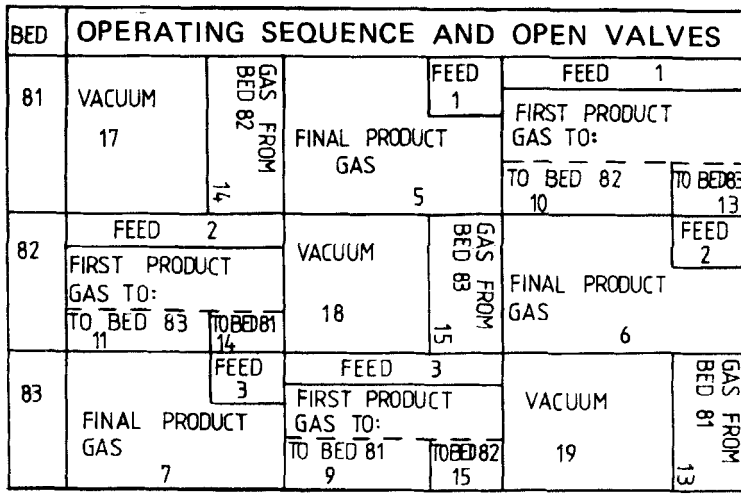


FIGURE 10.

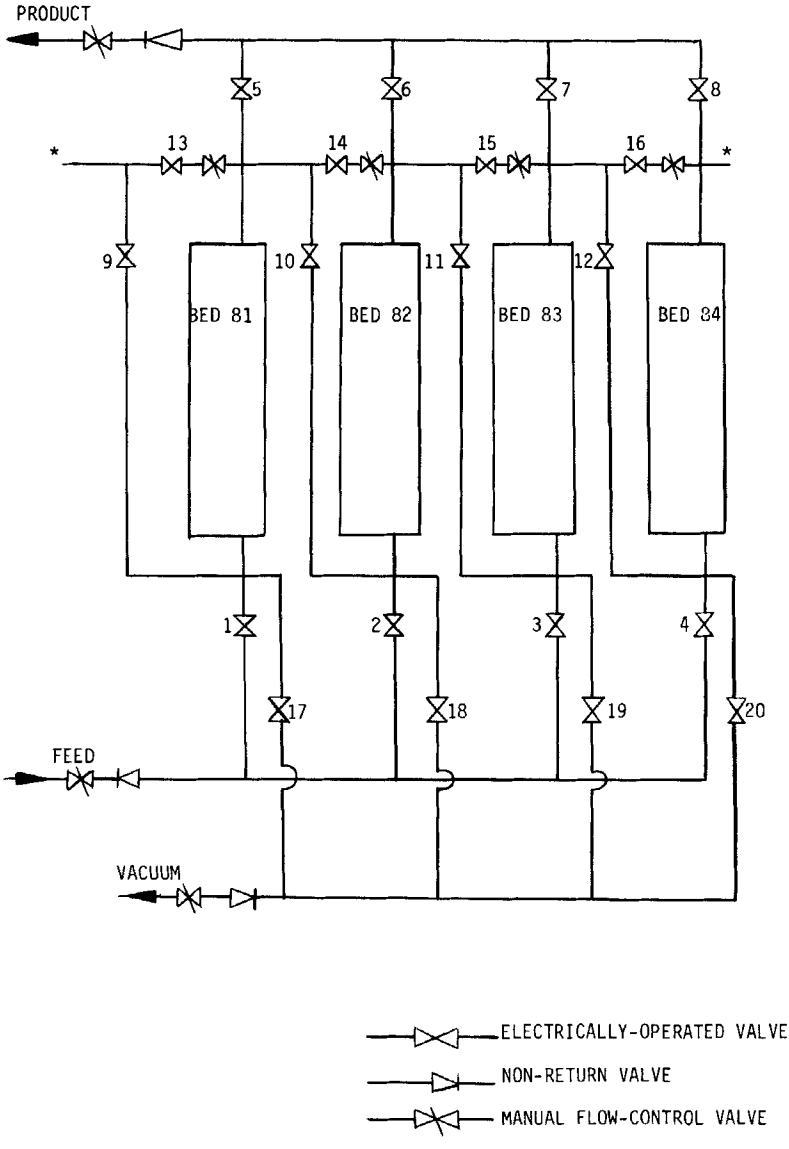


FIGURE 11.

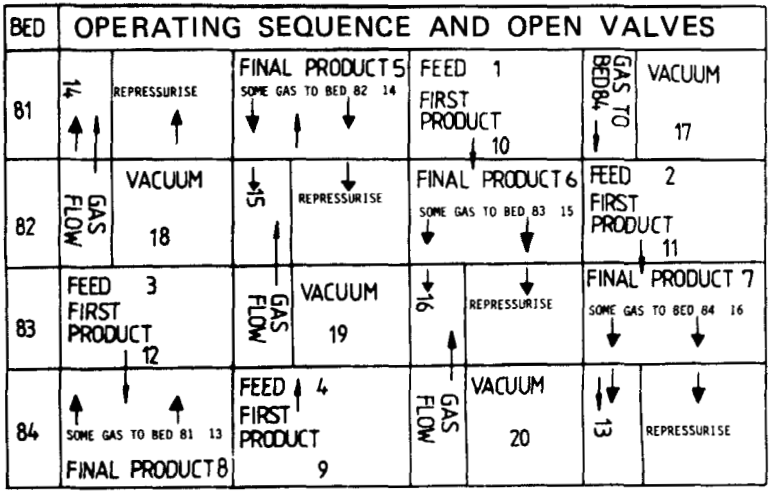


FIGURE 12.

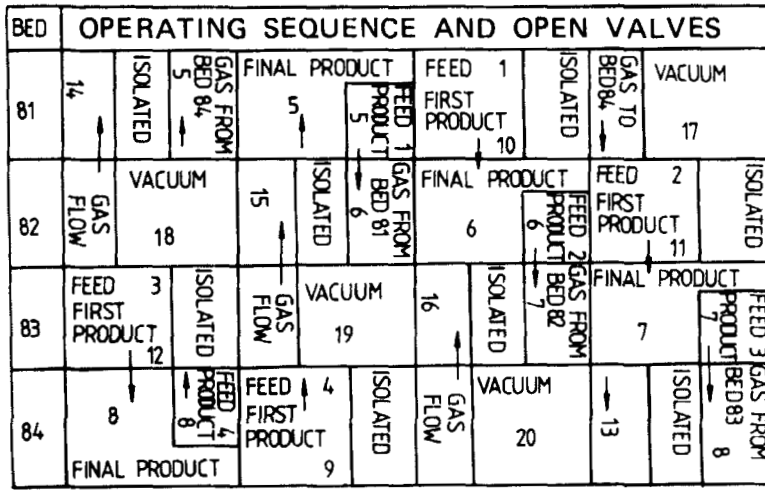


FIGURE 13.

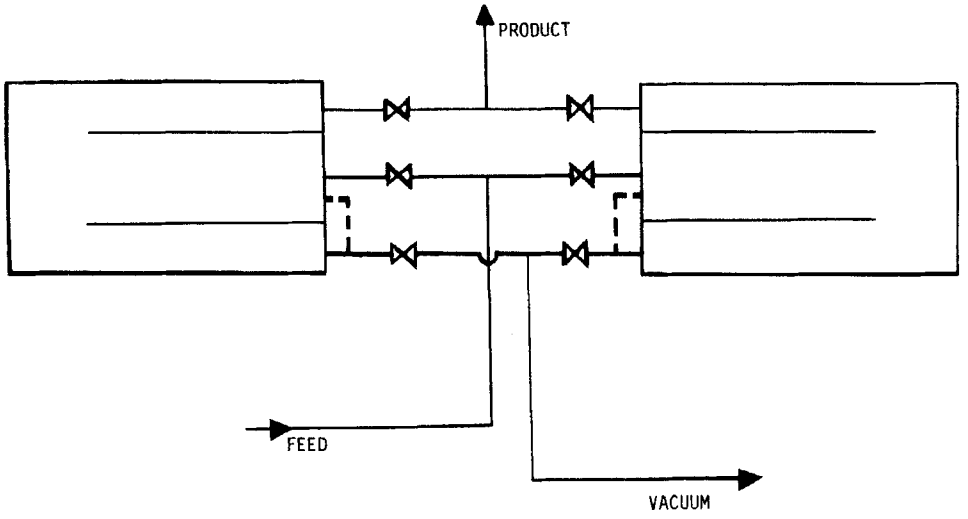


FIGURE 14.

impurities that are only adsorbed close to the feed inlet would be drawn through the remaining adsorbent bed length.

The bed design shown in Fig. 15 (*7*) also provides a compact plant arrangement and flexible piping layout. Both ends of the inner annular partition are fixed to the ends of the vessel. The main advantage is the ability for utilization of heat effects. The use of fins (high thermal conductivity) means that adsorption-desorption heat effects can be utilized between the two adsorbent regions (the outer vessel should be insulated). It also enables heat to be transferred from hot feed gas or purge gases to regions where desorption is occurring.

SUMMARY OF UK PATENT LITERATURE (1972-1984)

This section contains a review of UK patent literature published between 1972 and 1984. The survey is mainly restricted to PSA processes although some other related patents are included, e.g., temperature effects and miscellaneous applications. Copies of all UK patents are held at The Patent Office, London (*9*), from whom copies can be obtained upon payment of a fee. The *Official Journal (Patents)* is published weekly and contains details of all applications filed, specifications published, and patents granted in the UK. Abstracts of specifications published under the 1977 Patents Act (effective from 1 June 1978) are published weekly in

pamphlet form, sorted into the 25 units of the Classification Key and arranged in serial order within each unit. To perform a patent search it is necessary to determine which classifications are related to a particular subject. New editions of the Classification Key are introduced at regular intervals.

Prior to the 1977 Patents Act, a granted patent specification was assigned a seven digit designation (this terminated at UK patent specification 1 605 131). Patent applications published since 1 June 1978 have been assigned a seven digit designation suffixed by the letter A (starting at 2 000 001A). A granted specification has the same seven digits suffixed by the letter B. New patent applications that do not contain all the details required for a full specification are assigned an application number until the full specification is received (within 12 months).

The patents reviewed between 1972 and 1984 cover the designations 1 371 327 to 1 605 131, and 2 000 001 to 2 128 713. The date quoted with the patent (in the Reference section) is the date of filing for a patent application, or the date of granting for an accepted specification. The

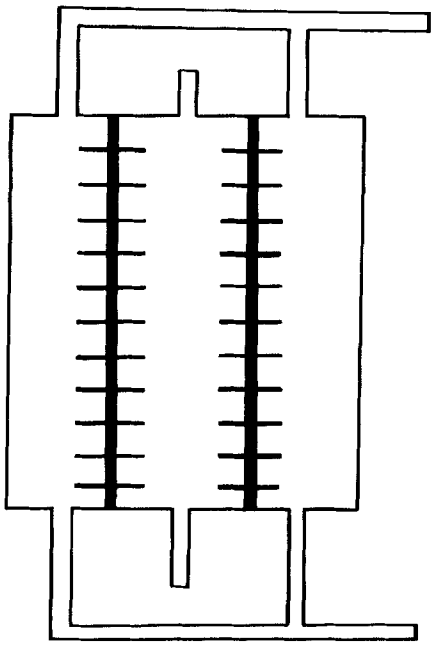


FIGURE 15.

patents reviewed here are grouped in the following categories: general PSA applications; 2-bed processes; 3-bed processes; processes using 4 or more beds; miscellaneous applications.

General PSA Applications

1 417 573. An early patent by BOC Ltd describing the use of PSA oxygen in sewage treatment. No specific details of PSA plant or its operation are given, but consideration of the application indicates a very simple adsorption-desorption process (*10*).

1 457 882. Describing a means of uprating an oxygen product (90%) obtained by PSA, using a cryogenic process (*16*).

2 003 742B. Description of a plant that can vary the oxygen supply to accommodate fluctuations in demand, e.g., an activated sludge reactor using PSA oxygen with liquid oxygen back-up supply (*26*).

2-Bed Processes

1 395 277. The cycle comprises adsorption, venting, purge with product gas, repressurization. Contains details of the control of a PSA process based upon pressures and flow rates. An example is the purification of hydrogen, producing a constant flow rate of gas (*83*).

1 413 509. A cycle comprising adsorption and hot gas purging (with venting); may also include a scavenging phase. Description is included of the use of cooling gas (*85*).

1 431 845. Pressure equalization adsorption system. Apparatus includes 2 beds and a gas storage tank. Describes a process for the separation of multicomponent gas mixtures using ZMS. Includes various stages of bed repressurization, with a primary and secondary product, i.e., oxygen-rich gas and waste gas (*53*).

1 452 242. 2 beds filled with CMS, and a storage tank. An oxygen product obtained by evacuation in three fractions. Some of the product gas (i.e., one fraction) is used for bed repressurization. The process produces an intermittent product flow rate. Data (*55*).

1 456 465. A 2-bed process, with a storage vessel containing gas to be used for repressurization. An example cited for oxygen production (*42*).

1 480 866. A process for nitrogen production using CMS. With a 2-bed process both ends of the beds are interconnected simultaneously for a pressure equalization stage. No product gas is obtained during this phase of the cycle.

A process is described using two pairs of adsorbent beds and two storage tanks. The cycle is:

First pair of beds: First stage purification, product enters first storage vessel; pressure equalization between beds; then repressurize a bed from the second storage tank.

Second pair of beds: Use gas from the first storage tank as feed while the first pair of beds are regenerated by evacuation (*56*).

1 529 701. Production of oxygen-enriched air using ZMS 5A (see also UK patent specification 2 104 409). A 2-bed process for at-home medical oxygen, using product oxygen gas to backfill a regenerated bed (*18*).

1 534 667. The purification of hydrogen by the removal of multi-component impurities; one bed is used to adsorb all impurities. Requires 2 beds for continuous operation. A CMS is used to adsorb CO_2, C_nH_m, CH_4, CO, and N_2 in stages up through the bed. During evacuation, the N_2 and CO are desorbed (higher up the bed) and then act as purge gases to desorb the other components (lower down). Examples are given for a feed gas containing approximately 55% hydrogen (*57*).

1 541 767. Nitrogen production from air using CMS. The use of a pressure equalization stage between both ends of the beds, hence a fluctuating product flow rate. Regeneration by evacuation (*58*).

1 551 732. The process experiences a period of no product flow unless a storage tank is included. A bleed of product gas is used for regeneration during evacuation (*19*).

1 559 325. An atmospheric pressure cycle producing a continuous flow of product, but some periods of reduced flow rate. Product quality gas is used to backfill a regenerated bed. No feed gas compressor required as gases are sucked through the bed, resulting in reduced power consumption. A 3-bed process is also described utilizing product gas backfill, and an LPPG fraction within the process (*21*).

1 562 636. A process for concentrating or liquefying a component in a gas mixture. Some product gas is used for purging, and an LPPG fraction is used within the process. Some desorbed gas is recycled and mixed with the feed gas. Contains examples and data, e.g., nitrogen containing 2% methyl ethyl ketone (*87*).

1 572 532. A 2-bed process with a storage tank, for oxygen production using ZMS. The cycle of operations is adsorption, pressure equalization between beds, desorption (vent and/or evacuation), purge with product gas, repressurize with product gas, pressure equalization between beds, and repressurize with feed gas (*81*).

1 586 961. A 2-bed process with a purge (effluent) gas storage tank, connected to a cryogenic process, e.g., adsorption process producing oxygen (<95%) followed by a cryogenic process to produce high purity oxygen. Nitrogen-waste gas from the cryogenic process is used to purge and regenerate the adsorbent beds. Use a storage tank for the first purging exit gas fraction (*23*).

1 593 538; 1 593 539; 1 593 540. Description of a 2-bed or 3-bed process, including a product gas storage reservoir and a purge gas storage vessel. Process includes product gas purge, LPPG storage and purging, and pressure equalization stage (between beds) (*61, 62*).

1 604 563. Uses 2 or more adsorbent beds, the operating pressure rises during adsorption (see also U.S. patents 3,636,679 and 3,738,087). Typical operating pressure is 40 psig although it can be much higher, e.g., up to 200 psig for a 3-bed process. The cycle includes pressure equalization between beds, depressurization, purging, and repressurization. Product is obtained during repressurization, hence the pressure change (*41*).

2 025 253B. Nitrogen production using CMS. Process includes pressure equalization (between both ends of the beds) and regeneration by venting and evacuation. Low and high pressure repressurization stages (slow final repressurization), hence a fluctuating product flow rate (*50*).

2 025 254B. As for patent 2 025 253B except no evacuation, variation in nitrogen product purity (*51*).

2 042 365B. Nitrogen production using CMS, no vacuum pump, and both ends of the beds are interconnected for pressure equalization, use of purge gas (*30*).

2 055 609A. The purification of natural gas by removal of CO_2, methanol, and water vapor using 2 beds in series; high pressure process (550 psig, 15°C). The first bed adsorbs water vapor and methanol, the second bed removes CO_2. Regeneration is achieved by using a purge of purified natural gas at 300°C (*70*).

2 055 610B. Nitrogen production using CMS. Regeneration by evacuation; pressure equalization between both ends of the beds. The LPPG fraction at the start of adsorption is either vented or recycled (*60*).

2 058 826B. A 2-bed or 3-bed purification process using activated carbon. Desorption by evacuation; the use of a purge and air stripping for bed regeneration (*88*).

2 066 693B. 2 beds and a product tank for oxygen production. The cycle is feed and adsorption, product purge and waste, and pressure equalization between the beds (*89*).

2 073 043A. Nitrogen production using CMS. Product storage tank and pressure equalization between both ends of the beds (*31*).

2 086 258A. Nitrogen production using CMS. Product storage tank. Can regenerate by using evacuation or just venting. Data included (*32*).

2 090 160A. A 2-bed process, mainly describing heat exchange. Use of product gas for backfilling (i.e., repressurization from the "top"). Data included (*79*).

2 091 121A. 2-bed process with a product gas storage tank. The cycle includes venting, purging, and backfilling (repressurization). A short cycle time (45 s) and lower power consumption. Data included (*33*).

2 104 409A. 2-bed process with a product gas storage tank. Does not describe a particular PSA process but is applied to the supply of "at-home" medical oxygen. Features include reduced noise level, improved design and constructional features, and annular beds (½-bed length) (*63*).

2 122 508A. At-home oxygen supply using ZMS. Uses one, two, or three pairs of beds, the number used depends upon the required product flow rate. Incorporates an analyzer alarm and operates on a 60-s cycle. Regeneration is achieved using an oxygen purge gas. Constant oxygen purity is obtained by operating more beds as a higher flow rate is required (*84*).

2 126 122A. Each bed is divided into sections; regenerate using hot gases. Utilization is made of heating and cooling effects (*77*).

2 126 917A. Removal of organic impurities such as benzene using activated carbon; two sieve layers in each bed. Use of a recycle gas stream which leaves the bed between the two layers (*78*).

2 127 710A. Separation of nitrogen and carbon monoxide (and carbon dioxide), includes a gas storage tank. The cycle is adsorption, depressurization (to the other bed), product gas purge, vacuum, repressurization (pressure equalization between beds), and feed gas repressurization. Includes data and examples (*99*).

3-Bed Processes

1 380 579. 2-, 3-, or 4-bed process. No evacuation stage, depressurization acts as desorption. With 4 beds a continuous product flow rate can be obtained. Use of a product-gas purge and pressure equalization (repressurization) stages (*34*).

1 380 580. 2-, 3-, or 4-bed process. Stages include depressurization, product purge, and repressurization (*34*).

1 424 457. 3- or 4-bed air separation process, nitrogen production using ZMS. Stages include pressure equalization, purge, and repressurization. Data included (*35*).

1 437 344. 3- or 4-bed nitrogen production process. Cycle stages are ambient pressure adsorption, evacuate (200 mmHg), air repressurization, nitrogen purge with venting, and nitrogen purging with the exit gas used as feed.

If the nitrogen purge is stopped at a high oxygen concentration in the bed (say 21%), the nitrogen product from the cycle is approximately 98% and gas recycle can be omitted. The efficiency of the purge step is inversely proportional to the purge rate. Process performance data are included in an example (*12*).

1 437 600. 3- or 4-bed process for nitrogen production (>99% purity). Features include a recycle compressor for nitrogen product purge, intermediate (bed height) feed inlet; use of three cuts (gas fractions), i.e., 40 to 75% oxygen is discarded, 21 to 40% oxygen is recycled, <21% oxygen is recycled separately (*13*).

1 439 614. Selective removal of one component in a gas mixture. Use of 3 beds in series: first bed (containing silica and ZMS 3A) removes water vapor, second bed (ZMS 5A) removes carbon dioxide, and third bed gives water vapor back to the gas. Data included in two examples (*69*).

1 440 155. 3 beds and a gas storage reservoir for purification or separation applications. Stages include venting to reservoir, bed interconnection, vent to atmosphere, and purge from reservoir. The reservoir gas is also used to increase the pressure in the other bed. Repressurization gas is introduced at an intermediate level in the bed (*67*).

1 443 973. 3 or more beds for an adsorbed product gas. The operating cycle is vacuum, air feed, and purge with product recycle. The product is passed through drying beds; these beds are regenerated by the dry oxygen waste gas (*14*).

1 449 864. 3-bed oxygen cycle. LPPG fraction used for backfilling and as second cut gas. A constant product flow rate is obtained (*15*).

1 461 569. Air separation process to obtain a nitrogen product (or for CO from a $CO-H_2$ mixture). At the end of nitrogen purging, the last exit gas is passed as feed to the other bed (adsorbing). Exit gas from the adsorbing bed (waste gas) is used to backflush an evacuated bed (*17*).

1 530 603. 2-, 3-, or 4-bed process for air separation. Utilization of the heat effects in the PSA cycle and heating of the inlet gas to achieve better adsorption (i.e., separation). Data are included, and temperature profiles in a bed (*37*).

1 530 604. 2-, 3-, or 4-bed air separation process using ZMS. Use of partitions in a bed to conduct heat, i.e., utilize the heat in the PSA cycle. Data are included (*37*).

1 533 566. At least 3 beds for SO_2 and water vapor adsorption using ZMS 4A. A hot gas purge is followed by a cooling purge (*38*).

1 537 285. Air separation for an oxygen product using 2 beds; three gas storage vessels for the gas fractions: oxygen product, nitrogen, and rinse gas. Use of product gas purge and repressurization. Data are included (*43*).

1 551 824. 2- and 3-bed processes for air separation. Use of CMS and ZMS beds in series for production of either 99% oxygen or 99% nitrogen.

For oxygen production, air is passed through CMS and an evacuated oxygen-enriched gas is passed through ZMS. A 99% oxygen product is obtained. Vent gas from the ZMS is used to regenerate the CMS bed.

For nitrogen production, air is passed through CMS and the enriched (nonadsorbed) nitrogen is fed to a ZMS bed. Pure nitrogen is obtained by evacuation. The waste oxygen from the ZMS is used to purge and repressurize the CMS bed (*20*).

1 562 595. 3-bed process for oxygen production from air. Use of a second-cut gas fraction and an evacuated nitrogen (second) product (closed-loop recirculation) (*90*).

1 574 801. 3-bed nitrogen product using ZMS. Gas fractions obtained by venting, evacuation, and recycled product purge (*22*).

1 587 485. 3-bed purification (CO_2/H_2O vapor removal) or separation (using two layers of adsorbent in the bed) process. Use of purge or vacuum for regeneration; 2 beds in series for repressurization (between the two adsorbent layers). Data are included (*48*).

1 591 798. 3-bed process for argon separation, e.g., 95% oxygen and 5% argon feed produces an argon product. Combined ZMS and CMS in each bed, cryogenic application (*24*).

1 594 454. 3-bed process using vacuum, backfilling, and a second cut gas fraction (*25*).

2 001 864B. 3-bed adsorption/desorption process for obtaining hydrogen; two-stage purification in each bed for removal of impurities. Typical cycle of vent, vacuum, and/or purge. Data are included (*59*).

2 011 272A. CMS-ZMS beds in series for obtaining high-purity oxygen (up to 99.7%) (*27*).

2 065 496B. 3-bed process with a product surge tank. Nitrogen adsorbed from air, also product nitrogen purge and regeneration (*92*).

2 089 675A. 3-bed process using an improved rapid-selective adsorbent for obtaining a higher purity of the adsorbed component. Data are given for hydrocarbons. Use of a vector (recycle) gas for purging, which may also be condensed out (*66*).

2 090 161A. 3-bed process, e.g., for air separation. Utilization of LPPG in various fractions. If no evacuation stage, backpurge with nitrogen product gas. Also use of repressurized vent gas. Data included (*79*).

2 090 162A. 3-bed process, e.g., for air separation. Use of two-stage venting and desorption, also product gas purging. Use of LPPG within the cycle. Data included (*79*).

2 109 266A. 3- or 4-bed PSA process for oxygen production. Some product gas is used to repressurize an evacuated bed (constant flow valve). Use of second cut (scavenging) gas while a bed is evacuated (*68*).

2 113 567A. 3-bed process, i.e., 2 beds and a common supplementary adsorber (bed 3); also includes a product tank. LPPG goes into bed 3; use of vacuum desorption. Data are given (*91*).

Processes Using 4 or More Beds

1 376 058. 4-bed process. Cycle is adsorption, depressurization, product purge, and product repressurization (*82*).

1 424 064. 4-bed process, i.e., 2 adsorbing and 2 desorbing, for removal of sulfur compounds. A hot gas purge (440°C) for desorption. The cycle is

high pressure adsorption, depressurization, reaction of sulfur compounds with oxygen, regeneration (440°C), bed cooling, and purging (*52*).

1 434 631. 6 beds filled with ZMS. The process is specifically designed for the separation of *n*-paraffins from a mixture with branched chain and/or cyclohydrocarbons (see also UK patents 944 441 and 1 026 116). Data are given (*73*).

1 444 231. 4-bed process (actually 2 beds in series) for PSA separations, e.g., H_2 and CH_4 purification. Includes data for the concentration profiles in a bed. While beds A and B are adsorbing, feed enters bed A and first product leaves and enters bed B. Final product from bed B is partially used to repressurize bed C and as a purge gas (expanded to low pressure) (*71*).

1 505 957. 7- to 10-bed process; 2 feed beds and three pressure equalization stages. Used for high feed gas pressure and high product purity. Data included (*36*).

1 506 161. 4-bed process, related to 1 444 231, same cycle except no purge gas (use vacuum). This cycle (or 1 444 231 for purge) can incorporate recycling of some waste (vent) gas to the feed. Examples and data are included for the purification of helium (*72*).

1 536 995. 4 pairs of beds, used for helium or hydrogen purification (see U.S. Patent 3,085,379 concerning air from a helium mixture). Cycle includes air feed (2 beds in series), part of final product used to repressurize 2 other beds in series, evacuate and waste gas is recycled through 3 beds in series to act as a scavenging purge (*47*).

1 579 549. 4-bed process used for the recovery of H_2 and N_2 from a mixture, e.g., ammonia plant purge gas. Use of an activated carbon sieve (including some data) for adsorption of NH_3, CH_4, N_2, and A.

Adsorption at 400 psig; pressure equalization (230 psig); depressurize (100 psig); pressure equalization (55 psig); depressurize (20 psig); purging (from bed depressurization); repressurize (from bed depressurization) in two stages; repressurize with feed gas (*40*).

1 579 783. Many beds (4+) and a rinse gas storage vessel. Purge desorption then evacuate, product repressurization. Data included (*45*).

2 033 777B. At least 4 beds, air separation for oxygen-rich and nitrogen fractions using ZMS. Evacuate to obtain a nitrogen product, and use a nitrogen purge. Air is passed into 2 beds in series. The main feature is a special rotary valve (*46*).

Miscellaneous Applications

1 406 178. Adsorber bed design (not process) using an annular slab of material (*86*).

1 432 132. Use of a charcoal adsorbent bed to remove odors, e.g., H_2S, from gas streams, such as the discharge from a sewage treatment plant (*11*).

1 443 197. Properties and data for a zeolite adsorbent, used to produce a high nitrogen adsorptivity (cf. oxygen). Not a process patent (*54*).

1 527 302. PSA and chromatography; use of an inert carrier gas. Mainly for the separation of *n*-paraffin/iso-paraffin mixtures. Includes examples and data (*64*).

1 529 779. A novel 1-bed process using a reciprocating piston in a chamber, acts as a compressor (improvement on U.S. patent 3,280,536) (*80*).

1 548 256. Selective adsorption of NO_x using silica gel and ZMS. Desorption effected with dry air, followed by gas absorption in a nitric acid tower (*39*).

1 551 348. Purification of gas mixtures, not describing a PSA process but temperature and pressure variations (*96*).

1 551 356; 1 551 357. Gas purification using a fluidized bed-type application (*97*).

1 553 780. Regeneration of drying beds; cycle and process control features (*93*).

1 564 464. Adsorption-absorption vapor recovery system (not describing PSA) (*95*).

1 572 968. A 2-bed process for the purification of argon by removal of oxygen and nitrogen. The process (as described) operates at 45 psia and below −250°F. Use of annular beds containing an inner layer of ZMS 4A for oxygen adsorption, and an outer layer of ZMS 5A for nitrogen adsorption. Regeneration takes about 3 to 4 h by passing nitrogen at 180°F through both beds for 3 h, followed by nitrogen at 80°F. A series of pressure–evacuation stages using feed argon is followed by pure argon at −275°F to cool the ZMS (*44*).

1 578 865. Removal of ammonia and/or amines from a gas (deodorizing). Uses an activated carbon-fluidized bed (not PSA) (*94*).

2 004 909B. A hydrocarbon separation process using ZMS followed by a water-ring pump to condense and separate the (adsorbed) *n*-paraffins. Data included (*74*).

2 006 041B. Describes bed construction for hot gas regeneration, an inner vessel with a flexible construction (not process design) (*49*).

2 018 153A. Regeneration of an adsorbent using pneumatic transfer of ZMS between 2 beds (*28*).

2 020 566A. Use of adsorbent beds for removal of condensible vapors, e.g., vinyl chloride (*29*).

2 054 403B. The use of induced temperature fluctuations to increase adsorption and desorption (*65*).

2 113 705A. Liquid-phase adsorption using ZMS and activated carbon (*75*).

2 124 103A. Process for separating and recycling NO_x gas components. Adsorption and desorption on ZMS (Zeolon 900H) with regeneration at 150°C. Feed is 0.5% NO_x, recycle is 50% NO_x, and at the end of regeneration only 1 ppm NO_x. The cycle comprises 15 min heating (no gas flow), 25 min regeneration, and 80 min adsorption (*98*).

2 126 706A. Description of a heat pump with combined adsorption and absorption (*76*).

FUTURE APPLICATIONS

The majority of the patent literature cited in this paper is concerned with either hydrogen purification or air separation, these being the original (and now traditional) applications of PSA processes. There is also a vast amount of literature published in research journals concerned with particular gas separations (*1, 2*) and mathematical modeling of the adsorption process.

It is relevant now to consider new applications of adsorption technology which will either adapt and use what is already known (in new situations), or will require new techniques to be developed.

Future applications should concentrate upon the following general priorities in order to extend the applications and improve the competitiveness of adsorption technology:

Reduce the amount of adsorbent required to effect a particular separation.

Develop separation processes with higher product recoveries (yields).
Reduce the power consumption of adsorption plants.
Develop processes or applications that can produce two (or more) industrially valuable products.

Although activated carbon has been used for many years as an adsorbent material, carbon molecular sieves are now being developed and used for industrial separations. An immediate requirement in this field is the production, in significant quantities, of these sieves with properties that have been specially "tailored" to effect particular separations for a wide variety of applications. More work also needs to be performed to obtain a better understanding of the basic adsorption process when using carbon sieves.

Major improvements are still needed in the use of solid adsorbents for pollution control applications, and for certain specific separations such as N_2/CH_4, CO_2/CH_4, and CO/N_2. Finally, future applications of adsorbents must surely include the field of biotechnology. Two examples that have been proposed (*100*) are the use of molecular sieves as supports for immobilized enzymes and the controlled release of biologically active materials from preloaded adsorbents.

CONCLUSIONS

Many processes have been developed which use adsorbents as the separation media. The majority of these processes requires three adsorbent beds (or two beds and a gas storage tank) and evacuation of the adsorbed species (or controlled pressure release for a high pressure process, with subsequent repressurization). It seems unlikely that major improvements will be achieved in process design for the traditional adsorption applications. Although more complex processes can be developed, they are invariably accompanied by increases in the costs of the plant and its control and operation.

Most new patents will probably be related to particular separation applications, which is really what is required.

REFERENCES

A reference to a UK patent (references numbered *10–99*) includes the date of granting (or date of publication of an application) and the name of the applicant (or assignee), rather than the inventor. Patents are listed here in groups according to the applicant (and in serial order within each group) in order to highlight those companies that are active in this field, and the extent of their patent cover. Cross reference is made within the paper between the groupings according to the number of beds and this reference list.

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