

50 Years of PSA Technology for H₂ Purification

The first industrial application of Pressure Swing Adsorption (PSA) went on stream in 1966 at a Union Carbide production facility. Today, more than 1,000 Honeywell UOP PSA systems have been designed, fabricated and delivered worldwide, representing about 25 million Nm³/h of pure hydrogen produced. This summary paper presents an overview of Honeywell UOP's PSA innovation over the past 50 years and highlights key developments that have led to UOP PSA systems being the process of choice in hydrogen generation and recovery systems.

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1. Introduction

In the 1950s, Union Carbide developed synthetic zeolites that enabled the development of the pressure swing adsorption process. It became possible to extract high purity hydrogen from a syngas mixture produced by the steam reforming of hydrocarbons. The new materials had the property to capture impurities while hydrogen was essentially not adsorbed. The ability to completely adsorb impurities allowed for the production of high purity hydrogen (typically 99.9+ mol-%) in a single unit with virtually little consumption of utilities, contrary to the traditional multiple-unit flow schemes utilizing acid gas removal wash systems and methanation reactors.

The main developments in PSA technology have been:

- Extension of the initial system featuring four adsorbers, to systems with 10 or more adsorbers;
- Development of high-performance adsorbents to achieve the higher hydrogen recoveries and purities;
- Addition of alternative operation modes (switchover) with a reduced number of adsorbers in service for full on-line maintenance;
- Development of the fully automatic operation of PSA systems for unattended operation, thanks to advancements in process controllers

2. Description of a PSA Unit

The basic flow diagram of a UOP Polybed™ PSA System is shown in Figure 1.

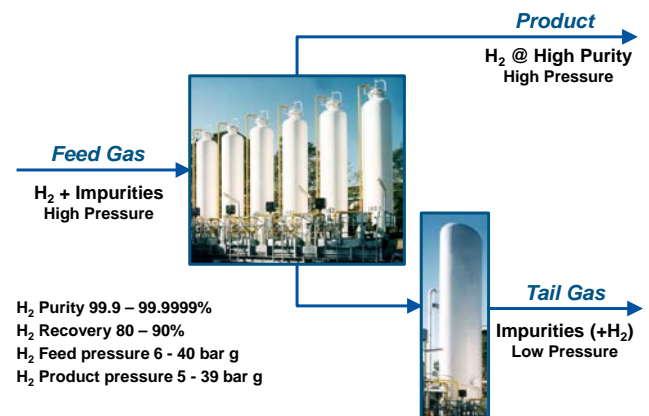


Figure 1: PSA Basic Flow Diagram

A PSA installation consists of five major components:

- Carbon steel adsorber vessels designed for fatigue service
- A selected mix of adsorbent materials
- A valve and piping skid that houses all automatic process switching valves, manual isolation valves, feed, product, tail gas pipe and internal connection headers and local instrumentation, connected to the adsorber vessels
- A tail gas drum to mix the tail gas and minimize the composition variations
- The control system ensuring the correct operation of the PSA unit

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

Feed Gas Composition: The PSA process can handle feed gas with a wide variety of impurities including but not limited to water, carbon oxides, methane, nitrogen and C₂⁺ hydrocarbons. Generally, feed gases containing less than 50 vol-% hydrogen cannot be economically upgraded in a PSA system.

Hydrogen Recovery: Recovery is the ratio of the quantity of hydrogen from the feed that is recovered in the product. Recovery is influenced by product purity, feed composition (nature and quantity of impurities) and pressure conditions.

Feed and Tail Gas Pressure: The adsorption pressure can be fixed by either the available feed pressure or the required product pressure. The feed pressure range is usually between 10 and 40 bar g, with extremes going as low as 6 bar g or as high as 67 bar g.

Product Purity: The product purity requirements influence the recovery, as the difference between 1 or 100 ppm mol of a controlling impurity (CO, N₂, CH₄) demands more or less adsorbent utilization during adsorption.

PSA Adsorbents: UOP develops and manufactures its own zeolites and has other adsorbents custom made. Adsorbents are tailored to meet the application specific demands and project requirements.

Process Cycle Time: The size of a PSA adsorber is proportional to the amount of impurities to be adsorbed per cycle. PSA adsorber size will increase with increasing impurities flow rate during the adsorption step and decrease with the adsorption time.

3. Historical Development of PSA Technology

The development of PSA technology by UOP and its predecessors can be described in terms of five periods (Figure 2).

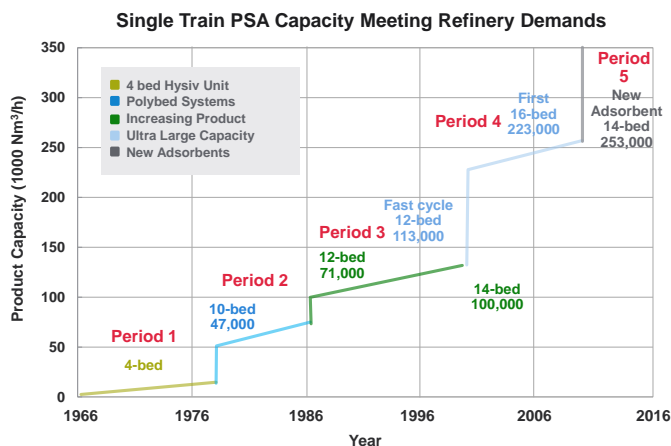


Figure 2: Single Train PSA Capacity Milestones

First Period [1966 – 1976]: 4-Adsorber Hysiv Systems

The industrial story of Pressure Swing Adsorption started in the early 1960s using a 5-step PSA cycle in a four-adsorber in-line configuration and a tail gas drum. The first commercial PSA unit was started up in 1966. The PSA cycle was performed by mechanical stepping switches while the controls relied on hard-wired electronic and pneumatic valves. Hydrogen recovery from feed varied between 65-75% depending on the operating conditions.

The demand for hydrogen in these applications was such that the majority of the PSA systems installed had a product rate between 400 and 1,000 Nm³/h with a few units reaching to 5,000 or even 7,000 Nm³/h.

By the end of the period about 70 units had been started up in the U.S. and Europe under the “Hysiv” trade name to purify syngas from steam reformers and to recover hydrogen from refinery off-gas and ethylene plants.

Second Period [1977-1986]: The Early Large Capacity Polybed™ Systems

PSA technology benefitted from Union Carbide’s developments of tailor-made synthetic zeolites that could be tested in a customized pilot test facility.

In 1976, the Polybed PSA process created an opportunity to go beyond the four-bed configuration and install units with 10 or more adsorber vessels. The first 10-bed PSA system (1975) produced 47,000 Nm³/h of pure hydrogen from synthesis gas from a steam reformer. The Polybed

cycle allowed the design of systems to take full advantage of the feed pressure and to recover more hydrogen. New PSA configurations were used including five-, six-, and eight-bed systems to optimize the performance, the size, and thus the cost control of the PSA system.

This development of PSA technology coincided with the quest for more environmentally friendly transportation fuels. As an increasing number of hydrotreating and hydrocracking units went on stream, more steam reformer units were installed to produce on-purpose hydrogen. The major steam reformer licensors quickly realized that the then standard hydrogen plant flow scheme treatment using two levels of water gas shift carbon monoxide shift reactors, a carbon dioxide wash system and a methanator to convert the remaining traces of carbon oxides to methane could be replaced by a PSA. PSAs produced a pure hydrogen stream that met the requirements of high conversion refinery processes and saved significant operating cost in terms of energy required to regenerate the CO₂ solvent. The PSA yielded higher purity product at 99.9%, compared with 95-97% for the “conventional” process. The PSA also improved energy-efficiency by utilizing the PSA tail gas as fuel to the burners of the steam reformer, hence reducing the intake of feed wasted as fuel. During the same time period, refiners started to understand that recovering hydrogen from secondary refinery streams containing more than 50- mol-% hydrogen at PSA feed pressure saved significant money. A new application known as Refinery Off-Gas PSA emerged and developed to become today’s second largest PSA application.

Developments in control system philosophy and equipment were instrumental to enable the improvements in the PSA technology. The introduction of programmable logic controllers (PLC) allowed for faster and more accurate control and reduction of cycle times. The first computer controlled PSA unit went on stream on a 10-bed PSA system in 1979. The concept of “stacked skid” (1984) introduced the installation of the PSA switching valves on two levels in the skid, coping with plot plan restrictions in crowded refineries.

More than 200 PSA systems were delivered spreading to new geographies such as the Middle East and Far East.

Third Period [1987-1999]: Ever Increasing Product Capacity

The development of high performance adsorbents (1989) produced a generation of units that were smaller and hence cheaper per unit of product, or a better adsorption capacity for specific contaminants. Stringent specifications on transportation fuels and dieselization of fuel market led to a large number of hydroprocessing units being installed together with a dedicated PSA-based hydrogen plant and additional hydrogen recovery from refinery off-gas dedicated PSA systems (Figure 3).



Figure 3: 12-bed Polybed PSA (Belgium)

More than 300 UOP PSA systems were delivered and started up worldwide between 1987 and 1999. Most units were in the U.S. and Europe with new growth in the Middle East, Far East and South America. About 20 PSA systems were installed in non-hydrogen services such as for methane and helium, or monomer recovery and purification. The Polybed PSA Systems commercialized in this period benefited from increased reliability and lower maintenance requirements through specific valve development programs, introducing the use of butterfly valves.

Further optimization of the skid design for maintenance access and reduced bed-mode operation with minimum capacity losses, resulted in the single central skid design as the best configuration. The isolation of vessels in pairs (1988) allow the simultaneous removal of a single pair of adsorbents for maintenance using manual isolation valves that isolate the adsorbents and their valves from the rest of the system, which remains in operation.

The concept of expandable PSA units (1999) resulted in a lower total cost by spreading CAPEX over time synchronized to scheduled future system capacity increases.

Further advances in PLC controller technology (e.g. CPU calculations capacity, memory size, redundancy, etc.), detailed understanding of vessel fatigue designs, the selection of specially designed, and high reliability components resulted in the “zero-downtime PSA” concept. No single failure inside the Polybed PSA system results in a PSA shutdown.

A large number of 10- and 12-bed Polybed PSA Systems started in this period. Some systems produce more than 110,000 Nm³/h pure hydrogen.

Fourth Period [2000-2013]: Ultra Large Capacity Units, First 16 Adsorber Polybed™ System

The demand for pure hydrogen continued to be strong in the first decade of the 21st century. Recovering and upgrading hydrogen from oil sands fields required very large amounts of hydrogen. A new patent enabled this challenge in the most cost effective way. A large PSA patent granted in 2001, resulted in the first (twin) 2x14-bed PSA system, which went on stream in Venezuela (2000). Each train produced 2x100,000 Nm³/h of pure hydrogen (Figure 4). Three years later, in 2003, the first single-train 16-bed PSA system went on stream in Alberta, Canada. This flagship system produces 223,000 Nm³/h of pure hydrogen from a single train steam reformer.

More than 300 Polybed PSA systems were started-up in this period primarily in the traditional three applications – steam reforming, refinery off-gas and ethylene – with plants in North America, Europe, the Middle East, India, South America and Russia. Non-refining applications emerged such as the removal of carbon dioxide at low feed pressure such as from DRI (Direct Reduction of Iron ore) came into being.



Figure 4: Twin 14-bed Polybed PSA (Venezuela, 2000)

Fifth Period [2014-onwards] New Adsorbents

The current generation of Polybed™ PSA systems is characterized by advancement induced by the availability of improved computational capabilities of personal computers and advanced adsorption simulation programs. A new generation of ultra-high-performance adsorbents allows further reduction in the installed adsorbent volume per ton of hydrogen recovered without sacrificing purity or recovery.

CFD (Computational Fluid Dynamic) models help optimizing the flow distribution in the adsorber vessels and designing more effective flow distribution internals.

Detailed piping stress calculations are used in the design of the skid to optimize the selection of pipe wall thickness for the material stress levels caused by the pressure swing.

Modern PLC's have calculation and memory capabilities that go beyond the requirements of a large PSA system. Proven standard PSA software applications interfaced with a fully detailed and customized Human-Machine Interface (HMI) have been developed on several PLC platforms.

UOP and Honeywell have optimized Honeywell's Experion PKS C300 DCS system for PSA sequencing applications, including all optimization algorithms, allowing advanced alarm management, asset management and remote process monitoring from the plant's main DCS. More than 10 PSA systems controlled by the Experion C300 DCS are currently in various stages of project execution, while

almost as many systems have been successfully commissioned and started through July 2015.

PSA's installed in H₂ plants make a separation between H₂ and all other impurities, in order to arrive at a product purity of 99.9% H₂. Executing the removal of CO, CO₂, N₂, CH₄ and H₂O, the PSA replaces the functions of a CO₂ solvent wash system and methanator. Changing the PSA adsorbent mix allows moving the key component for the purification from H₂ to CO₂. This was applied in a large steel plant in Korea (Figure 5) where PSA technology was used instead of a solvent wash for the removal of CO₂ from a reactor effluent, with the aim of maximizing the recovery of H₂ and CO for the downstream iron making.



Figure 5: 20-bed PSA in CO₂ Removal Service (Korea, 2013)

4. Conclusion

Pressure Swing Adsorption has become one of the refinery's key technologies to achieve its operational and economical objectives. In deep conversion refineries, the hydrocracking unit relies on a constant delivery of hydrogen at high purity and controlled impurity levels.

Next to refinery applications, which amount for about 65% of the installed PSA systems, and steam cracker applications (about 15% of the total), the technology has been used in a number of niche applications where sharp separation and high reliability are required (Table 1).

Since its advent in the 1960s, continuous technical developments have supported the wide use of PSA systems in demanding applications. The authors believe that the current state of the technology will continue to be surpassed and that PSA systems of the future will feature higher performance and will be even better integrated in the refining, petrochemical and chemical industry.

Feed Source	Product Largest Single Train Nm ³ /h	First Plant On Stream	No. Plants
Steam Reformer	253,657	1966	437
Refinery Streams	190,612	1971	246
Ethylene Off-Gas	122,793	1968	144
Methanol Off-Gas	39,595	1972	38
Misc. Off-Gas	50,155	1966	51
Partial Oxidation/Syngas	84,169	1974	28
Coke Oven Gas	12,201	1979	19
Natural Gas	7,691	1973	17
Oleflex™ Process Net Gas	56,194	1990	16
Ammonia Off-Gas	58,662	1970	14
Styrene Off-Gas	10,002	1970	12
Chlorine Off-Gas	24,637	1968	11
Steel Industry Gas	150,000	2006	2
Polyethylene	3,117	2001	2
Total Units			1037

Table 1: UOP Polybed™ PSA Applications (July 2015)



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