

# Pressure Swing Adsorption and Hydrogen Recovery Process

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## UNIVERSITY OF PETROLEUM & ENERGY STUDIES

### CERTIFICATE

This is to certify that the dissertation report on "**Pressure Swing Adsorption and Hydrogen Recovery Process**" completed and submitted to the University of Petroleum & Energy Studies, Dehradun by **Mr. Anmol Vickram Singh** in partial fulfillment of the requirement for the award of degree of **Masters of Technology (Refining and Petrochemical Engineering)**, 2005-07, is a bonafide work carried out by him under my supervision and has not been submitted for a degree elsewhere.

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**Anmol Vickram Singh**  
**M.Tech (R&PCE)**

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## 1: INTRODUCTION

Adsorption is the term used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. This is a fundamental property of matter, having its origin in the attractive forces between molecules. The force field creates a region of low potential energy near the solid surface and, as the result; the molecular density close to the surface is generally greater than in the bulk gas. Furthermore, and perhaps more importantly in a multicomponent system the composition of this surface layer generally differs from that of the bulk gas since the surface adsorbs the various components with different affinities. Adsorption may also occur from the liquid phase and may accompanied by a similar change in composition, although, in this case, there is generally little difference in molecular density between the adsorbed and fluid phases.

Most of the important applications of adsorption depend on the selectivity, i.e. the difference in the affinity of the surface for different components. As the result of this selectivity, adsorption offers, at least in principle, a relatively straightforward means of purification and a potentially useful means of bulk separation.

In general, adsorbents used in commercial adsorption process exhibit high surface areas per unit of weight (100-1000 m<sup>2</sup>/g). The commercial adsorbents which exhibit very high surface areas and which are generally used in separation process include the activated carbons, activated clays, silica gel, activated alumina, and the crystalline aluminosilicate zeolites (molecular sieves).

The design of regenerative adsorption system requires information of three specific types:

1. **Equilibrium Capacity:** How much of an adsorbate will be adsorbed under a given set of conditions.
2. **Adsorption Rate:** How fast will the adsorbate be adsorbed under these conditions.
3. **Life:** How many times can the operation be repeated.

**There are different types of adsorption process:**

1. Pressure Swing Adsorption (PSA)
2. Temperature Swing Adsorption (TSA)
3. Vacuum Swing Adsorption (VCA)
4. Rapid Pressure Swing Adsorption (RPSA)
5. Cyclic Batch Process
6. Periodic Countercurrent Process
7. Continuous Countercurrent Process
8. Simulated Moving Bed Process
9. Parametric Pumping
10. Chromatographic separation

## **2: PRESSURE SWING ADSORPTION**

A principal advantage of pressure swing cycles is that the desorbed material can be recovered directly as high purity product. With most other desorption techniques; additional downstream processing is required to separate the desorbed material from the purge fluid.

A pressure swing system can be designed to operate on relatively short cycles, on the order of 1 min to 1 hr. For these reasons a pressure swing cycle is attractive for bulk separation processes. Pure pressure swing cycles are not ordinarily used for drying and purification applications because low residual loading is not easily obtained.

Pressure swing cycles have some drawbacks. For significant amounts of desorption, a pure pressure swing cycle may require the use of a vacuum. However, the very nature of a packed bed makes the development of a high vacuum difficult. Also, vacuum equipment, operating cyclically, can be expensive and may require more operating attention than other types of regeneration equipment. An additional consideration involves control over the rate of pressure change so as to avoid particle movement.

Vacuum desorption can be used successfully in systems involving a weakly adsorbed material. Alternatively, an operating temperature level can be chosen sufficiently high so that desorption will readily occur upon a moderate reduction in pressure. Pressure swing cycles can consider for adsorbate systems when the isotherms exhibit steep slopes at relatively high adsorbate pressure levels.

### **2.1: Principle of PSA process:-**

The PSA process is based on a physical binding of gas molecules on adsorbent material, depending on:

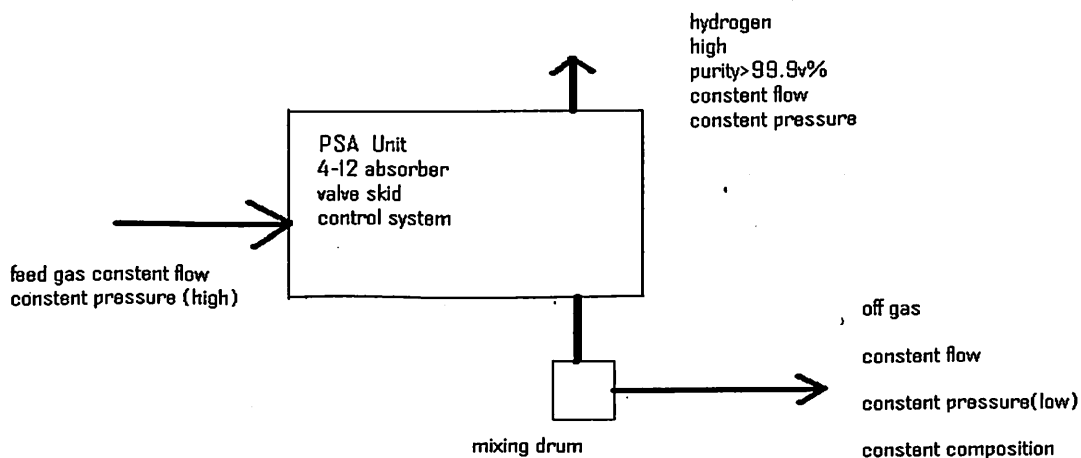
- a) Partial pressure of the gas component.
- b) Operating temperature.
- c) Type of components present in the gas.
- d) Type of the adsorbent material.

The separation effect is based on differences in binding forces of each gas components with low polarity such as hydrogen or helium, are practically non-adsorbate compared to molecules such as CO<sub>2</sub>, CO & N<sub>2</sub> and hydrocarbons. Hence most impurities for example in a hydrogen-containing stream can be selectively adsorbed by adsorbent material and high-purity hydrogen product is obtainable.

The adsorption equilibrium of a certain component on an adsorbent material determined by the partial pressure of this component and the operating temperature. Higher partial pressure and lower operating temperature increases the loading capacity of the adsorbent material and vice versa.

Adsorption of impurities is carried out at high pressure to increase the partial pressure and, therefore, the loading of the impurities on the adsorbent material. Desorption or regeneration takes place at low pressure to reduce the residual loading of the impurities as much as possible, in order to achieve high product purity, high delta loading adsorption/desorption and subsequently a high product recovery.

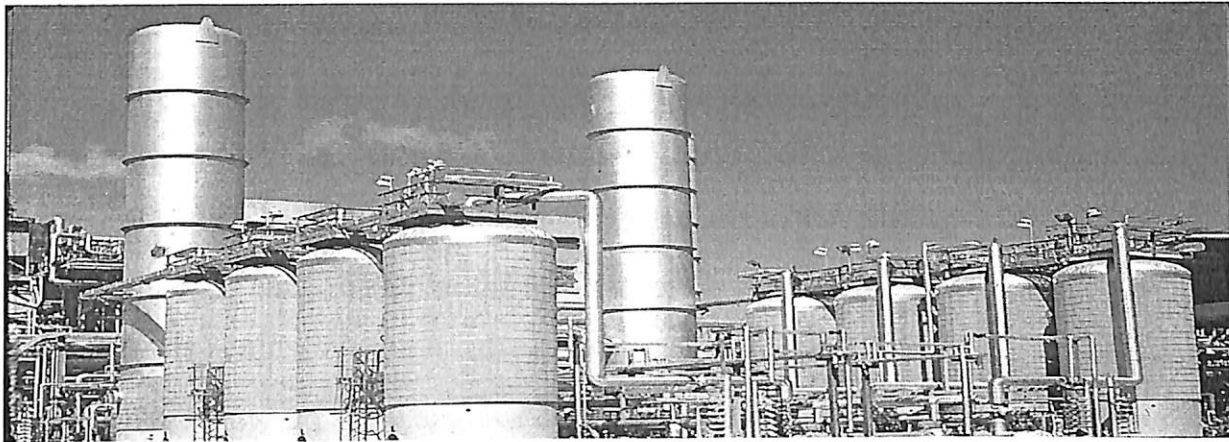
## 2.2: PSA Process:-



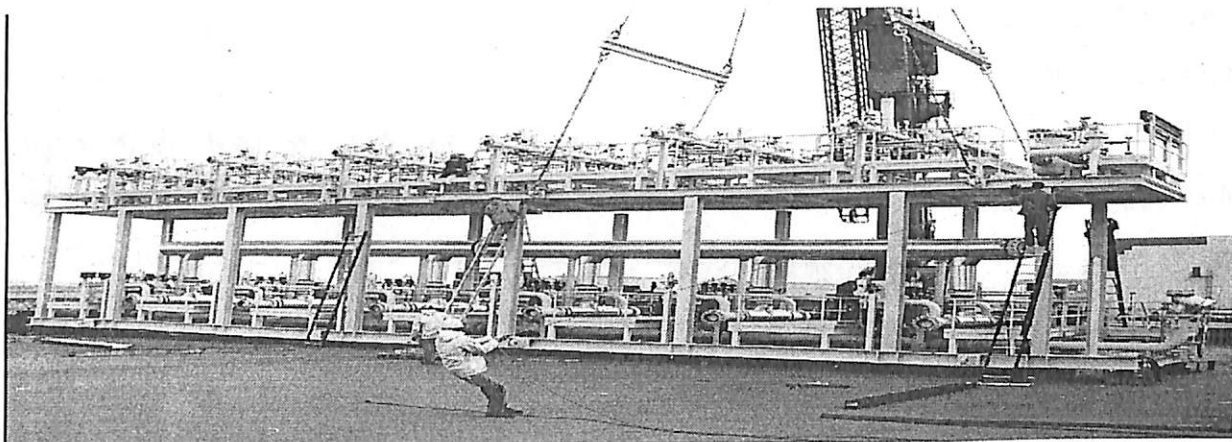
**Fig. 1 Basic Flow Diagram**

The PSA process is based on the principle that adsorbents are capable of adsorbing more impurities at a higher gas-phase partial pressure than at a lower partial pressure. The impurities are adsorbed in a fixed-bed adsorber at high pressure and then rejected as the system pressure “swings” to a lower level. Hydrogen is essentially not adsorbed. The





**Fig. 2 Installed PSA Units**



**Fig. 3 Stacked Skids**

### **2.3: Factors Affecting PSA Process:-**

- **Effect of pressure on PSA process:-**

The adsorption is normally carried out at high pressure (20-40 bars), which increases the respective partial pressure hence; the loading of the impurities on the adsorbent material also increases. Desorption or regeneration takes place at low pressure (1-4 bar), reducing the loading of the impurities adsorbed in one cycle corresponds to the difference of the adsorption loading and the desorption loading.

- **Effect of Temperature on PSA process:-**

The gas temperature is also an important parameter for the PSA process. With increasing temperature, the gradient of the adsorption isotherm decreases. This effect results in a lower differential loading, provided adsorption and desorption pressure remain constant.

The optimum gas temperature for the PSA process is in the range of 25°C to 45°C. Higher temperature is permissible but it reduces the differential loading.

Temperature below 5°C may aggravate the desorption at low pressure and can therefore result in low differential loading.

- **Effect of Impurities on PSA process: -**

The PSA system is designed for the absolute amount of impurities which can be removed from the gas which corresponds to the amount of adsorbent. If the impurity content increases, the feed gas flow rate shall be reduced correspondingly to keep the absolute amount of impurities constant. This will allow the system to produce a product gas with constant purity even with the variation in impurity contents.

### **3: HOW TO SPECIFY PRESSURE SWING ADSORPTION UNITS**

#### **3.1: Key component of PSA unit:**

1. Adsorber vessels
2. Provision of pressure swing
3. Valves, piping
4. Noise control

#### **Adsorber vessels:-**

The vessel in which adsorption and desorption take place can be horizontal, vertical or radial. The main design goal is the containment of the volume of adsorption needed to process a specific flow rate of gas.

The relationship between feed gas flow rate and adsorbent volume is generally called the specific feed rate (SFR), defined as the flow rate of gas divided by the adsorbent volume or mass.

The orientation and physical dimensions of the vessel play key roles in separation performance. Consider, for instance, adsorber vessels with the axis vertical such vessels have a height /diameter ratio greater than 0.5, typically in the range of 1 to 20. Because the economics of vessel fabrication and transportation tend to limit rolled diameters to 15-20 ft, large adsorbent volumes can not be placed in vertical vessels, and such adsorbers tend to be for small-scale use. (For example oxygen production at less than 70 tons/day)

For higher volume applications, a horizontal design may be used. In essence, the vessel is laid on its side and gasses flow perpendicular to its axis. In such cases, the bed height is less than the cross-sectional area of the vessel and the effective flow area is proportional to the true length of the vessel. Although this orientation leads to quite shallow beds, it can accommodate large volumes of adsorbent.

Radial bed designs are becoming increasingly popular as it gives opportunity to operate PSA units with high superficial velocities and short mass transfer zones. In such design

the gas flows radially between a distributor pipe running along the axis of the vertical cylinder vessel and another distributor covering its periphery. Although construction costs are higher for radial flow vessels as compared with horizontal ones, radial flow geometry may provide the lowest overall cost.

#### **Provision of Pressure Swing:-**

Depending on the nature of the gas mixture being separated, compressors or vacuum pumps are the usual choice for providing the pressure swing driving force for separation. For instance, most nitrogen generating plants require feed compression to produce a non-adsorbed product at high pressure; whereas oxygen-generating plants typically employ vacuum pumps to achieve low desorption pressures.

Compressors come in three types: centrifugal, rotary and reciprocating. The three have different pressure dynamics, which may affect upstream or downstream processing within the PSA plant. Furthermore, some adsorbents or feed gases can not tolerate the small amounts of contamination that may come from lubricated compressors, so it may be necessary to specify a non-lubricated design.

#### **Valves, piping:-**

Valves are used in several types of service within a PSA unit, such as flow control, pressure control, relief and isolation. Especially critical are the switching valves, which alternate the direction of gas flow in the different steps of the adsorption cycles. Leakage rate, response time, sealing pressure and pressure drop are important factors in specifying these valves.

#### **Noise control:-**

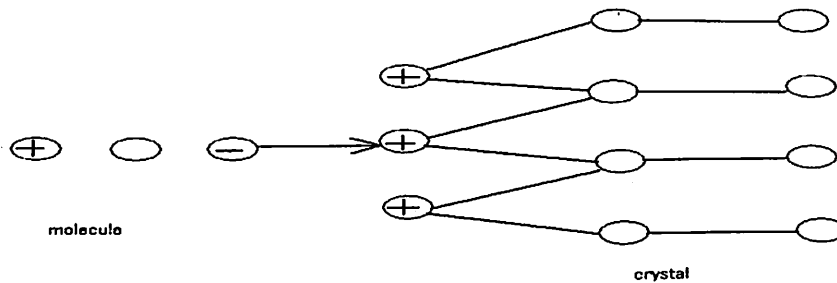
Because PSA process involves the cyclical compression and expansion of gases, they can be noisy. Typical solutions to this problem are to size the plant so as to avoid sonic velocities, to sound proof the compressors and vessels and to locate noisy equipment behind barriers or at remote distances. With air separation plants, where the waste stream is vented directly to the atmosphere, it is customary to route the waste through a silencer.

### 3.2: Process selection:-

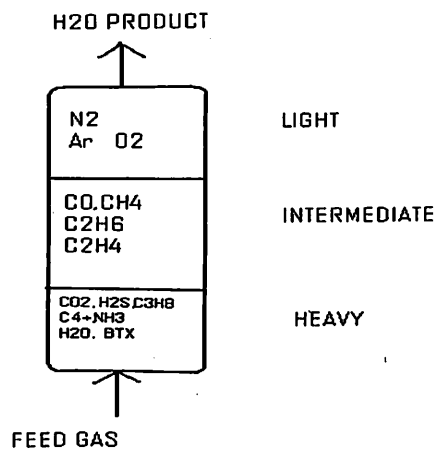
#### Fundamentals

Adsorption of gaseous components on commercial adsorbents such as **molecular sieves, silica gel, or activated carbon** is determined by several factors, of which volatility and polarity are the most important. As process conditions approach the dew point of a component, a less-volatile component is adsorbed from the gas phase. Adsorption is further aided by electrostatic forces. A strong preference by polar adsorbents is shown for polar or polarisable molecules. These molecules are attracted by the adsorptive forces of the positively charged cations contained in the crystal lattice of the adsorbent.

Highly volatile compounds with low polarity, as represented by hydrogen and helium, are essentially nonadsorbable compared with other molecules. Therefore, the PSA process performs a separation in a chromatographic fashion as shown in **Figure 5**. In general, the least strongly adsorbed impurities are the first to appear as contaminants in the hydrogen product.



**Fig. 4 Fundamentals of PSA**



**Fig. 5 Adsorption Spectrum**

### Selection of a PSA System:

Two parameters determine the choice of a PSA system: the required hydrogen recovery and the unit capacity.

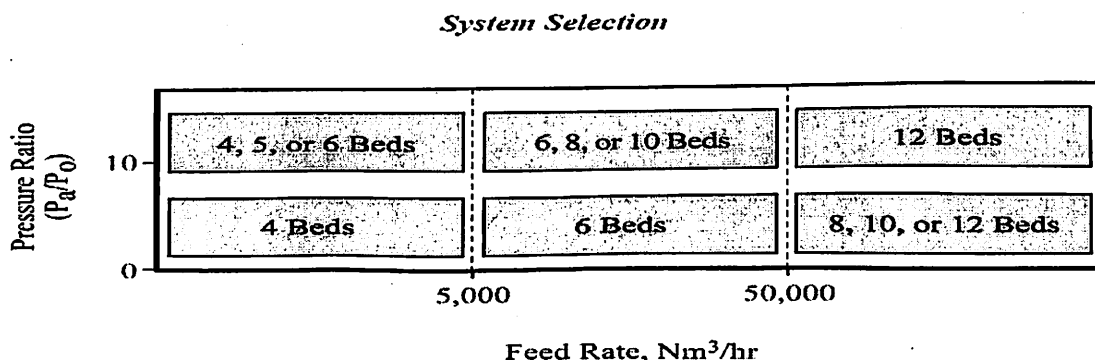
- **Small-capacity**

(Less than 5,000 Nm<sup>3</sup>/h of feed) PSA units are normally four-bed systems.

- **Large-capacity**

(Greater than 50,000 Nm<sup>3</sup>/h of feed) PSA units are normally designed for maximum hydrogen recovery, which requires three or more equalisations. Because the cost of a PSA unit increases with more pressure equalisations, small PSA units should be designed with one or two equalisations at the expense of small recovery loss.

Figure 6 can be used as a first guideline to select a PSA system based on the ratio of feed and offgas pressures over the feed gas flow rate. The PSA units for feed gas rates in the range of 5,000 to 50,000 Nm<sup>3</sup>/h require the evaluation of a number of possible systems. The investment costs have to be combined with the recovered hydrogen value to find the hydrogen recovery system with the lowest overall cost.



**Fig. 6 System Selection**

### Comparison of TSA and PSA

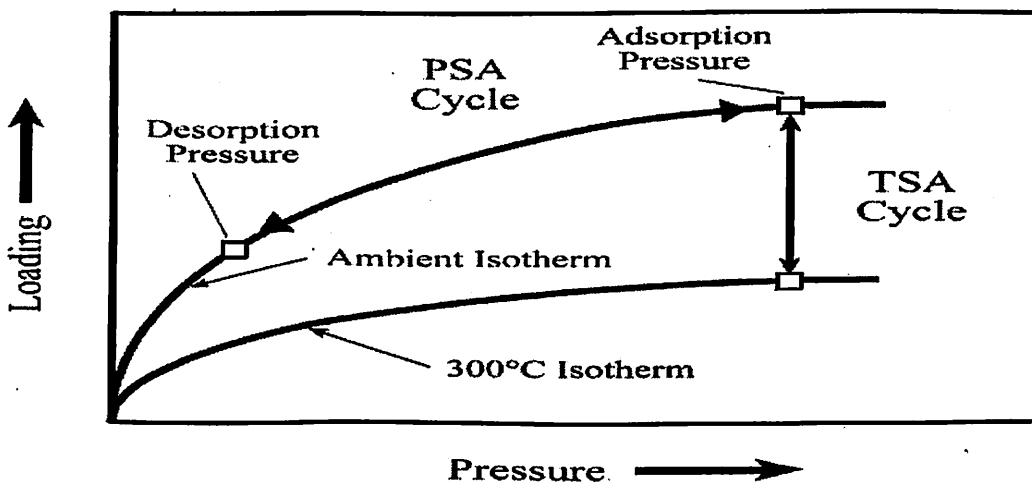
The classical method for the regeneration of an impurity-loaded adsorbent is to heat the adsorbent to high temperature by hot gas. At high temperatures the adsorbent's capacity is reduced, and impurities are desorbed.

After the adsorbent is regenerated, it must be cooled down to be ready for a new adsorption step. Although the cleaning effect of temperature-swing regeneration is effective, it has the disadvantage that the relatively slow heating and cooling process steps limit the number of cycles obtainable in any given time. For this reason, the temperature-swing process is limited to the removal of small quantities of strongly adsorbed impurities.

The removal of the adsorbed impurities in a pressure-swing adsorption system depends on reducing adsorptive capacity by lowering the pressure at essentially constant temperature. Because pressure-swing adsorption allows a much more rapid cycling, it can remove large quantities of impurities and also maintain the ability to remove impurities to low levels.

A comparison between temperature-swing and pressure-swing regeneration is graphically represented in **Figure 7**: the adsorption isotherms show the adsorbed impurity loading as a function of pressure and temperature. In a temperature-swing adsorption (TSA) cycle, the regeneration is carried out at constant pressure reducing the loading by increasing the temperature. The loading can also be reduced at constant temperature by lowering the pressure, which is the case in a pressure-swing adsorption (PSA) cycle.

### *TSA and PSA Regeneration Cycles*



**Fig. 7** TSA and PSA Regeneration Cycles

ability to completely adsorb impurities allows the production of a hydrogen product with very high (> 99.9 vol-%) purity. The basic flow scheme of the POLYBED PSA process is shown in **Figure 1**. The process operates at ambient temperature on a cyclic basis. The PSA process is a semibatch-type process that uses multiple adsorbers to provide constant feed, product, and offgas (for fuel) flows. The high-purity hydrogen product leaves the system close to the feed gas pressure. The offgas (impurities and the hydrogen losses) is available at low pressure as fuel.

In pressure swing process, the following steps occur successively.

1. Pressure buildup.
2. Adsorption of high pressure and hence production of pure component.
3. Depressurization.
4. Purging at low pressure or under vacuum.

### **Physical Description of a PSA Unit**

A PSA installation consists of four major parts:

- Adsorber vessels made from carbon steel and filled with adsorbent
- Valve and piping skid, including all valves and instrumentation, prefabricated and tested in the workshop
- Control system, which is normally located in a remote control room and contains the cycle controls
- Mixing drum to minimise the composition variation of the offgas

A packaged system approach is used. The process valves and piping are shop mounted on a steel frame and transported to the site as one or more pieces for quick and simple installation. An installed PSA unit is shown on **Figure 2**.

Recently, UOP has developed a stacked skid design to reduce the plot area requirements in particular for large POLYBED PSA units. A picture of this skid design is shown on **Figure 3**.



## PSA Process Steps

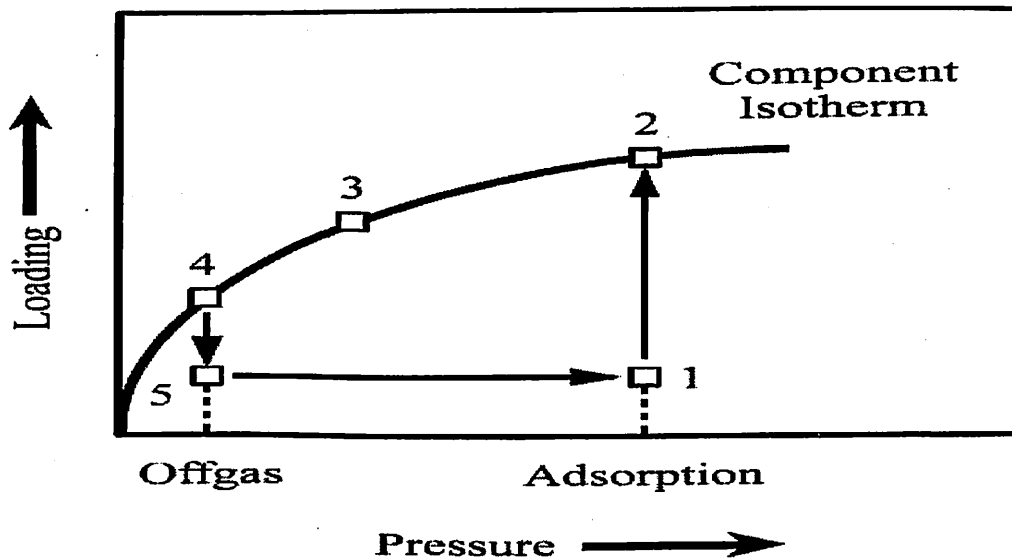
Although the PSA process is a batch process, it uses multiple adsorbers operating in a staggered sequence. Therefore, the process appears to be a continuous process at the battery limits.

A complete pressure-swing cycle consists of the following five basic steps:

- Adsorption
- Cocurrent depressurization
- Countercurrent depressurization
- Purge at low pressure
- Repressurisation

These basic steps apply to all PSA units regardless of the number of adsorber vessels (Figures 8 and 9).

### *PSA Loading as Function of Pressure*



**Fig. 8** PSA Loading as Function of Pressure

### PSA Process Steps

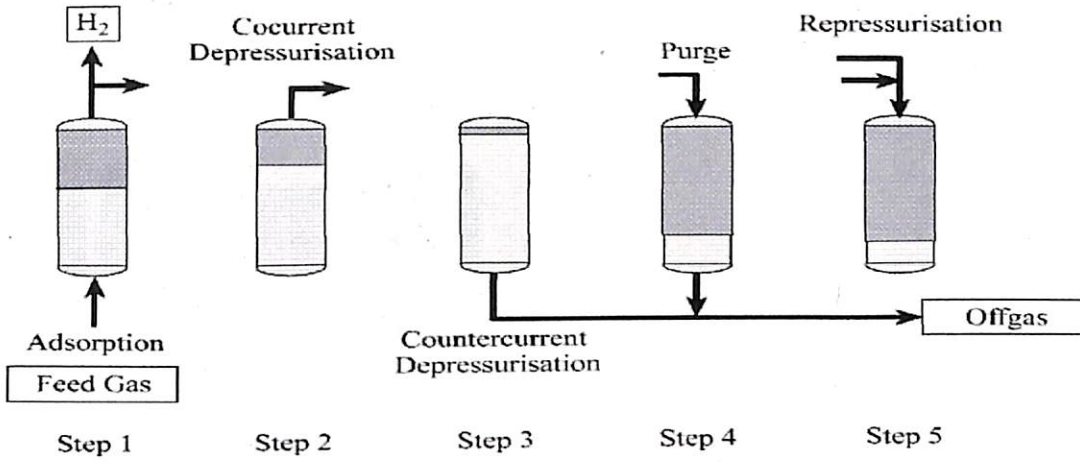
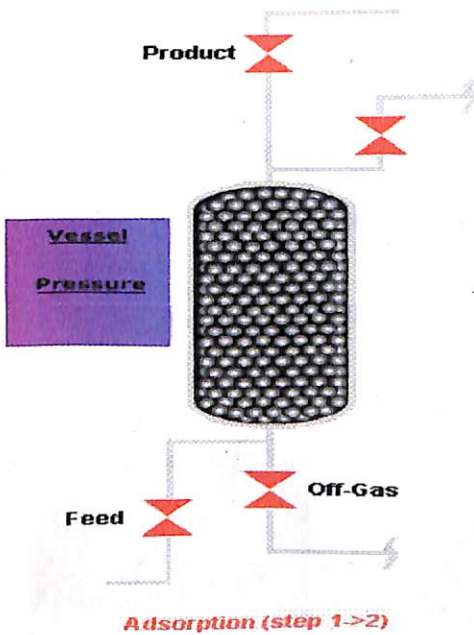


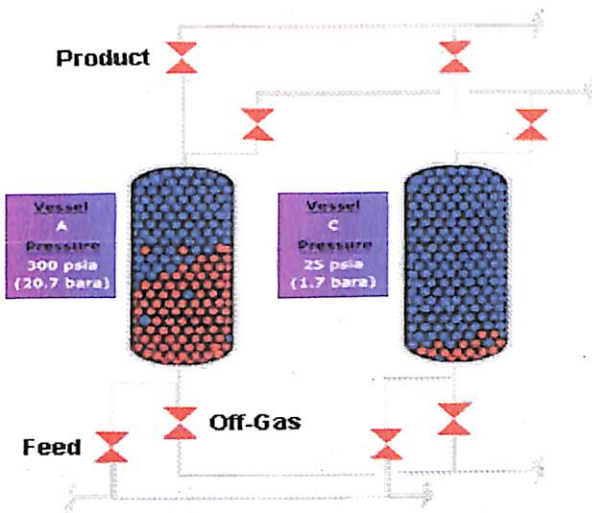
Fig. 9 PSA Process Steps

### Adsorption (Step 1 to 2)



The feed gas is introduced at the high adsorption pressure, impurities are adsorbed, and high-purity hydrogen is withdrawn as product. Flow is normally in the upward direction. When an adsorber has reached its adsorption capacity, it is taken off-line, and the feed is automatically switched to a fresh adsorber. This practice maintains constant feed and product flows.

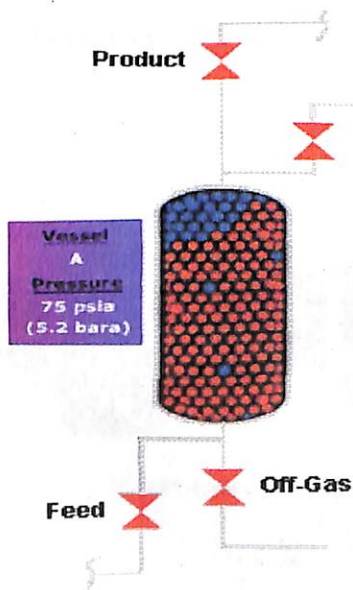
### Cocurrent depressurisation (Step 2 to 3)



**Cocurrent Depressurization (step 2->3)**

To recover the hydrogen trapped in the adsorbent void spaces in the adsorber, the adsorber is depressurized from the product side in the same direction as the feed flow (cocurrent), and high-purity hydrogen is withdrawn. This cocurrent depressurisation takes place in typically one to six discrete steps. The hydrogen is used internally in the system to repressurise (equalise) and purge other adsorbers.

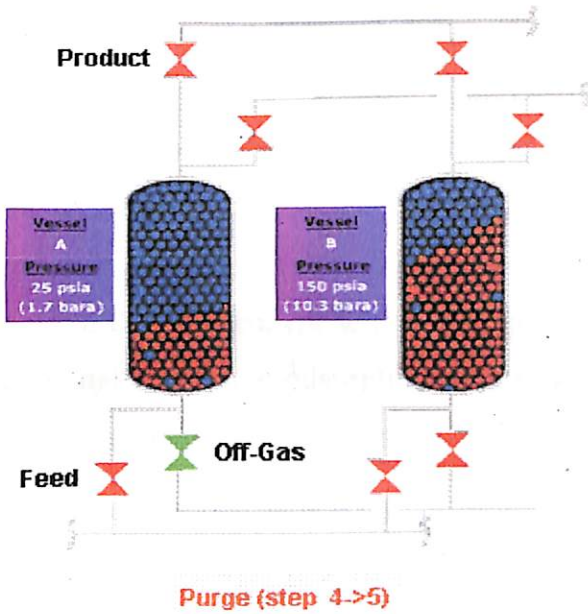
### Countercurrent depressurisation (Step 3 to 4)



**Counter-Current Depressurization (step 3->4)**

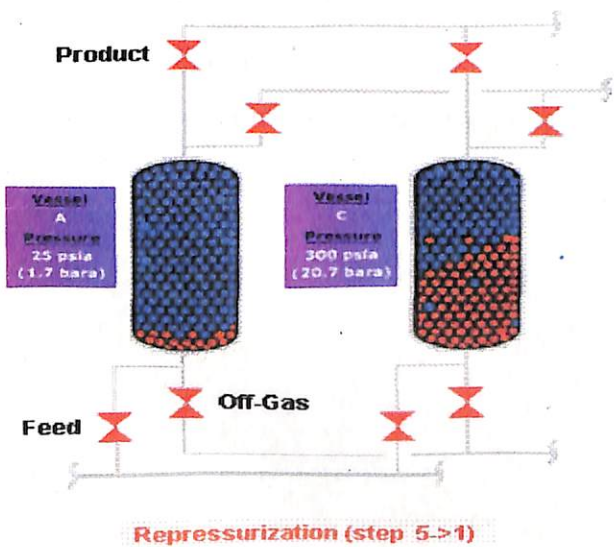
The saturated adsorber is then generated in a series of steps. After the hydrogen recovery steps are complete, the impurity fronts have migrated to the top of the adsorbent bed, and the bed has no remaining capacity. The bed is then partly regenerated by depressurising towards the feed end, and the desorbed impurities are rejected to the PSA offgas.

**Purge at low pressure (Step 4 to 5)**



The adsorbent is then purged with high-purity hydrogen (taken from another adsorber on cocurrent depressurisation) at constant offgas pressure to further regenerate the bed.

**Repressurisation (Step 5 to 1)**



The adsorber is then repressurised with hydrogen prior to being returned to the feed step. The hydrogen for repressurisation is provided from the cocurrent depressurisation (step 2 above) and with a slipstream from the hydrogen product. When the adsorber has reached the adsorption pressure, the cycle has been completed, and the adsorber is ready for the next adsorption step.

For drying and purification application usually involving contaminant concentrations less than 5 mole %, thermal -swing adsorption is generally preferred. Regeneration is relatively simple and requires purge-gas heating or bed changes and large adsorbent loading changes during the cycle. Unfortunately, the regeneration cycle in thermal-swing adsorption is apt to be inefficient and to take a long time, i.e. 8-24 hr. Low impurity concentrations lead to infrequent regeneration requirements. Thermal -swing adsorption is generally not suited for higher feed concentrations of the adsorbable component because of the bed heat capacity and long regeneration time. A non-isothermal adsorption process makes thermal-adsorption look promising, however, for dehydration of streams with water contents up to 20 wt %.

For bulk separations where the adsorbable component feed concentration is 7-50 %, pressure swing, purge gas stripping, and displacement are the preferred regeneration techniques. Pressure swing regeneration has the advantages of enabling direct recovery of a high purity product and permitting short cycle significantly with pressure at high pressure levels. Thus, it is best suited for low molecular weight, less polar molecules, e.g. low molecular weight hydrocarbons and gases such as hydrogen, helium, argon, air and natural gas. Pressure-swing regeneration can be made economical, however, even for the separation of C<sub>10</sub> and higher normal paraffins if operation is at high temperatures and pressures and desorption is at low pressures into a vacuum or compressor through a condenser.

### 3.3 Adsorbents:

#### Type of adsorbent

- **Silica gel**

Silica gel is a chemically inert, nontoxic, polar and dimensionally stable ( $< 400\text{ }^{\circ}\text{C}$ ) amorphous form of  $\text{SiO}_2$ . It is prepared by the reaction between sodium silicate and sulphuric acid, which is followed by a series of after-treatment processes such as aging, pickling, etc. These after treatment methods results in various pore size distributions on its surface.

Silica is also used for drying of process air (e.g. oxygen, natural gas etc) and adsorption of higher (polar) hydrocarbons from natural gas.

- **Zeolites**

Zeolites are natural or synthetic aluminum silicates which form a regular crystal lattice and release water at high temperature. Zeolites are polar in nature.

They are manufactured by hydrothermal synthesis of Sodium Aluminosilicate in an autoclave followed by ion exchange with certain cations ( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{++}$ , and  $\text{K}^+$ ). The channel diameter of zeolite cages usually ranges from 2 to 9 Å (200 to 900 pm). This process is followed by drying of microcrystal, which are palletized with a binder, to form macro pores and thermally activated at a temperature of  $6500\text{ }^{\circ}\text{C}$ . Zeolites are applied in drying of process air (only traces),  $\text{CO}_2$  removal from natural gas, CO removal from reforming gas and air separation. Non-polar zeolites are synthesized by de-alumination of polar zeolites. This is done by treating the zeolite with steam at elevated temperatures, greater than  $500\text{ }^{\circ}\text{C}$  ( $1000\text{ }^{\circ}\text{F}$ ). This high temperature heat treatment breaks the aluminum-oxygen bonds and the aluminum atom is expelled from the zeolite framework. Non-polar zeolites are used in non-polar organics removal

- **Activated carbon**

They are highly porous, amorphous solids consisting of microcrystallites with a graphite lattice. They are non-polar and cheap. One of their main drawbacks is that they are combustible. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, sub bituminous, and lignite), peat, wood, or nutshells (i.e.,

coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600 °C in an oxygen-deficient atmosphere that cannot support combustion.

The carbonized particles are “activated” by exposing them to an activating agent, such as steam at high temperature. The steam burns off the decomposition products from the carbonization phase to develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they are exposed to the steam. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product.

Activated carbon is used for adsorption of organic substances and non-polar adsorptive and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent. Its usefulness derives mainly from its large micropores and mesopore volumes and the resulting high surface area.

## **Property of adsorbent**

- **Advanced Adsorbents**

The adsorbents used in hydrogen PSA service are selected for their ability to remove specific feed components based on their relative adsorption strength and mass transfer characteristics. These adsorbents are provided in a compound-bed configuration, where they are loaded in layers and the impurities removed in a chromatographic manner as the gas flows through the bed of adsorbent.

The hydrogen recovery rate and cost of the PSA system are dependent on the performance achieved by the adsorbent used in the process. UOP has conducted hundreds of PSA pilot plant operations to evaluate adsorbents produced by all major worldwide adsorbent manufacturers. In the last 10 years, UOP has tested more than 200 different adsorbents and adsorbent combinations and has developed a complete database of the

performance of virtually all commercially available adsorbents. In addition, UOP has developed and commercialised new adsorbents specifically tailored to the hydrogen PSA process. This knowledge has been combined with UOP's fundamental understanding and practice of adsorbent manufacture, and the result is a family of improved PSA adsorbents.

The combination of advanced adsorbents and POLYBED PSA cycles in the design of PSA units has resulted in significant hydrogen recovery improvements and cost reductions compared to previous designs. The application of advanced adsorbents also opens the possibility of revamping existing PSA units for substantial capacity and hydrogen recovery improvements.

- **Adsorbent Lifetime**

As a result of the operation in the gas phase at ambient temperature, the adsorbents do not deactivate. The adsorbent layers in an adsorber vessel are selected to reject the heavy components at the bottom and the light components at the top. An overload, however, can transfer heavy components to the top adsorbent layers, where they can be difficult to desorb. Therefore, special precautions have to be taken for varying feed gas compositions.

The method is to select at the design phase an adsorbent split that can tolerate the highest expected quantity of heavy components. This approach may result in a marginally lower hydrogen recovery but will give protection for long adsorbent lifetime. The automatic purity control as described in the next section has been proven to reliably handle feed gas streams with varying composition. By careful design and good control methods, the adsorbent lifetime in hydrogen PSA units exceeds 20 years as demonstrated by many operating units.

### **Reliability and Fully Automatic Operation**

The fully automatic operation of a PSA unit includes automatic start-up; automatic control of capacity, product purity, and offgas; self-tuning; and zero downtime operation. These features have significance for the operation of a hydrogen plant and are discussed in more detail in this section.



- **Capacity Control**

For many years, PSA systems have incorporated automatic capacity control, which uses a feed flow signal to adjust the PSA unit's process parameters. Because the PSA adsorbent bed has a fixed capacity for impurities, operation at reduced capacity is optimised by increasing the cycle time to maintain constant product purity at varying feed rates.

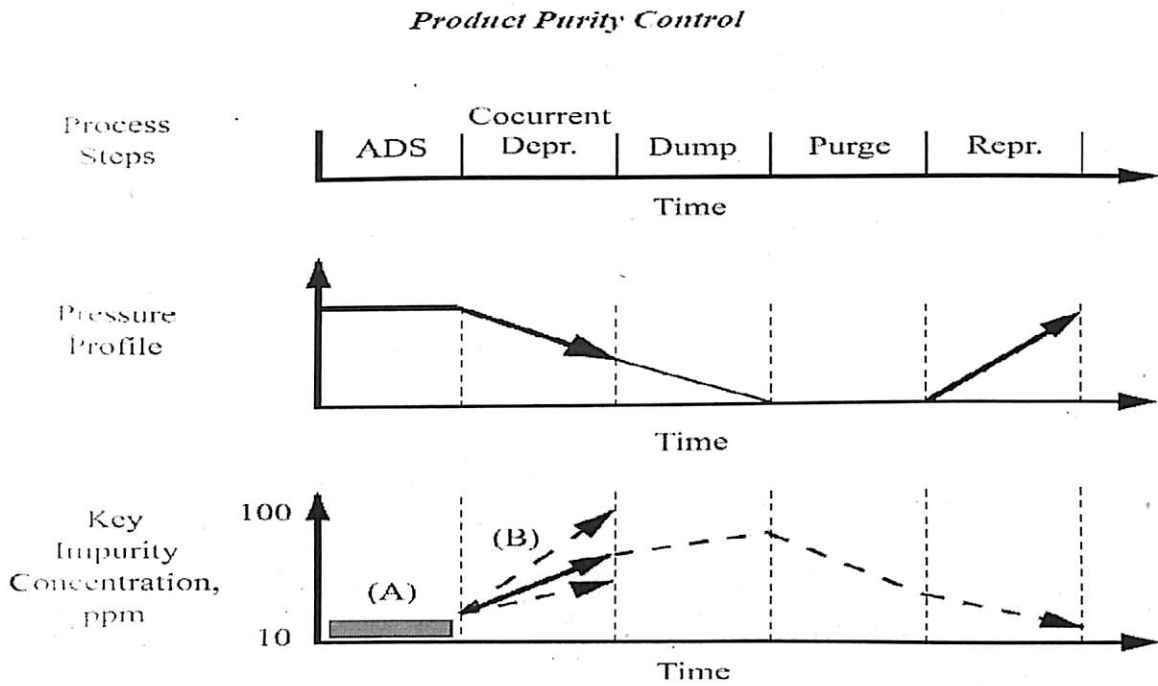
Hydrogen recovery marginally improves at turndown to 30% of the design rate. The PSA unit can be turned down further, even to 0% of the design rate, but below about 30%, valve control limitations may result in operation at a reduced recovery rate.

The automatic turndown control system works well and allows smooth capacity changes of the PSA unit. However, it does not account for changes in feed composition, temperature, or other process variables and is often set by conservative operators to provide higher hydrogen purity than is required at the expense of lower hydrogen recovery. Operation in this manner increases hydrogen production cost. Conversely, if the unit is operating at the maximum allowable impurity limit, the system is susceptible to feed changes that can lead to the production of off-specification product. These concerns can be addressed by the use of a patented automatic purity control system, which is described in the next section.

- **Automatic Purity Control**

In 1988, UOP commercialised a patented automatic purity control system that allows the PSA unit to be operated at constant product impurity levels in spite of changes in feed conditions. Automatic purity control uses either hydrogen product analysis or hydrogen analysis at the end of cocurrent depressurisation. The purpose is to adjust the cycle time so that the specified hydrogen product purity can be maintained at varying operating conditions. For feed streams with a rather constant composition, the hydrogen sampling is done only in the hydrogen product gas to reach the highest hydrogen recoveries (Point A on Figure 10). For feed streams with varying compositions, such as refinery vent gases, the hydrogen sampling is performed at the cocurrent depressurization (Point B on Figure 10). Automatic product purity control also protects the adsorbent against an overload of heavy hydrocarbons and permanent deactivation. It also gives an early indication of a potential impurity breakthrough. It allows the PSA unit to safely operate at the maximum

recovery point over a wide range of conditions. The impact of changes in process conditions is minimized, and the system can be operated at a product impurity level close to the maximum allowable level under any conditions. **Table 1** can be used as a guideline to select the preferred purity control system.



**Fig. 10 Product Purity Control**

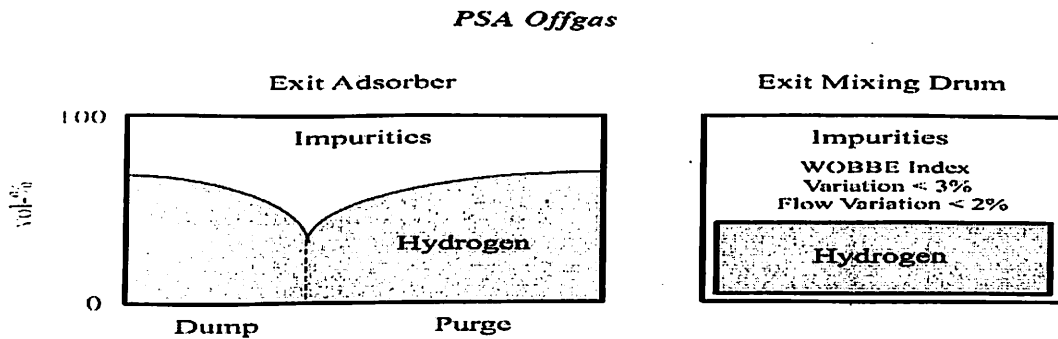
**Options for H<sub>2</sub> Purity Control**

Table 1  
*Options for H<sub>2</sub> Purity Control*

	H <sub>2</sub> Product Control	Cocurrent Depressurisation Control
Feed Gas Conditions:	Steady	Fast Flow Variations and Composition Varies
Typical Feed Gas:	Steam Reformer Ethylene Offgas	Refinery Offgas
Adsorbent Lifetime:	Not Vulnerable to Overload	Long Lifetime as a Result of Overload Protection

- **Off gas Control**

The offgas leaves the adsorber vessels with varying composition and flows through a mixing drum to dampen the composition variation.



**Fig. 11 PSA Offgas**

In the past, variations in the flow into the PSA offgas mixing drum could cause significant pressure variations in the mixing drum. Controlling the flow to the burners or fuel gas header required a control valve. Today, any pressure changes in the offgas mixing drum are used to change the counter-current depressurization-purge split, so that the flow into the drum is constant. The pressure variations in the drum are minimised, and the result is a constant flow to the fuel gas system. The advantage of this improved Offgas control is a reduction in the pressure drop in the tail gas line and an increase in the hydrogen recovery rate.

- **Automatic Switchover**

The automatic switchover feature is based on monitoring the combined valve and pressure pattern of all adsorbers. The valve positions are monitored by proximity switches. The pressure changes in the system are also monitored. If both the valve position and pressure change are in error, the unit automatically removes the faulty adsorber and continues with a reduced number of adsorbers in operation.

UOP designs the automatic switchover for minimum disturbance to all flows and to maintain the hydrogen product purity specification at all times.

• **Zero-Downtime POLYBED PSA Units**

As a result of UOP's long-term vendor development, POLYBED PSA units are highly recognized in the market for their reliable operation and low maintenance requirements. On-stream factors approach 100% when switchover to an operation with a reduced number of adsorbers is included. However, from a quality viewpoint, switchover should be avoided for two reasons. First, performance reduction, however small, is associated with an operation using fewer adsorbers. Second, any component malfunction requires maintenance, which should be avoided.

**Reliability**

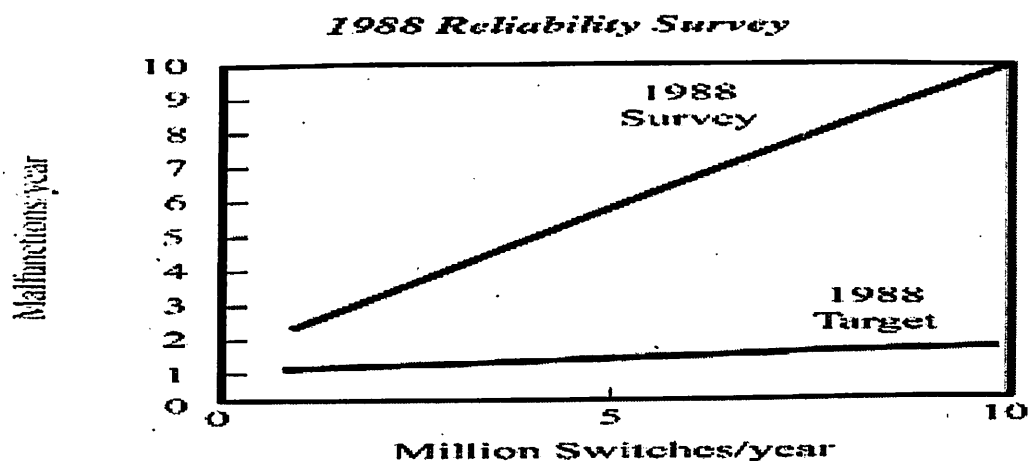
In 1988, UOP performed a fundamental investigation of the causes of component malfunction in the PSA systems by analysing 10 randomly selected units. The different PSA units consisted of 4-, 6-, and 10- adsorber systems. Data on component malfunction (Table 2) were analyzed and incorporated into a program to improve the quality of PSA units.

TABLE 2  
*1988 Reliability Survey*

	Clients										Total	Total %
	A	B	C	D	E	F	G	H	I	J		
Operation: Million Switches/Year	8.4	5	5	4.5	4.4	3.6	3.3	3.2	3	2.4	42.8	—
Total Failures/Year	9	6	10	5	1	2	2	1	2	4	42	—
Valve Actuators	0	1	0	1	0	0	1	0	2	3	8	19
Solenoids	3	2	6	2	0	0	0	0	0	0	13	31
Positioners	5	2	2	0	0	1	1	1	0	0	12	28
IO Cards	0	0	0	1	0	0	0	0	0	1	2	5
Transmitters	1	1	2	1	1	1	0	0	0	0	7	17

The most unreliable components proved to be the valve actuators, solenoids, positioners, and transmitters. In 1989, UOP implemented a vendor quality assurance program. This program included the selection of vendors with the most reliable components and UOP participation in improving the components further by redesigning and implementing quality standards for the manufacturing process.

An example of the reliability improvement of this program is demonstrated by the upgrading of a 10-bed system (unit A) that previously demonstrated an unacceptably high average of nine malfunctions per year. After the improved components were incorporated into the unit, the failure rate dropped to 1.5 per year. **Figure 12** indicates a correlation of the total malfunction rate per year versus the total number of valve operations per year.



**Fig. 12** 1988 Reliability Survey

### Redundant Hydrogen Valve Header

To maintain a constant hydrogen product flow, UOP patented the repressurisation to product pressure in 1964. A constant, controlled flow is withdrawn from the hydrogen product for the repressurisation to product pressure. However, a malfunction of the required repressurisation control valve causes a complete shutdown of the PSA unit.

In 1989, UOP obtained a patent to improve the reliability of PSA units by eliminating the repressurisation control valve. The final repressurisation to product pressure is now achieved through product control valves (**Figure 13**).

This improvement provides a redundant valve header for the hydrogen valves. The redundant valve header can be used to eliminate the need for switchover to reduced bed operation. At a malfunction of a hydrogen valve, the redundant hydrogen valve header takes over automatically. The use of hydrogen product valves for the final repressurisation has improved the reliability of PSA units significantly.

### Improved Repressurization Control

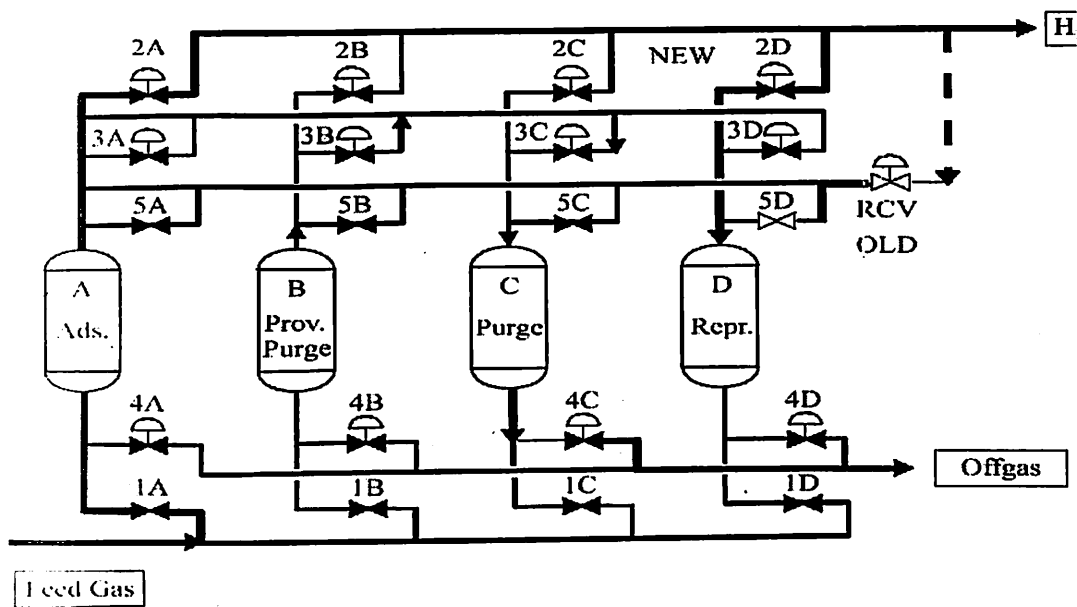


Fig. 13 Improved Repressurisation Control

#### PSA Control Systems

State-of-the-art PSA units contain more adsorbers and up to 75 valves, which operate in a precisely controlled fashion. These PSA units have multiple switchovers to cycles that use fewer adsorbers to bypass a malfunctioning valve or instrument. For example, a 12-bed system can be designed to operate as a 10-bed or 8-bed unit. The control requirements take full advantage of the power of today's control system technology to allow for smooth and precise analog and digital control, multiple switchovers, improved diagnostics, and ease of operation.

Most POLYBED PSA units are controlled with microprocessor-based programmable logic controllers (PLC's). This equipment offers the advantages of off-the-shelf, manufacturer-supported hardware, worldwide service, high-level control capability, and standard data highway links to a distributed control system (DCS), options for redundancy, operator familiarity, and a modem to link to the UOP engineering centre for remote troubleshooting.

Incorporated into the PSA control system are features of automatic capacity and purity control, offgas flow or pressure control, self-adaptive tuning, automatic start-up and

shutdown, and automatic switchover in the event of a valve or instrument malfunction. Today, approximately 60% of the POLYBED PSA units use a DCS interface. The remaining 40% use a dedicated PC interface supplied with the unit.

### **3.4: Adsorber design consideration:-**

#### **Pressure Equalisations**

The hydrogen removed during the cocurrent depressurisation steps is used to repressurise other adsorbers by pressure equalisations and this reduces the hydrogen losses to fuel. As a general rule, increasing the number of pressure equalisations increases the hydrogen recovery. However, a minimum hydrogen purge is required to reject the impurities. Thus, for every application, an upper limit of equalisations required to achieve maximum hydrogen recovery exists. Once this maximum is reached, adding more pressure equalisations does not improve the hydrogen recovery.

#### **Polybed PSA Units**

- **Four-Bed Cycle**

The classical PSA cycle, which is still widely applied today to smaller units (**Figure 9**), was developed in 1965 and used four adsorber vessels. More than 400 PSA units using this cycle have been supplied.

#### **Importance of Cycle Time**

Because the PSA process is a semibatch-type operation, the size of a PSA unit in terms of total adsorber or adsorbent volume is determined by the process cycle time. The cycle time is the time required for an adsorber to complete all the steps in a cycle (**Figure 14**). The reduction in cycle time, and hence the reduction in adsorbent inventory and associated cost, has been one of the main targets in UOP's PSA technology development. The first PSA units were designed for cycle times between 16 and 20 minutes. With the invention of the POLYBED PSA units, the process steps could be staggered in a more-efficient way when compared to the four-bed systems. Consequently, cycle time was substantially reduced.

### Standard 4-Bed Cycle Sequence

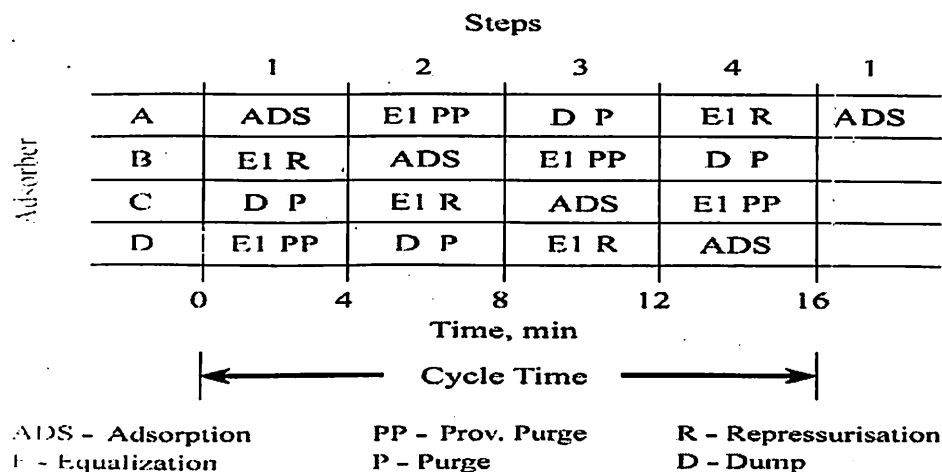


Fig. 14 Standard 4-Bed Cycle Sequence

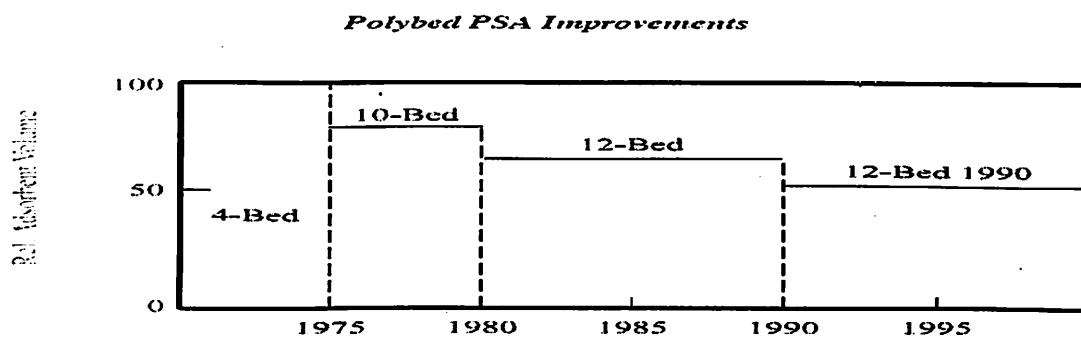
### POLYBED PSA Units

UOP achieved the first major breakthrough of the PSA technology in 1976 with the commercialisation of POLYBED PSA units. High hydrogen recoveries and the possibility of designing POLYBED PSA units for capacities in excess of 100,000 Nm<sup>3</sup>/h met the increasing hydrogen demand of refineries. The invention of the POLYBED PSA units resulted in three significant improvements over the 4-bed systems:

- **Enhanced hydrogen recovery.** A greater number of adsorbers combined in one train give greater freedom to sequence the cycle for higher recoveries. POLYBED PSA units are designed for two or more pressure equalisation steps to enhance the hydrogen recovery.
- **Unlimited capacity.** As the second main feature, POLYBED PSA units have more than one adsorber on the adsorption step at the same time. The feed gas flow distributes over a number of adsorbers, and thus the unit can be designed for any feed gas capacity without the limitation of the four-bed systems.
- **Increased unit utilization.** In 1985, UOP began to develop improvements that allow POLYBED PSA systems to operate with reduced cycle times. As a result of UOP's stepwise improvements in adsorbents and PSA cycles, today's PSA units require less than 50% of the adsorbent volume that was necessary in the PSA



designs of 1975 (Figure 15). This improvement has led to significant reductions in capital costs.



**Fig. 15 Polybed PSA Improvements**

### Process Parameters

The following process parameters influence the design and performance of a POLYBED PSA unit:

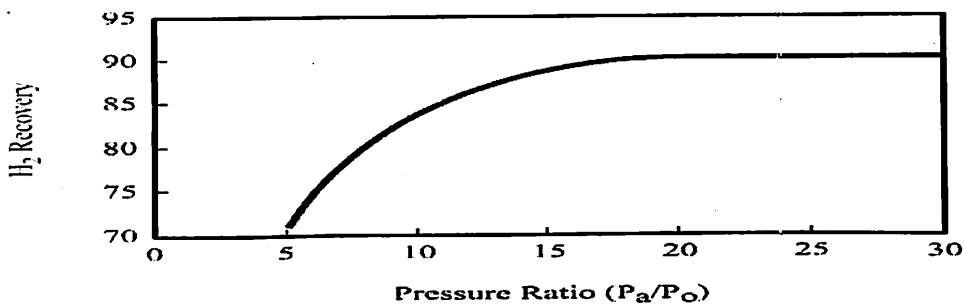
- Feed and offgas pressure
- Feed gas composition
- Required product purity

The effect of these parameters is discussed in this section.

### Feed and Offgas Pressure

The adsorption pressure can be fixed by either available feed pressure or the required product pressure. The feed pressure range is usually between 10 and 40 bar. A high feed gas pressure is always preferred for high hydrogen recovery and low investment costs. The pressure drop from feed to product is relatively small, and the product is available at a pressure about 0.5 bars lower than the feed. Offgas pressures range between atmospheric and 10 bar. This parameter has the strongest influence on hydrogen recovery. The lower the offgas pressure, the higher the hydrogen recovery possible, and the lower the investment costs for a fixed product rate. A ratio of at least 4 to 1 is typically required between the absolute feed pressure and the absolute waste pressure. The combined influence of feed pressure and waste pressure on the product recovery is indicated in **Figure 16**.

*Effect of Pressure Ratio on H<sub>2</sub> Recovery*



**Fig. 16 Effect of Pressure Ratio on H<sub>2</sub> Recovery**

**Feed Gas Composition**

The PSA process can handle feed gas with a wide variety of impurities (Table 3). The process performance varies accordingly with the adsorption-desorption properties of a specific component on the selected adsorbent. In all cases, larger impurity concentrations affect the performance only marginally. Generally, feed gases containing less than 50% by volume hydrogen cannot be economically upgraded in a PSA system.

**Product Purity**

High hydrogen product purity is obtainable with a PSA process. However, some small advantages with respect to hydrogen recovery and investment cost can be gained at the expense of a less-severe purity specification. Generally changing the product specification by an order of magnitude changes the hydrogen recovery by 1% (Table 4).

*Typical Impurities of PSA Feed Gas Streams*

Component	Steam Reformer Raw Gas	CCR Offgas	Ethylene Plant Offgas	Styrene Plant Offgas	Coke Oven Gas
CO	X	—	X	X	X
CO <sub>2</sub>	X	—	—	X	X
CH <sub>4</sub>	X	X	X	X	X
C <sub>2</sub> H <sub>6</sub>	—	X	X	X	X
C <sub>3</sub> H <sub>8</sub>	—	X	—	—	—
C <sub>4</sub> H <sub>10</sub>	—	X	—	—	—
O <sub>2</sub> , Ar	—	—	—	—	X
N <sub>2</sub>	∞	—	—	—	X
NH <sub>3</sub>	—	—	—	—	X
H <sub>2</sub> S	—	—	—	—	X
H <sub>2</sub> O	X	—	—	—	X
BTX	—	X	—	X	X
Styrene	—	—	—	X	X
HCl	—	∞	—	—	X

**Table 3 Typical Impurities of PSA Feed Gas Streams**

## Product Specification H<sub>2</sub>-Recovery,

Key Impurity,	ppm % Points
1	-1
10	Base
100	+1

**Table 4 Hydrogen Recovery Sensitivity**

### • Two bed PSA unit

A two-bed six-step pressure swing adsorption (PSA) process using zeolite 5A was performed experimentally and theoretically for bulk separation of H<sub>2</sub>/CO and H<sub>2</sub>/CH<sub>4</sub> systems (70/30 vol %) as major components in coke oven gas. When the pressure is cycled between 1 and 11 atm at ambient temperatures, 70% H<sub>2</sub> in the feed could be concentrated to 99.99% in the product with a recovery of 75.87% in the H<sub>2</sub>/CO mixture and 80.38% in the H<sub>2</sub>/CH<sub>4</sub> mixture. The effects of adsorption pressure, P/F ratio, adsorption/purge step time, and pressure equalization step time were investigated experimentally. If the product end of an adsorption bed was not contaminated during the adsorption and depressurizing pressure equalization steps, elongation of both the adsorption and purge steps gave good adsorbent productivity and recovery without any decrease in purity. Certain elongations of step time in the pressure equalization step resulted in a better performance of a PSA process. When the H<sub>2</sub> mole fraction of effluent stream during the pressure equalization step was not high, the initial H<sub>2</sub> purity of the adsorption step was not good because of the contamination of the product end section. A mathematical model incorporating heat and momentum balances analyzed these results.

### Basic Adsorbent Properties: -

#### 1. Isotherm Data

1. Uptake, release measurements
2. Hysteresis observed
3. Pretreatment conditions
4. Aging upon multicomponent cycles

5. Multi-component effects

## **2. Mass Transfer Behavior**

1. Interface character
2. Intraparticle diffusion
3. Film diffusion
4. Dispersion

## **3. Particle Characteristics**

1. Porosity
2. Pore size distribution
3. Specific surface area
4. Density
5. Particle size distribution
6. Particle shape
7. Abrasion resistance
8. Crush strength
9. Composition stability
10. Hydrophobicity

## **Application Considerations**

### **1. Operating Conditions**

1. Flow rate
2. Feed and product concentrations
3. Pressure, temperature
4. Desired recovery
5. Cycle time
6. Contaminants

## **2. Regeneration Technique**

1. Thermal: steam, hot fluid, kiln
2. Chemical: acid, base, solvent
3. Pressure shift
4. Regenerate, adsorbate recovery or disposal

## **3. Energy Requirements**

### **4. Adsorbent Life**

1. Attrition, swelling
2. Aging, fouling

## **Equipment, Flow sheet**

### **1. Contactor Type**

1. Fixed: axial, radial flow
2. Pulsed, fluidized bed

### **2. Geometry**

1. Number of beds
2. Bed dimensions
3. Flow distribution
4. Dead volumes

### **3. Column Internals**

1. Bed support, ballast
2. Flow distribution
3. Insulation

### **4. Miscellaneous**

1. Instrumentation
2. Materials of construction
3. Safety, maintenance
4. Operation, start-up, shutdown

The three critical considerations in the design of a pressure swing adsorber are adsorbent bed pressure gradient, the bed volume, and the regeneration purge. The pressure gradient in an adsorbent bed influence the power required to operate the system, the life of the adsorbent, and flow distribution through the adsorbent.

Sizing the adsorbent bed in a pressure swing process is based on maintaining both the mass-transfer front and the heat-transfer front within the adsorbent bed during the on-stream period of the operating cycle. Effluent purity depends on maintaining the mass-transfer front within the bed while effective bed regeneration depends on retaining the heat-transfer front. Retaining the heat-transfer front is the principal consideration in the design of a pressure swing adsorber. A sufficient purge flow is critical during the regeneration phase to assist in the removal of all of the contaminant adsorbed during the on-stream phase of the cycle.

A pressure swing adsorber is evaluated in terms of the effluent purity, the operating power requirement, the size, the reliability of the system's components, and the life of the adsorbent. The design of a pressure swing adsorber is based on the velocity effects, adsorbent size and regeneration purge, and the choice of the adsorbent influences all aspects of design.

**Velocity effect:**

The fluid flows through tortuous interstitial passages between the granules in an adsorbent bed resulting in viscous and kinetic energy losses that create pressure gradients within bed. The pressure gradient affects the service life of the adsorbent and the flow distribution within the bed. The drag forces acting on the adsorbent bed will fluidize the granules in an up-flow condition if the pressure gradient exceeds the product of the bulk density of the adsorbent and gravitational acceleration. Fluidization results in abrasion

and rapid attrition of the adsorbent granules, which leads to the failure of the adsorption process. The fluidization velocity limit determines the minimum bed diameter.

Even at velocities below the fluidization limit, granule attrition can be severe. In addition to the drag forces, the adsorbent is subjected to alternating lateral forces, which can cause oscillatory motion of the granules. Any motion of the granules will cause abrasion and loss of adsorbent. The attrition velocity limit depends on the shape, size distribution, and hardness of the granules and the direction of flow. For most commercial grade adsorbents, the up-flow velocity limit is 75-80 % of the fluidization limit. In down-flow adsorbent beds, the drag forces tend to nestle the granules in a more stable. Settled configuration that has resistance to the lateral forces, and the down-flow attrition velocity limit is twice that of the up flow.

High velocities result from the large differential pressures that are often encountered at the initiation of the depressurization and re-pressurization steps. Continual pressure cycling, external mechanical vibrations and compressor pulsation can also contribute to adsorbent attrition. When immobilized, an adsorbent bed can withstand much higher flow rates with smaller adsorbent granules and faster cycling rates. Adsorbent immobilization is used in compact, high-throughput pressure swing adsorbers.

Pressure gradients in an adsorbent bed tend to produce an uneven flow distribution, which reduces the effectiveness of the adsorption processes and allows a premature break-through of the contaminant into the effluent. Wall effects and flow channeling result from pressure gradients that cause uneven flow distribution. Wall effects are produced by a disparity in the void fraction in the adsorbent bed.

The packing of adsorbent granules near the vessel walls is more ordered than in the central region of the bed, which results in a higher interstitial, voids fraction and higher flows rate near the walls.

Wall effects can be controlled by limiting the minimum adsorbent bed diameter to at least 30 times the granule diameter, which reduces the fraction of the total flow passing through the high velocity region. The minimum bed length should also be limited to at least 100 times the granule diameter to promote intermixing of the flow streams in the two velocity regions.

**Adsorbent bed size: -**

The pressure swing adsorption process is dependent on retaining both the mass-transfer and heat-transfer fronts within the adsorbent bed during the on-stream phase of the cycle. The heat and mass transfer fronts advance at different velocities that depend on the operating conditions and properties of the adsorption system. The velocities of the transfer fronts are much greater at elevated pressures where the density of the gas is higher.

When the heat-transfer front advances at a faster rate than the mass transfer front (as can happen in the removal of trace condensible contaminants from air), the adsorbent bed must be sized to retain the heat transfer front through out the on stream period. The bed length is often increased by additional 10 % to provide for the retention of both the mass and heat transfer fronts.

When the mass transfer front advances at a faster rate than the heat transfer front, which can happen in the bulk separation of coal gasification products, the bed length is determined by the retention of the mass transfer front. If the contaminants are noncondensable, as is the case in the fractionation of air, retaining the heat of adsorption is of minor consequence and the system, essentially, is a purge stripping adsorption process. While most commercial adsorbents have about the same heat capacity (approx. 1005 J/K.g.K), which is relatively constant with temperature and pressure. Excess length contributes to the purity of the effluent, but it does not decrease the quantity of purge required for regeneration.

**Regeneration purge:-**

In the pressure swing adsorption process, purge flow is required to convey the heat of adsorption into the contaminated region of the adsorbent bed and to sweep the desorbed components out of the system during regeneration. The capacity of the purge for the contaminant and the quantity of contaminant adsorbed during the on-stream phase of the cycle determine the minimum amount of purge flow required to regenerate the off-stream adsorbent bed.

To achieve a high purity effluent, the purity of the outlet end of the adsorbent bed must be maintained and the mass-transfer front must be returned to the inlet portion of the bed



during the regeneration phase. A countercurrent purge of purity equal to the effluent is admitted into the outlet end of the adsorbent bed and the contaminated purge is exhausted from the influent end of the bed. To maintain purity at the outlet end of the bed, it is necessary to depressurize the off-stream bed through the inlet end and to repressurise through the outlet end with a high purity purge.

A loss effluent purity can result from cocurrent depressurization and repressurization caused by contaminant penetration through the bed under the high flow rate conditions at the initiation of the changeover steps. When the outlet end of the bed is contaminated, effluent purity is degraded. When the environment is warmer than the influent, or when external heat is applied indirectly to the purge exhaust end of the adsorbent beds during regeneration, the purge exhaust vapor pressure and contaminant partial pressure in the most contaminated region of the beds are elevated. This significantly reduces the purge flow required to regenerate the adsorbent. Indirect heating can be accomplished with embedded, finned heating tubes or external heating jackets using a low-grade heat source such as hot water, hot lubricating oil, or the hot air discharge from the compressor.

In the adsorption of condensible vapors such as water and oil vapors, equilibrium established at the inlet ends of the adsorbent beds limit the partial pressure of the contaminant vapor in the purge exhaust. The adsorbent comes into equilibrium with the condensible vapor in the influent during the on-stream phase. The purge exhaust approaches the same equilibrium condition during regeneration. Because the heat required for desorption is provided by the retained heat of adsorption under isentropic conditions, the purge exhaust temperature and its vapor pressure are equal to the influent temperature and vapor pressure. In pressure swing adsorption systems designed to remove noncondensable gases such as carbon dioxide, nitrogen, or oxygen, the partial pressure of the contaminant gas in the purge only the purge exhaust pressure limits exhaust. There is no theoretical minimum purge in this case.

### 3.5: Equipment sizing: -

- **Adsorber beds:**

Sizing the adsorber beds is the first step in design of PSA plant.

- **Data Gathering:**

It is desirable to have data on the adsorption equilibrium conditions as well as the rates of adsorption of the gas-mixture components in the adsorbents to be used in the bed.

Adsorption equilibrium for single slowly adsorbing components (ones in which it takes more than 10 sec to achieve one half of the equilibrium loading) is usually measured gravimetrically. Faster adsorption is more difficult to measure, requiring more-advanced techniques. When gravimetric methods are inappropriate, one convenient technique is to measure the elution front from an adsorber column and fit the shape of the front to a simulated experiment to determine the parameters of the assumed form of rate expression.

- **Bench and Pilot units:-**

Once the required adsorption equilibrium data are in hand, the development of a PSA process usually starts at the laboratory or bench scale, employing beds in vertical columns of 0.05 - 0.1 m diameter and 1-3 m in length. Solenoid valves are typically used to change the flow directions and needle valves to contact the critical flows. The unit is typically outfitted with a microprocessor based controller, a data acquisition computer, mass flow rates and gas analyzers. In some facilities, plastic tubing is employed to make the gas flow connections, in order to facilitate changes of the cycle as new ideas emerge on how to improve the process performance.

Typically, the bed height should be the same as in the desired full scale plant, typically around 2 m and in order to observe fully developed temperature profiles, the bed diameter should be at least 0.6 to 1 m (in full scale plants, by contract, beds with diameter as great as 6 m are not common). The controllers, valves, analyzers and compressors or vacuum pumps should be of the same type as in the desired full-scale plant. Care should also be taken that the void spaces above and below the adsorbent be in

same proportion as in the full-scale plant (for example top and bottom voidage each at 12 % of the total vessel volume) The pilot plant should be instrumented to measure all flows (inlet, outlet and all internal streams such as those for equalization, purge, depressurization and venting) as functions of time, temperature (inside the beds, axially and radially) gas compositions, pressures and pressure drops.

**The calculation sequence for sizing the bed is: -**

(Standard volumetric product flow desired)

$$\text{Volume of adsorbent} = \frac{\text{-----}}{\text{Specific product}}$$

Volume of adsorbent

$$\text{Total vessel volume} = \frac{\text{-----}}{(1 - \text{percent voidage}/100)}$$

[(Product flow rate desired) (1-percent purity/100)]

$$\text{Feed flow rate} = \frac{\text{-----}}{[(\text{Yield}) (1 - \text{percent feed purity}/100)]}$$

Waste gas flow rate = feed flow rate - product flow rate

**Scale up factors:**

Several factors affect the performance of a PSA adsorption bed as the Scale of operation increases. One is gas distribution. At the bench scale and even in a pilot plant, it is relatively easy to obtain uniform, gas distributions, so deviations from the desired plug-flow distributions are not large. As scale increases however uniformity of gas distributions becomes more problematic.

Thermal non-uniformity in the bed increases with increasing the scale of operation. If examined, many operating PSA plants would show a relatively cold region close to the bottom of bed and a relatively warm region close to the top of the gas-exit region. Simulation and pilot plant experimentation can considerably reduce the risk of this scale-up effect.

### **Anticipating Operating Constraints:-**

There are three operating constraints.

1. Diffusion
2. Gas velocity
3. Pressure drop

One constraint involves diffusion. In most cases, PSA process is operated as fast as the diffusion limitations permit, which is usually some fraction of the characteristic diffusion time (defined as one half of the time needed to achieve equilibrium loading). At the point where diffusion becomes an important limitation, the product yield starts dropping and further attempts to speed up the cycle make the operation less economic.

Another related constraint involves gas velocity. As the cycle time falls, gas velocities increase. At a particular velocity, the adsorbent particles begin to fluidize, which is highly undesirable. The high velocities can be forestalled by making the bed larger in cross-section (and correspondingly shorter). This strategy is more prudent and economical than a sometimes-suggested alternative: making provision to immobilize the bed in the face of the fluidization velocities.

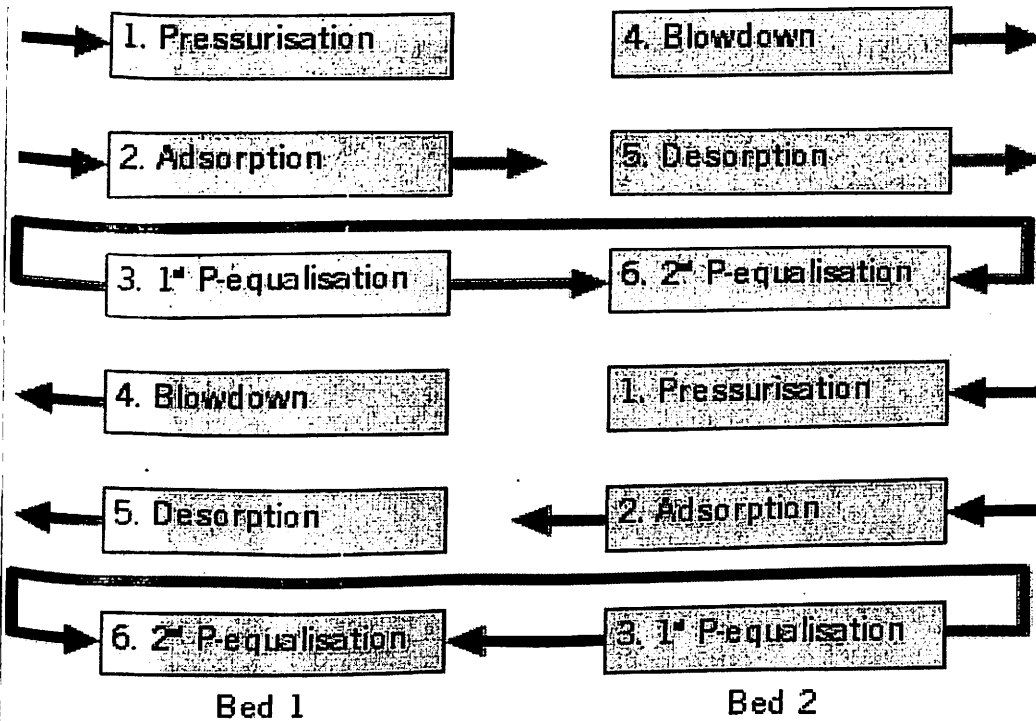
The third constraint is pressure drop through the bed. This accounts for a significant part of the power consumption of the plant, so high-pressure drop (even when the unit is below fluidization conditions) may not be acceptable. As with fluidization specifying a shorter bed and increasing its cross-sectional area can lessen the problem.

#### 4. SINGLE COLUMN PSA EXPERIMENT

##### DATA AVIALABLE

- Total half life cycle = 128 sec.
- Diameter of adsorption vessel = 76 cm.
- Height of vessel = 2.1 meter.
- Volume of adsorbent = 165 lit.
- Diameter of pellets = 2 mm.
- Beds are operated at = 180°
- Feed gas pressure = 8.4 bar.
- Regeneration pressure = 1 bar.

The following two beds, six step process are used for the production of hydrogen using carbon sieve adsorbent.



<u>Cycle</u>	<u>Time</u>
Pressurisation.	2 sec
Adsorption	60 sec
1 <sup>st</sup> pressure equalization	2 sec.
Blow down	2 sec.
Desorption	60 sec.
2 <sup>nd</sup> . pressure equalization	2 sec.
<hr/>	
Total	128 sec.

Room temp. = 28 °C

PSA temp. = 50 °C

Adsorption temp. = 46.2 °C (mini.)  
49.5 °C (maxi.)

Desorption pressure = 0.38 kg/cm<sup>2</sup>

cycle no	feed flow (lpm)	product flow (lpm)	adsorption pressure (kg/cm <sup>2</sup> )	H2 in product	H2 in blowdown		H2 in evacuation		H2 in evac.+purge	
					time	wt %	time	wt %	time	wt %
1	3.4	1.8	3.01	0						
2	3.2	1.8	3.05	0	0	19.2	0	7.1	0	38.8
3	3	1.6	3.16	0	5	7.3	5	7	5	39.8
4	3	1.6	3.05	0.2			10	7.4	10	35.2
5	3.2	1.6	3	0.6					20	28
6	3.2	1.6	3.02	0.8					30	23.9

## RESULTS

Adsorb. + Pressure flow = 4.5 lit/sec.

Product flow = 3.55 lit/80sec.

Desorption prod. Flow = 2 lit/60sec.

Rinses prod. Flow = 0.2 lit/5sec

Blow down prod. Flow = 2.7 lit/40sec.

Purges prod. Flow = partially open = 6.75 lpm

= totally open = 7.8 lpm

N<sub>2</sub> purity (wt %) = 98.9

H<sub>2</sub> recovery (wt %) = 77.98 %

## CALCULATION

	wt % H2	wt % N2	mol fraction H2
feed	12.2	87.8	0.08124
product	1.1	98.9	0.00702
rinse with drawl	7.1	92.9	0.04637
blow down	7.3	92.7	0.0477
depressurisation	26.45	73.55	0.186
depressurisation + purge	24.3	75.7	0.16962

$$\text{H}_2 \text{ in rinse with drawl input} = 0.95(\text{vol. flow rate lpm}) * 0.16 (\text{cycle time})$$

$$= 0.152 \text{ lpm}$$

$$\text{Feed input} = \text{total by pass flow} - \text{by pass during adsorption}$$

$$= 7.8 \text{ lpm} - 3.8 \text{ lpm}$$

$$= 4.0 \text{ lpm}$$

$$\text{H}_2 \text{ in feed input} = \text{feed input} * \text{mol fraction of hydrogen in feed}$$

$$= 4 (\text{vol. Flow rate}) * 0.08124 (\text{from table})$$

$$= 0.325 \text{ lpm}$$

$$\text{Total H}_2 \text{ input} = \text{H}_2 \text{ in feed input} + \text{H}_2 \text{ in rinse with drawl input}$$

$$= 0.325 + 0.152$$

$$= 0.477 \text{ lpm}$$

$$\text{H}_2 \text{ in depressurizations output} = \text{depressurization product flow} * \text{H}_2 \text{ in depressurizations}$$

$$= 2 (\text{vol. flow rate}) * 0.186 (\text{from table})$$

$$= 0.372 \text{ lpm}$$

$$\% \text{ H}_2 \text{ recovery} = \text{H}_2 \text{ in evacuation output} / \text{total H}_2 \text{ input}$$

$$= 0.372 / 0.477$$

$$= 77.98 \%$$

**VOLUME OF ADSORBENT** = standard volumetric product flow desired / specific product

$$= 1.8 / 0.011$$

$$= \mathbf{163.63 \text{ lit.}}$$

**TOTAL VESSEL VOLUME** = volume of adsorbent / (1-% voidage/100)

$$= 163.63 / (1-85/100)$$

$$= 163.63 / 0.15$$

$$= \mathbf{1090.86 \text{ lit.}}$$



## 5. SIMULATIONS AND OPTIMIZATION OF AN INDUSTRIAL PSA UNIT

### INTRODUCTION

The pressure swing adsorption (PSA) systems have received increasing attention from the specialized literature. Several articles have been published in the past years, with focus on the numerical simulation of such units and on experimental results. In general, these studied units are very simple, and have too many simplifications when compared to industrial units. This fact reflects the required computational complexity when working with real industrial systems, mainly when the objective is to optimize some process parameters.

In the past years, some works on optimization of pressure swing adsorption units have been done. Almost all those works are related to simple experimental units. Kvamsdal and Hertzberg (1995a) have worked with three systems of trace separation to investigate the effect of mass transfer during the blowdown step. They presented another work (Kvamsdal and Hertzberg, 1995b) on optimization of a trace separation system, where the importance of model simplifications to save time was emphasized, and the adsorption pressure, purge rate and column length was optimized. Chlendi et al. (1995) have proposed a method to characterize the behavior of pressure swing adsorption cycles based on experiments design and polynomial fittings to represent the system. The objective of this work was to make the problem easier to be optimized. There are some studies (Park et al., 1998; Kumar, 1994) on the optimal height of different kinds of adsorbents to separate multicomponent mixtures. Nilchan (1997) presented a more systematic approach to solve optimization of periodic adsorption process. It is proposed the discretization of the time domain with the inclusion of cyclic steady state conditions. The main disadvantage of this method is the increase in the computer memory requirement.

In the present work, modeling and simulation of an industrial hydrogen purification unit is made. The system is fed with a stream containing about 95% hydrogen, almost 5% methane, and traces of carbon monoxide, humidity and benzene. The product has about 99.99% purity in hydrogen, and the unit recovers about 90% of the hydrogen fed. The beds have three adsorbent layers, at feed entrance there is one composed of alumina,

followed by an activated carbon layer, and after that, there is a zeolite layer. The alumina is used as a guard bed, in order to prevent irreversible contamination of the other adsorbents with water or benzene. This occurs because of the strong interaction of these heavier compounds with the adsorbents. As alumina has weaker adsorption strength, they can be desorbed by pressure reduction, which would be impossible for the activated carbon or for the zeolite.

This work does not consider the presence of water or benzene in the feed, and the adsorption of carbon monoxide or methane in alumina is not considered too. Thus the alumina bed has no influence in the model results. Because of the weak interaction of hydrogen with all adsorbents, it is treated as an inert.

First of all, a model to describe an industrial pressure swing adsorption unit for hydrogen purification was made. All the process characteristics are considered for the model conception, in order to describe the system behavior correctly. After verifying that the model is in accordance with plant data, the influence of some process parameters were studied, enabling the identification of optimal points. The main focus is the influence of the pressure swing steps on the process performance, which is represented by the relation of two characteristic times,  $T_1$  and  $T_2$ . In the industry, for this particular system, the cycle time is manipulated to control the product purity, but the relation of the pressure swing steps is set to constant value. The objectives of this work are to study the influence of variations on the relation of the pressure swing steps and to identify its optimal value.

#### **Process description:-**

The hydrogen purification plant has six vessels and operates in twelve steps. Each vessel is filled with three different adsorbents, alumina, activated carbon and zeolite. The sequencing of the different steps follows a predefined rule, which is best understood in **table 5**.

Table 5

BED	STEP													
	1	PE1	HD	PE2	PE3	PP	BD	P	RE3	RE2	RE1	REP	ADS	
2	ADS			PE1	HD	PE2	PE3	PP	BD	P	RE3	RE2	RE1	REP
3	RE1	REP	ADS			PE1	HD	PE2	PE3	PP	BD	P	RE3	RE2
4	RE3	RE2	RE1	REP	ADS			PE1	HD	PE2	PE3	PP	BD	P
5	BD	P	RE3	RE2	RE1	REP	ADS			PE1	HD	PE2	PE3	PP
6	PE3	PP	BD	P	RE3	RE2	RE1	REP	ADS			PE1	HD	PE2
Time (s)	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2	T1	T2

Sequence of the steps of a complete PSA cycle (PE – Provide pressure equalization, HD – Hold, PP – Provide purge, BD – Blowdown, P – Purge, RE – Receive pressure equalization, REP – Product repressurization, ADS – Adsorption).

The steps performed for each bed in a complete cycle are the following: pressure equalization 1 (provide), hold, pressure equalization 2 (provide), pressure equalization 3 (provide), provide purge, blowdown, purge, pressure equalization 3 (receive), pressure equalization 2 (receive), pressure equalization 1 (receive), repressurisation, and adsorption. Figure 1 show the duration of each step, which is a composition of two characteristic times,  $T_1$  and  $T_2$ . The pressure equalization 1 has a fixed duration of 25 seconds, thus the hold step take  $(T_1 - 25)$  seconds, and the repressurisation step take  $(T_2 + T_1 - 25)$  seconds. A typical pressure variation with time is shown in fig. 17.

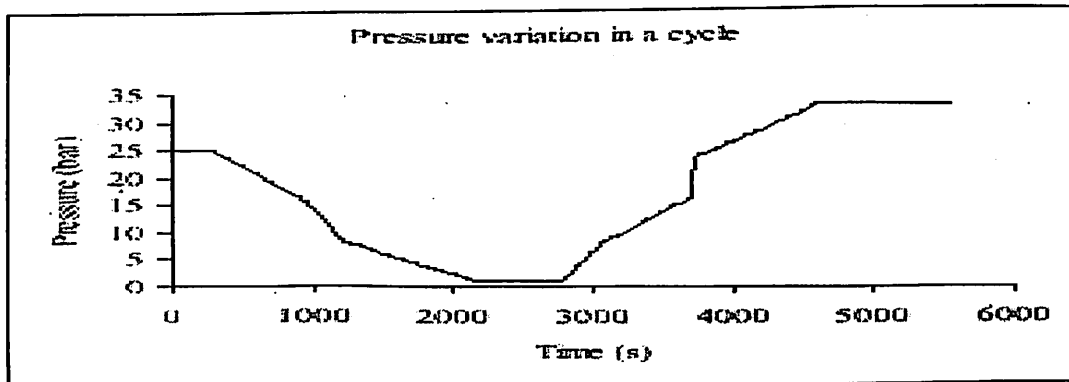
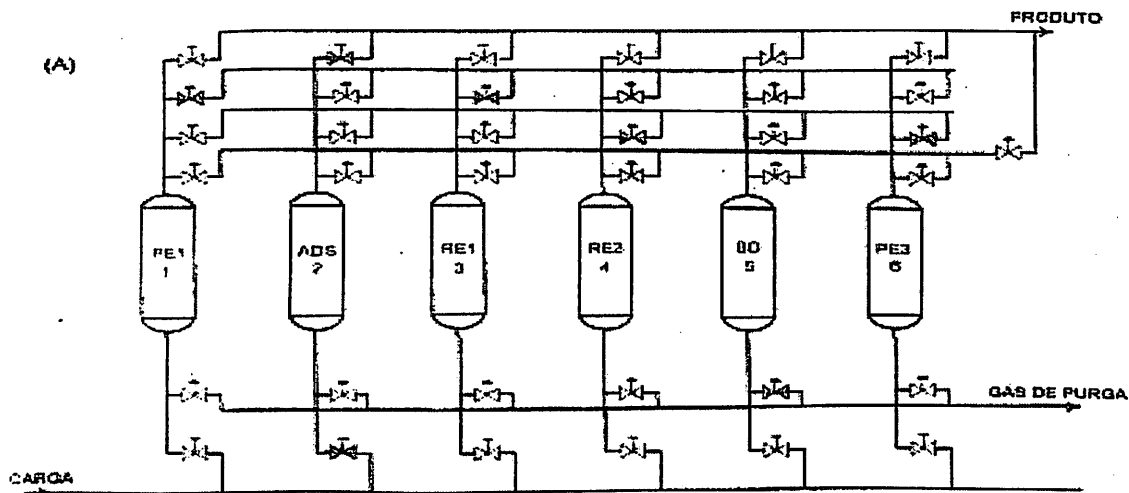


Fig. 17 Typical pressure variation with time.

The purge is the main regenerating step, which enables the desorption of the adsorbed material. The other steps are used basically to reduce the bed pressure to the purge pressure, and, after the purge step, to increase it to the adsorption pressure. The equalization steps are used to improve recovery, because they use the gas that is living a

bed at a higher pressure and has to be depressurized to fill a bed that is increasing pressure to enter adsorption step. It is obvious that in the pressure equalization step the receiving pressure vessel cannot reach the adsorption pressure, once the final pressure of that bed must be lower or equal to the final pressure of the providing pressure vessel. In order to reach the adsorption pressure, the bed receives a fraction of the product gas in the repressurization step.

**Figure 18** represents a brief description of the unit. The valves marked are open. This diagram shows the way the beds are connected one to another. The valves have to open and close synchronized to change the system from one step to another, in accordance with the necessary connections between the beds. The different bed connection schemes can be known by the analysis of **table 5**.



**Fig 18 : Simplified diagram of the process.**

The pressure variation in the variable pressure steps has a linear dependency with time. There is a control system that controls the interconnection valves in order to follow a predefined linear set point. In the diagram described in **Fig. 18** the bed 1 is equalizing pressure with bed 3, bed 6 is equalizing pressure with bed 4, bed 5 is in blowdown, and bed 2 is in adsorption step. This configuration corresponds to the first step in the **table 5**.

**Mathematical model and optimization strategy:-**

The PSA is a distributed system that can be modeled using a set of partial differential and algebraic equations. Although it has an intrinsically dynamic behavior, it can achieve a

cyclic steady state after a certain number of cycles. A mathematical model for a complex commercial PSA unit is developed. The assumptions adopted are summarized below.

1. The flow model adopted is the plug-flow with axial dispersion. No radial gradients are considered.
2. The system is non-isothermal, with thermal axial dispersion. Is considered local thermal equilibrium between the gas and the solid phases.
3. To maintain the model generality, the system is considered a bulk separation process, then the change of velocity due to adsorption (or desorption) is taken into account by the overall material balance.
4. The multicomponent adsorption equilibrium is computed adopting the extended Langmuir model. The isotherm constants are taken from literature, obtained from experiments with a single component (Park et al., 1998). No consideration was made concerning interaction among different molecules.
5. The adsorption of hydrogen is considered negligible.
6. A linear driving force model is adopted to compute the mass transfer dynamics, with constant overall mass transfer coefficient.
7. Darcy's Law is used to compute the pressure drop across the bed.
8. The ideal gas law is assumed.
9. A linear time dependence of the pressure in the pressure equalization, provide purge, and repressurization steps is known from plant data.
10. All transport parameters, as well as physical properties of gas and solid phases are taken from the literature or estimated from empirical correlations.
11. Heat transfer to the surroundings is negligible.

The different layers obey the same balance equations, but with different sets of physical properties and equilibrium parameters. Thus a balance equation must be done for each adsorbent layer.

The adsorption isotherm parameters are taken from Park et al. (1998).

## Balance Equations

With the preceding assumptions, the balance equations to model the system are given below.

a) **Overall material balance** applied to the gas phase, where the latest term on the right hand side of the equation takes into account the adsorbed quantity:

$$\frac{\partial \rho}{\partial t} = - \frac{\partial(v\rho)}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \sum_{i=1}^{n-1} \frac{\partial q_i}{\partial t}$$

Where  $\rho$  is the gas density,  $v$  is the gas interstitial velocity,  $\varepsilon$  is the bed porosity,  $q_i$  is the amount of component  $i$  adsorbed,  $z$  is the axial dimension, and  $t$  is the time.

b) **Component material balance**, for the gas phase:

$$\frac{\partial C_i}{\partial t} = D_z \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial(v \cdot C_i)}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\partial q_i}{\partial t} \quad i = 1, \dots, n-1$$

Where  $n$  is the number of components,  $D_z$  is the axial dispersion coefficient, and  $C_i$  is the molar concentration of component  $i$  in the gas phase.

c) **Energy balance:**

$$\left( C_{p_g} \varepsilon + \frac{1-\varepsilon}{\varepsilon} \cdot C_{p_s} \right) \frac{\partial T}{\partial t} = K_z \frac{\partial^2 T}{\partial z^2} - v \cdot C_{p_g} \cdot \frac{\partial T}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \cdot \sum_{i=1}^{n-1} \Delta H_{ads,i} \cdot \frac{\partial q_i}{\partial t}$$

where  $C_{p_g}$  is the mean heat capacity of the gas,  $C_{p_s}$  is the heat capacity of the adsorbent,  $K_z$  is the thermal axial dispersion coefficient,  $T$  is the temperature, and  $\Delta H_{ads,i}$  is the heat of adsorption of component  $i$ .

d) **Adsorption isotherm for adsorbed components:**

$$q_{i,eq} = \frac{q_{i,sat} b_i \cdot P_i}{1 + \sum_{j=1}^n b_j \cdot P_j}$$

$$q_{i,sat} = a_{1,i} + \frac{a_{2,i}}{T}$$

$$b_i = b_{0,i} \cdot \exp \left( \frac{b_{1,i}}{T} \right)$$

where  $a_{1,i}$ ,  $a_{2,i}$ ,  $b_{0,i}$ ,  $b_{1,i}$  are the adsorption isotherm parameters for the component  $i$  in each adsorbent material,  $P_i$  is the partial pressure of component  $i$  in the gas phase, and  $q_{i,eq}$  is the amount of  $i$  adsorbed in equilibrium with the gas phase partial pressure of  $i$  at system temperature in that point.

e) **Linear driven force equation**, to model the mass transport between gas and solid:

$$\frac{\partial q_i}{\partial t} = k_i \cdot (q_{i,eq} - q_i)$$

where  $k_i$  is the overall mass transfer coefficient for the component  $i$  in each adsorbent material.

f) **Darcy's equation**:

$$\frac{\partial P}{\partial z} = - \frac{180 \mu v}{d_p^2} \frac{(1 - \epsilon)^2}{\epsilon^2}$$

where  $P$  is the pressure,  $\mu$  is the viscosity, and  $d_p$  is the mean particle diameter.

g) **Ideal gas equation**:

$$P = \sum_{i=1}^n C_i \cdot R \cdot T$$

where  $R$  is the universal gas constant.

### Initial conditions

The solution of the previous equations needs some initial conditions to solve the equations with temporal derivatives. The bed is considered initially clean, and the pressure is equal to the initial pressure of the first step of the bed. The temperature is assumed to be equal to the feed temperature.

The following initial conditions are used to solve the set of differential and algebraic equations.

$$C_i(z) = 0, \quad i = 1, \dots, n-1 \quad z = (0, L)$$

$$T(z) = T_F \quad z = (0, L)$$

$$P(z) = \text{initial pressure of bed} \quad z = (0, L)$$

$$q_i(z) = 0, \quad i = 1, \dots, n-1 \quad z = [0, L]$$

where  $T_F$  is the temperature of the feed stream.

### Boundary Conditions: -

The balance equations are applied to all the steps of the process. The differences from one step to another are accounted by the boundary conditions. On pressure variable steps, the pressure changes are assumed to have a linear dependency with time, here represented by  $P(t)$ . This linear dependency is used as a boundary condition on the pressure. The boundary conditions used in the model are shown below.

### Fluid entering a bed:

$$X_i = X_{i,in} \quad T = T_{in}$$

where  $X_i$  is the molar fraction of component  $i$  in the gas phase,  $X_{i,in}$  is the molar fraction of component  $i$  and  $T_{in}$  is the temperature in the stream that is entering the bed.

### Fluid leaving bed and closed end:

$$\frac{\partial C_i}{\partial z} = 0 \quad \frac{\partial T}{\partial z} = 0$$

For pressure and velocity, the boundary conditions are the following:

### Adsorption

$$z = 0 \rightarrow v = v_f$$

$$z = L \rightarrow P = P_{ads}$$

Where  $v_f$  is the interstitial velocity at feed entrance, and  $P_{ads}$  is the adsorption pressure.

Pressure equalizations, repressurization and provide purge:

$$z = 0 \rightarrow v = 0$$

$$z = L \rightarrow P = P(t)$$



where  $P(t)$  is the previously known pressure variation with time.

**Blowdown:**

$$z = 0 \rightarrow P = P(t)$$

$$z = L \rightarrow v = 0$$

**Purge:**

$$z = 0 \rightarrow P = P_D$$

$$z = L \rightarrow v = -v_{out} \cdot \frac{P_{out}}{P(L)}$$

Where  $P_D$  is the purge pressure,  $P_{out}$  is the pressure and  $v_{out}$  is the interstitial velocity in the exit of the bed which is providing purge gas.

**Intersection of the Layers**

The intersection of the layers is modeled with a set of continuity equations. In order to avoid numerical problems when calculating the derivatives near the border between the two adsorbent layers, the axial dimension is divided in two parts, related to each adsorbent. Then the derivatives near the borderline are calculated without using values of the other axial distribution domain, because the software calculates these derivatives with backward or forward finite difference formula, in exception of the centered finite difference approximation used on the points inside the interval. This way, there is a separation of the two axial distribution domains. They must be connected by a set of continuity equations.

$$\begin{aligned}
 F_1(x_i) &= F_2(x_i) & \frac{\partial F_1(x_i)}{\partial z_1} &= \frac{\partial F_2(x_i)}{\partial z_2} \\
 V_1(x_i) &= V_2(x_i) & \frac{\partial V_1(x_i)}{\partial z_1} &= \frac{\partial V_2(x_i)}{\partial z_2} \\
 T_1(x_i) &= T_2(x_i) & \frac{\partial T_1(x_i)}{\partial z_1} &= \frac{\partial T_2(x_i)}{\partial z_2} \\
 C_{i,1}(x_i) &= C_{i,2}(x_i) \quad i = 1, \dots, n & \frac{\partial C_{i,1}(x_i)}{\partial z_1} &= \frac{\partial C_{i,2}(x_i)}{\partial z_2} \quad i = 1, \dots, n
 \end{aligned}$$

where the subscripts 1 and 2 indicate the activated carbon and the zeolite layers respectively.

## Optimization Strategy

Due to the mathematical complexity of the problem, the strategy selected to achieve the optimal point is the simplest possible. The complete discretization method, described in the work of Nilchan (1997) has required an unavailable amount of computer memory, because of the elevated number of variables generated by the time discretization. The objective is to study the combined effect of the cycle time, here represented by the  $T_1 + T_2$  parameter, and of the  $T_1/T_2$  ratio on the system behavior. A mesh with different values for these parameters was generated, as can be seen in Table 6, resulting in twenty-five different simulation cases.

Table 6 : Values of  $T_1/T_2$  and  $T_1 + T_2$  used in the simulation.

$T_1 + T_2$	650	789	928	1068	1206
$T_1 / T_2$	.15	.35	.48	.60	.75

With the results of product purity and recovery for these cases it is possible to find an optimal value for the two parameters for this specific case study.

## Numerical Solution of the Model

To solve the set of partial differential and algebraic equations (PDAE) the gPROMS (Pantelides, 1996) software is used. This program is a general-purpose process simulator that can work with models involving distributed systems.

The set of equations has to be changed when a bed goes from one step to another, due to the change on the boundary conditions. This work is also executed by the simulator. The user should just implement a routine that defines when the step changes should be made. This way, any modification to be done in the simulation can be made quickly.

The spatial discretization of the set of partial differential and algebraic equations (PDAE) results a set of differential and algebraic equations (DAE) which is integrated in relation to time using the SRADAU code.

## Results and discussion: -

The first objective of the work is to reproduce the plant behavior by numeric simulation, and then to find the optimal cycle time and optimal ratio of the characteristic times ( $T_1$  and  $T_2$ ). The operational parameters optimized in this study are the sum of the characteristic times  $T_1$  and  $T_2$ , and its ratio,  $T_1/T_2$ . The analysis of the plant behavior is made with two main parameters, the product purity and the hydrogen recovery. The product purity is defined as the ratio between the molar amount of hydrogen collected in the product during the last cycle and the total molar amount of the product.

$$\text{Product Purity} = \frac{\int_0^{T_{\text{cycle}}} \pi \cdot R_i^2 \cdot \varepsilon \cdot V_p \cdot X_{H_2,p} \cdot dt}{\int_0^{T_{\text{cycle}}} \pi \cdot R_i^2 \cdot \varepsilon \cdot V_p \cdot dt}$$

where  $T_{\text{cycle}}$  is the cycle time,  $R_i$  is the adsorbent vessel internal radius,  $\varepsilon$  is the bed porosity,  $V_p$  is the gas velocity at product end, and  $X_{H_2,p}$  is the hydrogen molar fraction at product stream.

The hydrogen recovery is defined as the ratio of the molar amount of hydrogen collected in the product during the last cycle and the molar amount of hydrogen fed to the bed in the last cycle.

$$\text{Hydrogen Recovery} = \frac{\int_0^{T_{\text{cycle}}} \pi \cdot R_i^2 \cdot \varepsilon \cdot V_p \cdot X_{H_2,p} \cdot dt}{\int_0^{T_{\text{cycle}}} \pi \cdot R_i^2 \cdot \varepsilon \cdot V_f \cdot X_{H_2,f} \cdot dt}$$

where  $X_{H_2,f}$  is the hydrogen molar fraction at feed stream.

Thus the product purity and the hydrogen recovery are calculated at the beginning of a cycle, remaining constant until another cycle starts. **Table 7** shows that the product purity and the hydrogen recovery in the simulation agree with plant data, for the same operational conditions.

**Comparison and validation with plant data: -**

Table 7 : Comparison with plant data.

	Plant		Simulation
	analyser	laboratory	
recovery	68.19	99.83	70.06
purity			99.85
molar fraction of CO in product	$8.67 \times 10^{-7}$	$2.9 \times 10^{-5}$	$2.07 \times 10^{-6}$
molar fraction of CH <sub>4</sub> in product		$1.7 \times 10^{-3}$	$2.1 \times 10^{-3}$

A basic case was first simulated. **Figure 19** shows the product purity and hydrogen recovery of the system as a function of time. The plant is assumed to start with a hundred percent purity and recovery. This simulation is made with the cycle time equal to 5568 seconds. The system is considered to achieve the cyclic steady state (CSS) when the difference of product purity between one cycle and the proceeding is less than  $10^{-5}$

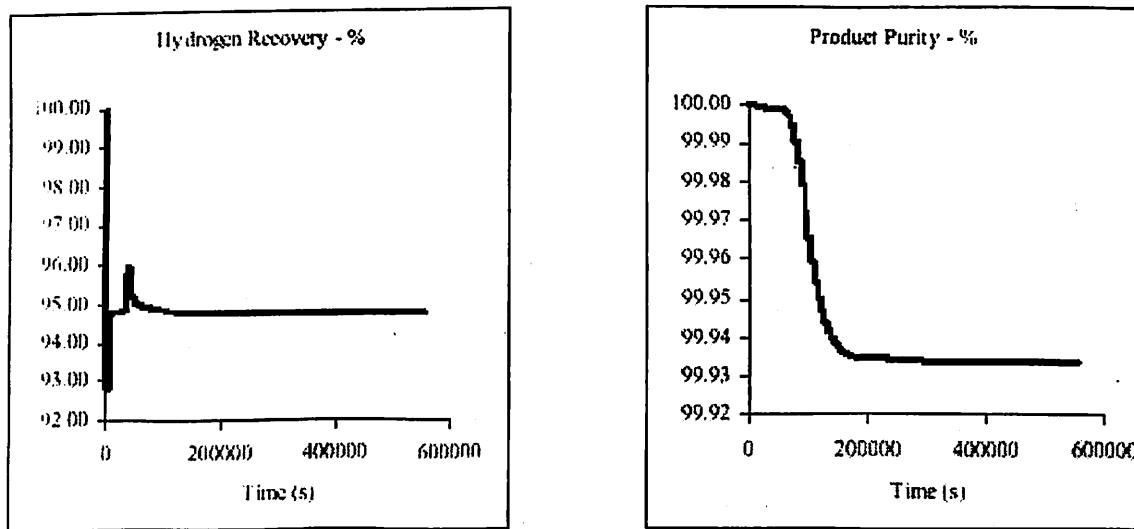


FIG.19 : Product purity and hydrogen recovery as functions of time.

The cyclic steady state is achieved, and then used as initial condition to the other simulations. All perturbations on the values of  $T_1$  and  $T_2$  are done as step variations, after initializing the system with the cyclic steady state with  $T_1 + T_2$  equal to 928 seconds and  $T_1 / T_2$  equal to 0.48. Then the values of  $T_1$  and  $T_2$  are 302 and 626 seconds respectively, and the cycle time is 5568 seconds. The variations of the cycle time are based on variations of  $\pm 30\%$ , and the variations on  $T_1 / T_2$  are chosen to cover a wide operational range.

**Figure 20** shows the variation of hydrogen recovery and product purity with the parameter  $T_1 + T_2$ , which reflects the value of the cycle time. The results showed that product purity decreases with the increase of the cycle time, while the hydrogen recovery presented low reduction. This relationship among cycle time, recovery and purity is qualitatively well known. The utility of this kind of work is to identify the optimal cycle time in order to avoid product over specification. The optimal cycle time would be the value that brings the product inside specification limits with the greatest possible recovery. The optimal cycle time may be related to different feed conditions.

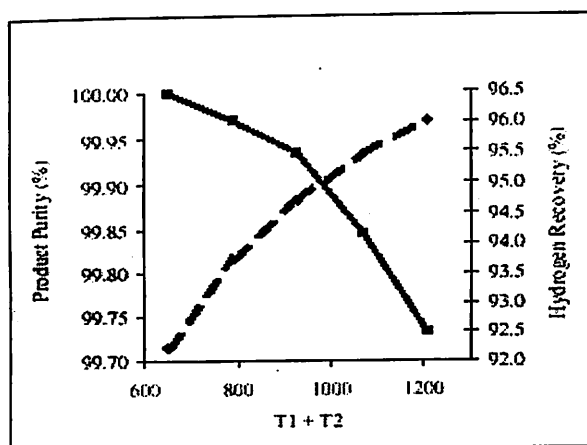


Fig 20 Variation of the product purity and hydrogen recovery with the parameter  $T_1 + T_2$ .

In the industrial unit there is a feed forward control to automatically change the cycle time when the feed flow rate is changed, acting in a linear way. Such relationship assumes that, reducing the feed flow rate in fifty percent, the cycle time will be increased by two times. A very interesting study would be the investigation of the variation of the optimal cycle time with the feed flow rate, the feed temperature, and the adsorption pressure, in order to verify if the optimal value is really inversely proportional to the amount fed to the unit. Such study is going to be done as a continuation of this study, once the investigation of the optimal value for the ratio  $T_1/T_2$  seems to be unnecessary.

**Figure 21** shows the variation of the product purity and the hydrogen recovery with the ratio  $T_1/T_2$  for two different values for the  $T_1 + T_2$  parameter. The variations are verified only in the fourth decimal.

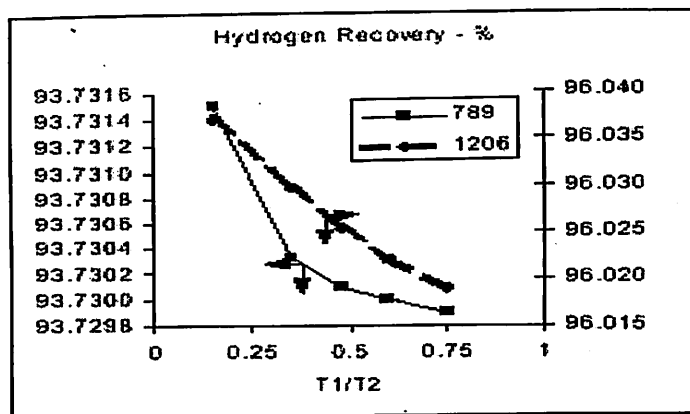
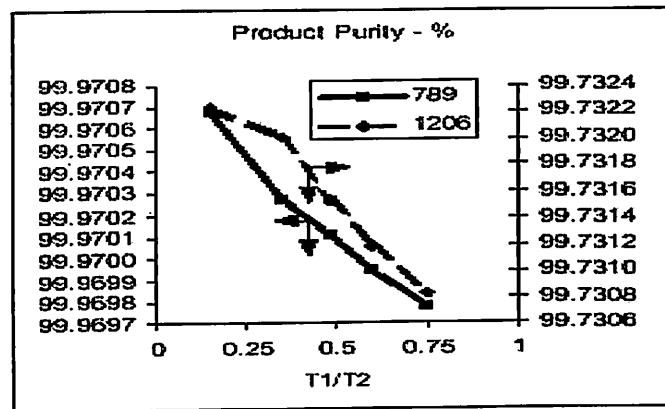


fig 21 Variation of the product purity and the hydrogen recovery with T<sub>1</sub>/T<sub>2</sub>.

The variations of the purity and recovery showed a very low dependency with the variations made in the ratio T<sub>1</sub>/T<sub>2</sub>. It can be attested that, in this specific case, variations on the ratio T<sub>1</sub>/T<sub>2</sub> cause no effect on the product purity or on the hydrogen recovery. In fact, the amount of gas used to purge the bed is the same, because the difference of the initial and the final pressure of the provide purge step is equal, only the rate of variation of the pressure with time is changed. The difference on the time to depressurize the bed causes different purge gas velocities, which presented no effect on the product purity or hydrogen recovery in this case. The choice of the ratio T<sub>1</sub>/T<sub>2</sub> to be used is probably made based on mechanical aspects of the system. A fact that is also observed is the simultaneous increase in hydrogen recovery and product purity when the ratio T<sub>1</sub>/T<sub>2</sub> is reduced. Obviously, if the cycle time remains unchanged and the hydrogen purity is increased, then the additional hydrogen transferred to the product stream will reflect in reduction of the amount of hydrogen purged, increasing also the recovery.

## 6. Applications

Generally the PSA process should always be considered whenever a high-purity hydrogen stream has an advantage. Such advantages would be:

- A higher hydrogen partial pressure in the downstream reaction section
- Compression cost savings due to the smaller amount of inert gases in the makeup hydrogen and in the reaction section recycle gas
- Reduction of the reactor loop purge gas quantities
- Better quality of the hydrogenated products

A few examples classified according to the type of feed gas are provided. The reference list in Table 8 gives a complete hydrogen applications overview.

*PSA Applications and Experience List*

Feed Source	H <sub>2</sub> in Feed, vol-%	Largest Unit in Operation, Nm <sup>3</sup> /h H <sub>2</sub>	First Unit On-stream	Number of Units Built
Steam Reformer	64-96	113,000	1966	201
Refinery Streams	45-92	90,900	1971	104
Ethylene Offgas	35-95	129,800	1966	86
H <sub>2</sub> /CO Cold Box	72-99	58,000	1967	17
Partial Oxidation	54-94	43,800	1976	17
Methanol Offgas	58-84	39,300	1972	17
Chlorine Cell Offgas	98-99	26,100	1968	8
Ammonia Plants	51-88	37,500	1970	12
Styrene Offgas	79-88	10,600	1970	11
Coke Oven Gas	50-59	12,400	1979	19
Cosorb Offgas	43-93	12,400	1977	7
Misc. Offgases	60-98	16,400	1966	33
Total Units	—	—	—	532

**Table 8. PSA Applications and Experience List**

### Steam Reforming

The PSA process for the purification of steam reformer gas has replaced the traditional purification process. The reasons for the change to PSA are summarised below:

#### High-purity hydrogen.

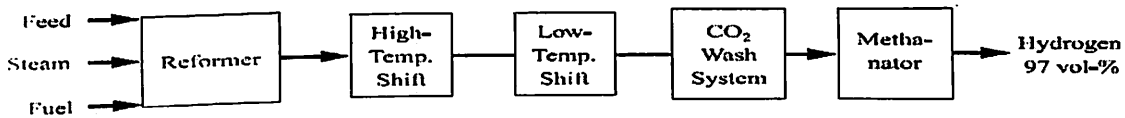
A less complex operation as a result of the reduced number of unit operations in series. The PSA process involves only steam reforming, high temperature shift conversion, and PSA (Figure 22 for comparison).

The PSA process is more easily optimised with reforming conditions than the traditional purification process. Thus, the hydrogen plant designer can vary the steam-to-carbon ratio in the reformer, the outlet temperature, and the outlet pressure to achieve optimal feedstock and fuel consumption. Also, a considerable increase in the quantity of export steam is obtained.

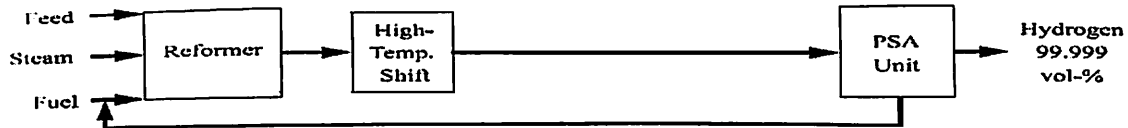
Typical reforming conditions and economics are compared in **Table 9**.

*Steam Reforming Flow Schemes*

Traditional



PSA



**Figure 22 Steam Reforming Flow Schemes**

**PSA and Conventional Purification in Steam Reforming**

Table 9

*PSA and Conventional Purification in Steam Reforming*

	PSA	Convention
<b>Reforming Conditions:</b>		
Severity	LOW	HIGH
Steam-to-Carbon-Ratio	3 / 1	4.5 / 1
Outlet Temperature, °C	850	850
Outlet Pressure, barg	20	20
Methane Slip, vol-%	5	2.5
<b>H<sub>2</sub>-Production:</b>		
H <sub>2</sub> , Nm <sup>3</sup> /hr	15,000	15,000
H <sub>2</sub> Purity, vol-%	99.999	97
Feedstock (NG), Nm <sup>3</sup> /hr	5,300	4,300
Fuel (NG) Nm <sup>3</sup> /hr	800	2,600
Export Steam, t/hr	11.8	6.6
<b>Production Costs, \$1000 Nm<sup>3</sup>/hr of H<sub>2</sub>:</b>		
Total	110	126
Feed and Fuel	85	96
Investment	25	30



## **Upgrading Refinery Hydrogen Streams**

Large quantities of hydrogen are produced as a by-product of catalytic reforming. The hydrogen stream coming from the catalytic reformer (or from hydroprocessing vent gases) can be purified in one single process step by a PSA unit, and all impurities can be removed. The concept of upgrading refinery vent streams for pure hydrogen has been described in the UOP paper "The Efficient Refinery: Hydrogen Management in the 1990's."

## **Ethylene Plant Offgas**

The hydrogen rich gas coming from an ethylene plant is an excellent feedstock for a PSA unit. The low carbon monoxide content permits an economical design for high hydrogen recovery. The installation of a PSA unit with hydrogen purification for acetylene hydrogenation simplifies the cold box design and eliminates the installation of a hydrogen compressor.

## **Ammonia Syngas**

Ammonia production is the largest consumer of hydrogen, and as would be expected, the PSA process plays a role. Three applications for ammonia production incorporate PSA technology:

- The first is upgrading refinery or chemical plant off gases (such as that available from ethylene and methanol plants) for the production of high purity-hydrogen. In those cases, the PSA product is normally added to conventional ammonia plants, except where the PSA product unit is large enough to justify a stand-alone facility.
- In the KTI-PARC process, the PSA unit provides a nitrogen-enriched hydrogen product using nitrogen as purge and repressurisation gas. The use of nitrogen purge results in hydrogen recoveries of above 95%.
- In the ICI LCA ammonia process, excess air is introduced into the reformer. The resultant excess nitrogen is then rejected along with carbon dioxide by a PSA unit.

## **Other Applications**

Various other hydrogen purification applications exist, including the purification of coke oven gas, ammonia synthesis, and methanol synthesis purge gas to recover valuable hydrogen; the upgrading of cold box products and styrene plant offgas; the purification of ammonia dissociator gas; and the **ultrapurification** of electrolytic hydrogen for blanketing gas in semiconductor production.

### **Hydrogen Recovery from Reformed Gas:-**

The gas from the steam reformer consisting of about 75 % by hydrogen. This mixture is saturated with water vapor, also contains CH<sub>4</sub>, CO, N<sub>2</sub> and CO<sub>2</sub>. With the exception of the hydrogen itself, all the components of the hydrogen rich gas mixture are adsorbed at adsorption pressure usually up to 30 bars in the PSA unit. In this process hydrogen yield of more than 90 % can be obtained and if necessary hydrogen of the purity up to 99.9999 %. Linde has supplied such type of PSA plants in IOCL, Baroda and GSFC, Baroda. Linde is presently executing two identical hydrogen PSA units with 1, 33,000 Nm<sup>3</sup>/h capacity of feed gas flow for their client in Gujarat State.

### **Hydrogen Recovery from Refinery Gas:-**

The increasing demand for high purity hydrogen for hydrogenation purposes in refineries has resulted in pressure swing adsorption becoming the method of choice for gas separation or purification, thus recovering high quality hydrogen from refinery gases. The hydrogen content of refinery gases may be up to 95 % by volume. Linde has supplied a single train PSA plant operated by UK Wesseling, which produces 57,000 Nm<sup>3</sup>/h hydrogen with 99.5 % purity grade. Linde has also designed and erected such plants to handle 100,000 Nm<sup>3</sup>/h refinery gases.

### **Hydrogen Recovery from Coke Oven Gas:-**

PSA process can also be utilized for the recovery of hydrogen from coke oven gas. Pre-purified coke oven gases consist mainly of hydrogen and methane, but they also contain the higher boiling hydrocarbons, sulfur compounds, BTX, naphthalene and tar. Linde has designed and erected a PSA based hydrogen recovery unit for the Ruhrkohle AG based

on coke oven gas. This PSA plant is capable of handling 20,000 Nm<sup>3</sup>/h feed gas from which 10,000 Nm<sup>3</sup>/h hydrogen of a purity of 99.9 % by volume is being recovered.

#### **Carbon Dioxide Recovery:-**

Linde PSA systems are successfully employed for the bulk removal of carbon dioxide in direct reduction plants in the iron manufacturing industry. For certain, direct reduction processes a vacuum regenerated pressure swing adsorption (VPSA) system is the optimum choice. These Linde plants represent the world's largest adsorption plant ever built. Linde VPSA plants are also used for the recovery of carbon dioxide from various raw gases in order to make them suitable for liquefaction or other consumers. For example, Linde has designed and erected a PSA system for the removal of carbon dioxide in a direct reduction plant in South Africa.

#### **Methane Recovery: -**

Considering the requirement of petrochemical industries, Linde has designed and erected methane recovery units from the natural gas with purity up to 25-ppmv C<sub>2</sub> + content in the methane product.

#### **Ethylene Recovery:-**

To reduce the production cost of ethylene oxide (EO) plant, it is required to recover ethylene from the purge gases of the EO plant. A typical EO purge gas contains about 30 % ethylene and 50 % methane, plus oxygen, nitrogen, argon and carbon dioxide. Linde has supplied such PSA plant of 700 Nm<sup>3</sup>/h capacities and it has been successfully in operation since 1983.

#### **Nitrogen Recovery: -**

The separation of nitrogen and oxygen from air takes place in an adsorber vessel filled with carbon molecular sieve (CMS). The nitrogen can be purified up to 99.99 % by PSA process, and standard Linde nitrogen PSA units are available with a capacity from 10 to 6000 Nm<sup>3</sup>/h. The application of nitrogen PSA units are for biological preservation, experimental research, as an inert in chemical & petrochemical industry, metallurgical industry, construction and glass industry, electrical or electronic industry and food industry.

### **Oxygen Recovery:-**

For the oxygen separation, ambient air is compressed to slightly over pressure and pass through one of three adsorbers packed with zeolite molecular sieves. Water and carbon dioxide are adsorbed preferentially in the inlet zone after which nitrogen is adsorbed. The resulting oxygen gas is compressed to the required pressure depends on its further application. A maximum oxygen purity of 95 % can be achieved with the PSA process and it is available with a capacity from 10 to 5000 Nm<sup>3</sup>/h. The field of application of oxygen PSA units is for medical purpose, oxygen enrichment processes, metallurgical industry, glass industry, food industry and environmental treatment.

### **Removal of Radioactive Nuclides:**

Exhaust gases of nuclear power stations contain gaseous radioactive nuclides such as tritium, nitrogen, oxygen, argon, krypton and xenon in concentrations or below 10<sup>-6</sup> vol %. Hydrogen containing tritium is burned catalytically, the water is purified. Short live nitrogen, oxygen, krypton, and xenon nuclides are adsorbed on activated carbon, the bed providing lag time for radioactive decay. Heating can regenerate the loaded adsorbent, by lowering the pressure or by purging with inactive gas.

### **Adsorptive purification of Methane:**

Methane must often be separated from methane containing gases such as biogas, mine gas and deposit gas. In addition components like water, carbon dioxide, hydrogen sulfide, sulfur dioxide and mercaptans may have to be removed from natural gas. The adsorption pressure for the separation process is between 0.2 and 0.8 Mpa. The yield of methane is > 95 % with less than 8 % air.

### **Separation of Isomers:**

Normal and isoalkanes can be separated by PSA process. Process conditions are 580 KPa for adsorption and 7 KPa for desorption at 300°C.

## 7. DEVELOPMENTS OF PSA

### **PSA Technology Development**

This paper presents an overview of UOP's PSA development work and also addresses the key role of the PSA technology for hydrogen purification. The main development steps have been the extension of four adsorber units into systems with 10 and more adsorbers for unlimited plant capacity, the development of high-performance adsorbents to achieve the highest hydrogen recoveries, and the development of the fully automatic operation of PSA units for unattended operation.

The main PSA application has been recovery of hydrogen from a wide range of gas streams. Since its commercialisation in 1966, more than 530 PSA units have been installed worldwide. Between 1966 and 1976, the plant capacities did not exceed hydrogen product rates greater than 20,000 Nm<sup>3</sup>/h generally provided by four-bed PSA systems. The hydrogen was mainly used in chemical and petrochemical plants.

The major breakthrough of the PSA technology was achieved in 1976 with the commercialisation of POLYBED PSA units. Hydrogen recoveries exceeding 90%, and the possibility of designing POLYBED PSA units for capacities of 100,000 Nm<sup>3</sup>/h met the increasing hydrogen demand of refineries. The inherent capability of POLYBED PSA units to maintain design capacity with a reduced number of adsorbers in operation provided the on-stream reliability required for the downstream process units.

In the late 1980s, UOP added two important patented control features to the POLYBED PSA units: improved repressurisation control and automatic purity control. The improved repressurisation control allows the PSA units to be designed for "zero downtime operation." The automatic purity control completely removes any need for operator attention. The latest control development features self-tuning of the most-critical Components. Important progress has been made in the reduction of the total adsorbent volume required to purify a specific feed gas rate. Today's PSA units require less than 50% of the relative adsorbent volume used in PSA designs of 1975, as a result of stepwise improvement in adsorbent and PSA cycles.

### **Distillation adsorption hybrid system:**

The conventional distillation plant, which is being used in industries, gives separation of ethanol from azeotropic mixture of ethanol-water up to 94-mol %. PSA plays important role to reach purity of ethanol up to 99.5 mol%. The basic mechanism relies on high-pressure adsorption of one or more components followed by reduced pressure desorption of the bed. The desired products from the bed can be the strongly adsorptive or weakly adsorptive components. PSA offers the flexibility to start-up and shut down quickly. The use of PSA, however, forces the conversion from a continuous process to one that includes a cyclic process. Control valves and instrumentation associated with a cyclic process will require more frequent maintenance. And using adsorption requires feed streams to be clean and free of suspended solids.

The conventional process to recover and purify ethanol consists of three distillation columns. In the first column, the ethanol-water azeotrope is produced as an overhead product. In the second, entrainer is added and water is removed as part of an azeotrope at the top of the column and ethanol product is produced and removed at the bottom. The third column is used to recover entrainer.

The PSA unit replaces the entrainer distillation and entrainer recovery columns. The estimated total capital investment is \$ 1,000,000 for a PSA unit that will produce 7,500 lb/h of fuel-grade ethanol. The capital investment of the PSA unit will vary considerably depending on size and also on equipment options, such as inclusion of heat recovery equipment.

Installation of PSA allows a reduction in steam consumption from 7.7 to 0.5 million Btu/h. New electrical energy in the amount of 788,000 KWh/y is required to drive the vacuum pumps and other equipment for the PSA unit. The use of benzene or cyclohexane entrainer is eliminated, along with storage tanks, pumping and piping needed to operate entrainer storage and supply. It is assumed that the adsorbent will have to be changed out every three years. As illustrated in fig, ROI increases from 10 % at reboiler energy of \$3/million Btu to about 25 % at \$6/million Btu. The hybrid begins to give acceptable ROI's at values of reboiler energy of \$5-6/million Btu.

## **Support for cryogenics:**

### **Prepurification:**

About 85 % of the world supply of oxygen, nitrogen, argon and essentially the entire supply of neon, xenon and krypton, are produced by cryogenic fractional distillation of air. Control of the air contaminants such as water, carbon dioxide and light hydrocarbons (present in some areas) which can foul the primary heat exchanger or form combustible solids in the oxygen rich environment is essential for the design of cryogenic systems.

For decades, these impurities were controlled by periodically reversing flow in the heat exchanger passages, and by liquid phase adsorption of the low solubility species from the oxygen rich liquid streams. PSA process widely used, replacing conventional method to remove impurities. The Prepurification receives air that has been compressed and cooled. Its temperature may vary from 40 to 100 °F, its pressure from 5 to 15 atm. IN a Prepurification system, water, carbon dioxide and most of the hydrocarbons (including acetylene) are adsorbed in the bed during high pressure adsorption. Flow continues through a given adsorber until a preset concentration of carbon dioxide (such as about 0.25 ppm) begins to break through at the product end. The feed is then switched to an adsorber just completing regeneration. The contaminated adsorber is depressurized, and then purged with waste gas from the air separation plant. Regeneration normally takes place at reduced pressure, the temperature varying from ambient up to as high as 600 °F.

## **8. Summary**

Although the POLYBED PSA process was commercialized more than 30 years ago, it is the preferred route for the majority of hydrogen purification applications. UOP's PSA systems are highly reliable, flexible and easy to operate. In addition, the ability of the process to remove all impurities, especially oxides of carbon, to very low levels and to produce the hydrogen product at essentially feed pressure makes POLYBED PSA the process of choice. This paper has discussed the development of the PSA process by UOP and has outlined the major applications of the PSA process in terms of feedstocks.

The report has also presented some of the more recent improvements to this process. These improvements, together with current development activities, ensure that this process will continue to be efficient and economical in the future. The recent improvements in adsorbent technology lead to more efficient PSA units.

Continued PLC and DCS development is likely to lead to further improvements in troubleshooting and ease of operation.



## 9. CONCLUSIONS

Reliable service and high efficiency fractionation can be provided by properly designed process swing adsorption systems. High residual loading and thus low operating loading characterize it. PSA system provides rapid cycling of process with efficient use of adsorbent. It can be hybridized with other separation processes easily. High purity product can be obtained within a single jump and thus it differs from other separation processes. It is highly dependent on cycle time of sequence rather than dependent on flow rate and sizing of bed.

A model to simulate and optimize an industrial PSA unit was developed. All the features concerning with a complex industrial plant were considered. The characteristics of the process were well represented by a non-isothermal model using the extended Langmuir isotherm to represent the adsorption equilibrium and a linear driving force model to describe the adsorption dynamics.

The effects of the cycle time and the ratio  $T_1/T_2$ , two characteristic parameters of the process, were studied. The influence of the cycle time on product purity and hydrogen recovery was studied, showing that it is possible to foresee the optimal cycle time to achieve a defined product specification with maximum recovery. The effect of the ratio  $T_1/T_2$  showed a negligible influence in product purity and hydrogen recovery.

## VARIABLES

$p$  = gas density

$v$  = gas interstitial velocity,

$e$  = bed porosity,

$q_i$  = amount of component  $i$  adsorbed,

$z$  = axial dimension

$t$  = time

$n$  = number of components,

$D_z$  = axial dispersion coefficient

$C_i$  = molar concentration of component  $i$  in the gas phase

$C_{p_g}$  = mean heat capacity of the gas,

$C_{p_s}$  = heat capacity of the adsorbent,

$K_z$  = thermal axial dispersion coefficient,

$T$  = temperature

$\Delta H_{ads,i}$  = heat of adsorption of component  $i$ .

$a_{1,i}$ ,  $a_{2,i}$ ,  $b_{0,i}$ ,  $b_{1,i}$  = adsorption isotherm parameters for the component  $i$  in each adsorbent material,

$P_i$  = partial pressure of component  $i$  in the gas phase

$q_{i,eq}$  = amount of  $i$  adsorbed in equilibrium with the gas phase partial pressure of  $i$  at system temperature in that point.

$K_i$  = overall mass transfer coefficient for the component  $i$  in each adsorbent material.

$P$  = pressure,

$u$  = viscosity

$d_p$  = mean particle diameter.

$R$  = universal gas constant

$T_F$  = temperature of the feed stream

$X_i$  = molar fraction of component  $i$  in the gas phase,

$X_{i,in}$  = molar fraction of component i and

$T_{in}$  = temperature in the stream that is entering the bed.

$v_f$  = interstitial velocity at feed entrance

$P_{ads}$  = adsorption pressure.

$P(t)$  = previously known pressure variation with time

$P_D$  = purge pressure,

$P_{out}$  = pressure

$v_{out}$  = interstitial velocity in the exit of the bed which is providing purge gas.

1 and 2 = indicate the activated carbon and the zeolite layers respectively.

$T_{cycle}$  = cycle time,

$R_i$  = adsorbent vessel internal radius,

$\epsilon$  = bed porosity,

$V_p$  = gas velocity at product end

$X_{H_2,p}$  = hydrogen molar fraction at product stream.

$X_{H_2,f}$  = hydrogen molar fraction at feed stream

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