



BREAKING THE HYDROGEN BARRIER WITH PSA REVAMPS

INCREASING HYDROGEN PRODUCTION OF PSA UNITS





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ABSTRACT

Recent advances allow refiners to revamp PSA units to recover hydrogen at a higher rate or purity with essentially the same equipment through the use of high performance adsorbents and other state-of-the-art techniques. This paper presents the basis for potential changes and discusses five revamp cases of commercial units.

PSA PROCESS

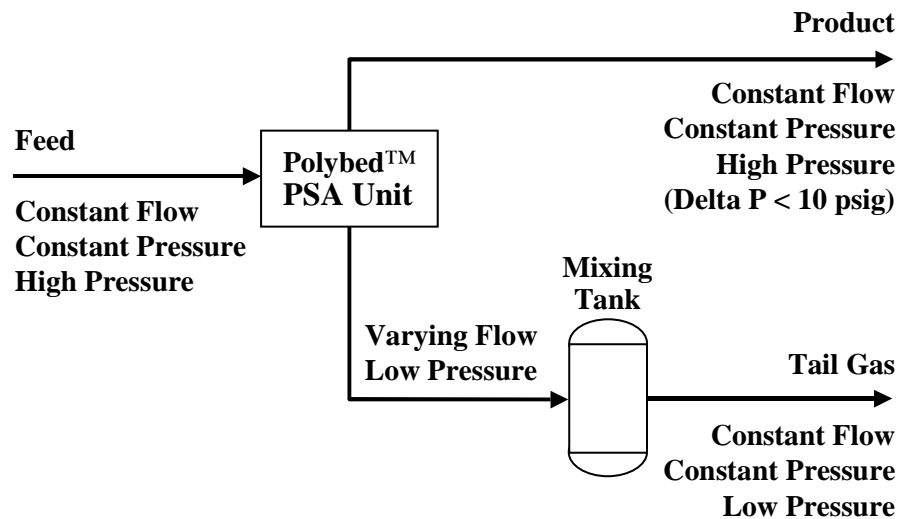
Pressure Swing Adsorption (PSA) units are the industry standard worldwide for purifying synthesis gas in hydrogen plants and extracting hydrogen from valuable off-gases from refining process units. The hydrogen purity is typically over 99.9% with the low concentrations of carbon oxides (CO and CO₂) required for downstream processing units. UOP has provided PSA technology to many industries for over thirty years, with the first unit coming on-stream in 1966, and over 600 others following since then.

The main components of a PSA installation are the adsorbers (steel vessels containing

adsorbents), the valve and piping skid (for all valves and instrumentation), the control system (normally located in a remote control room), and the mixing tank (to minimize the composition variation of the tail gas). A process block diagram follows (Figure 1). Feed gas enters the PSA unit at high pressure; the product is delivered with minimal pressure drop through the unit while the tail gas is typically rejected at low pressure. A PSA unit can be designed to accommodate a wide range of operating pressures, from low pressure up to units approaching 1000 psig.

Figure 1

PSA Installation – Basic Flow Diagram



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The driving force for the separation is the partial pressure of the impurities. The operating principle is simple: at high pressure, impurities are adsorbed from the feed gas, resulting in a high-purity gas product. By stopping the feed and “swinging” the adsorber to low pressure, the impurities are desorbed, exiting in the tail gas. Although the PSA process is a batch process, it uses multiple adsorbents operating in a staggered sequence, so that the unit operates as a continuous process at the battery limits.

A complete pressure-swing cycle consists of the following five basic steps that apply to all PSA units regardless of the number of adsorber vessels:

- Adsorption
- Depressurization
- Cocurrent-countercurrent depressurizations
- Purge at low pressure
- and Re-pressurization

ADSORPTION

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 sequence maintains constant feed and product flows.

COCURRENT DEPRESSURIZATION

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. The hydrogen is used internally in the system to repressurize (equalize) and purge other adsorbers.

COUNTERCURRENT DEPRESSURIZATION

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 depressurizing towards the feed end, and the desorbed impurities are rejected to the PSA tail gas.

PURGE

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

REPRESSURIZATION

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

PRESSURE EQUALIZATIONS

Hydrogen recovery is a function of the number of equalizations (co-current depressurizations) that can be achieved within the system. As a general rule, increasing the number of pressure equalizations increases the hydrogen recovery. For every application there is an upper limit of equalizations required to achieve maximum hydrogen recovery. Once this maximum is reached, adding more pressure equalizations does not improve the hydrogen recovery.

RECOVERY VERSUS CAPACITY

During the design of a new PSA unit, hydrogen recovery is typically maximized so that the sizes of upstream process units can be minimized. Invariably, after installation and startup, refinery demands and hydrogen balances change. This usually requires finding ways to produce additional pure hydrogen for the new needs.

Increasing the hydrogen production of an existing PSA unit is possible without extensive hardware changes. The original design of a PSA unit places the impurity front at the top of the adsorber bed by the end of the cocurrent depressurization step. By modifying the process cycle and reducing the number of equalizations, the impurity front can be located at an intermediate level in the bed. This gives the unit the capacity to handle an increase in feed rate such that the front advances back to the top of the bed again. Essentially, this trades hydrogen recovery for feed capacity. A two to three point decrease in hydrogen recovery as a result of fewer equalizations can lead to capacity increases of 15 to 20%, the net result being a substantial increase in hydrogen production.

Depending on the installed charge of adsorbents, improved hydrogen recovery is accomplished by using high performance adsorbents. In many cases, the recovery can be maintained through a partial adsorbent replacement while the production rates are increased. Recently developed cycles also allow for increased capacity with minimal impact on hydrogen recovery. In all cases, the unit continues to produce on-spec hydrogen product.

For a successful unit revamp, a complete new process design is necessary to check the hydraulics of the unit, and to ensure no adsorbent attrition. Changes in the system can range from simple to complex. Some areas for change are:

- Re-ranging of instrumentation
- Replacement of valve trims
- Replacement of skid valves and piping
- Modifications to adsorber vessel flow distributors
- Partial adsorbent replacement, and in some cases
- Expansion with additional adsorber vessels

The following cases illustrate how UOP helped various refineries break the hydrogen barrier through PSA revamps. In some instances, a simple revamp satisfied local processing needs for many years. In other cases, the PSA unit underwent a continuing transformation throughout its life as the refinery hydrogen needs continued to change.



It is possible to revamp an existing PSA unit to increase the hydrogen production without extensive hardware changes.

CASE 1

A revamp has been completed for a large twelve bed Polybed™ PSA unit in a refinery on the US West Coast. The PSA unit was originally designed in 1987 to produce 85 K Nm³/h (76 MMSCFD) of hydrogen product. After modifications to both the steam reformer and the PSA unit, the PSA unit was revamped to produce an additional 13 K Nm³/h (12 MMSCFD) of hydrogen, for a total product rate of 98 K Nm³/h (88 MMSCFD).

A number of options were considered for expansion of the PSA unit. The greatest capacity and highest recovery were available from a combination of cycle changes coupled with the installation of advanced adsorbents. This refiner selected the lowest-cost route. Modification of the PSA cycle and software with minimal hardware changes allowed for an increase to the 98 K Nm³/h capacity; however, this capacity increase resulted in lower hydrogen recovery. The lower hydrogen recovery also required re-balancing the supplemental fuel to the furnace. The output of the hydrogen plant was then based on the ultimate limit of steam reformer production combined with the PSA improvements. The PSA modifications were completed and the unit restarted within the 2 weeks downtime allowed during a scheduled turnaround.

The benefit of using high performance adsorbents was analyzed as the refiner sought to minimize the impact of the lower hydrogen recovery. The analysis concluded that with the incorporation of higher performance adsorbents, the hydrogen recovery rate would be improved and the ultimate capacity of the PSA unit even further increased. However, the refiner is currently in the design

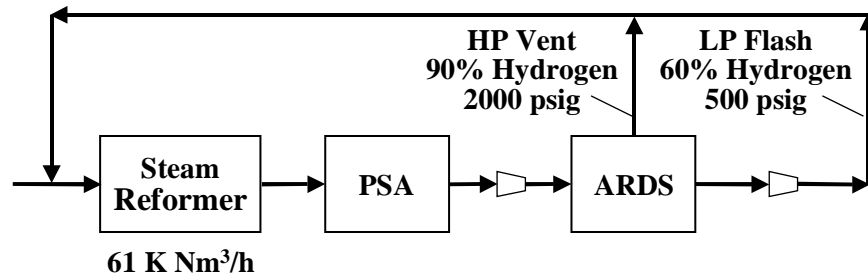
phase of a revamp with a new process cycle requiring piping changes in combination with a partial adsorbent replacement that will achieve hydrogen production rates of over 112 K Nm³/h (100 MMSCFD), while maintaining hydrogen recovery.

CASE 2

In 1983, a large atmospheric resid desulfurization (ARDS) facility in North America was commissioned. The hydrogen make-up for this plant came from a steam reformer hydrogen plant with a product flow of 61 K Nm³/h (55 MMSCFD). The hydrogen plant employed a large 10-bed PSA unit that removed essentially all the impurities, including nitrogen, from the steam reformer effluent.

As designed, the feed gas to the steam reformer was predominately natural gas, and supplemental feed was derived from the high-pressure vent and the low-pressure flash of the ARDS unit. The high-pressure vent was scrubbed of H₂S and throttled down to steam reformer feed pressure, and the low-pressure vent was compressed to match the steam reformer feed pressure. Figure 2 shows the overall flow scheme.

Figure 2
Original Flow Scheme



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To meet the increasing hydrogen needs of the refinery throughout the years, various revamps have taken place as summarized in the table below.

History of Hydrogen Requirement, in Nm³/h

Year	Phase	Steam Reformer	Membrane	CCR	Total
1983	1	61	—	—	61
1987	2	72	6	—	78
1990	3	72	6	56	134
1995	4	95	6	56	157
1995	5	95	6	67	168
Planned	6	95	6	84	185

PHASE 2 - FIRST REVAMP OF STEAM REFORMER PSA

In 1987, a plant expansion was undertaken in which the target hydrogen capacity was increased from 61 to 78 K Nm³/h (55 to 70 MMSCFD). The first capacity increase was achieved through the debottlenecking of the steam reformer and SMR PSA unit to increase the hydrogen output by 18% from 61 to 72 K Nm³/h (55 to 65 MMSCFD).

The SMR PSA debottlenecking was achieved through a process redesign and changes to the control system software with virtually no hardware modifications. This was achieved by reducing the number of pressure equalizations. The unit was able to process more feed gas while still maintaining the original design product specification. This increase in feed capacity more than compensated for the decrease in hydrogen recovery. The net result was an increase in hydrogen production of 18%.

Later, the high-pressure vent stream at over 2,000 psig was routed to a membrane system. The hydrogen product was delivered to the suction of the hydrogen make-up compressor. This change added an additional 6 K Nm³/h (5 MMSCFD) of hydrogen to the refinery hydrogen header.

PHASE 3 - A NEW PSA UNIT

In 1990, a continuous catalytic reforming (CCR) unit was installed and the net gas was fed to a new ten-bed PSA unit. Compressing the tail gas made it possible to maximize the hydrogen recovery in the PSA while still sending the tail gas to the refinery fuel system. This new CCR

PSA unit added an additional 56 K Nm³/h (50 MMSCFD) of hydrogen to the hydrogen balance. Five years later, this unit was revamped, as discussed below (in Phase 5).

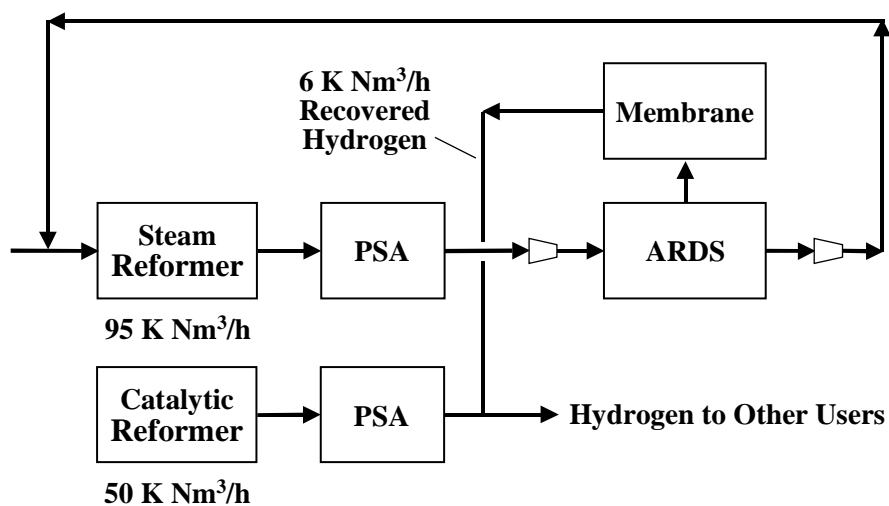
PHASE 4 - SECOND REVAMP OF STEAM REFORMER PSA

A second revamp took place in 1995 to increase the capacity of the Steam Reformer and its PSA from 72 to 95 K Nm³/h (65 to 85 MMSCFD). This additional debottlenecking required modifications to many of the control valves and piping on the piping skid, but maintained the existing adsorber vessels and mixing tanks. As the flow rates had increased by over 50% since the original design, pressure drop problems encountered in the feed, product and tail gas piping had to be overcome. The pressure drops through the unit were reduced to acceptable levels by installing valves with larger discharge coefficients to replace some of the existing valves.

The unit as built had a few common control valves malfunction that caused switchovers to an alternate operating mode that resulted in reduced feed rates. The new cycle was designed so that these common valves were eliminated and the remaining valves on the skid assumed new functions.

Therefore, the reliability of the unit was also increased, as malfunction of any control valve now would cause a switchover to an alternate cycle that could still process full feed rates. Minor modifications were made to the skid instrumentation and the entire control system software was reprogrammed to implement the new cycle. A close working relationship between the refiner, UOP and the valve vendor allowed the revamp design and hardware to be completed, ready for installation, less than six months after the project was authorized. All field modifications were completed during a two-week turnaround.

Figure 3
Revamped Flow Scheme after Phase 4



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PHASE 5 - REVAMP OF CCR PSA

In 1995, the CCR PSA unit was debottlenecked, as additional feed was available from the catalytic reformer. By installing additional tail gas compression and updating the PSA cycle, the unit's hydrogen production was increased to 67 K Nm³/h (60 MMSCFD) while maintaining the original design specifications. The fabrication and installation of the new compressors determined the overall project schedule and the PSA changes were implemented well within the time frame.

PHASE 6 - PLANNED FURTHER EXPANSION

Due to changing demands, the refinery is still hydrogen short and UOP has been asked to evaluate options to further increase the CCR PSA capacity. The 1995 PSA revamp resulted in being able to process all the feed available, and at the time there was some spare tail-gas compression capacity still available. The CCR PSA unit can be further revamped to meet the current capacity demand by fully utilizing the existing compression. UOP and the refiner are in the process of evaluating this additional expansion.

One approach being considered is to make a similar type of cycle change as implemented in the Steam Reformer PSA unit at this plant. Hydrogen production is predicted to increase to 84 K Nm³/h (75 MMSCFD). This revamp will reuse the existing adsorber vessels and adsorbents but would require changes to the existing valves and piping skid. These changes will allow the CCR PSA to produce 50% more hydrogen than the original design and will maintain the hydrogen recovery already obtained from the previous revamp. This revamp design will fully use all the tail gas compressors to their full capacities.

Implementing Phase 6 will bring the total hydrogen availability for this refinery to 184 K Nm³/h (165 MMSCFD), three times the original capacity in 1983.

CASE 3

In 1984 a major refiner in Western Canada started up one of the world's largest facilities at the time, for the production of pure hydrogen. The plant consisted of two identical steam reformer-Polybed PSA based hydrogen plants [each with a product capacity of 31 K Nm³/h (27.5 MMSCFD)] and a Polybed PSA unit to upgrade catalytic reformer off-gas [with a product capacity of 32 K Nm³/h (28.3 MMSCFD)]. The product hydrogen from the three PSA units (SMR1, SMR2 and CCR PSA) was combined and used as make-up to a hydrocracker processing synthetic crude oil.

The refiner wished to process more synthetic crude and, therefore, the demand for hydrogen increased. The catalytic reformer off-gas purity was greater than 90% hydrogen and was deemed

acceptable for direct feed to the hydrocracker when blended with high purity PSA hydrogen. Re-routing the catalytic reformer off-gas from the PSA to the hydrocracker reduced the hydrogen loss to the PSA tail gas, but more importantly, it freed up this PSA for some other use.

The refiner first modified the various PSA units in a number of stages. It debottlenecked the two steam reformers which were then producing over 20% more raw hydrogen than originally designed. The “CCR” PSA was revamped by changing the software and design conditions to allow it to operate on SMR gas in parallel with the original two SMR PSA units. The adsorbent in the CCR PSA was, however, far from optimum for service on SMR gas. Since the three PSA units could easily handle the amount of flow, capacity was not a problem, so a study was made to explore increasing the amount of hydrogen recovered.

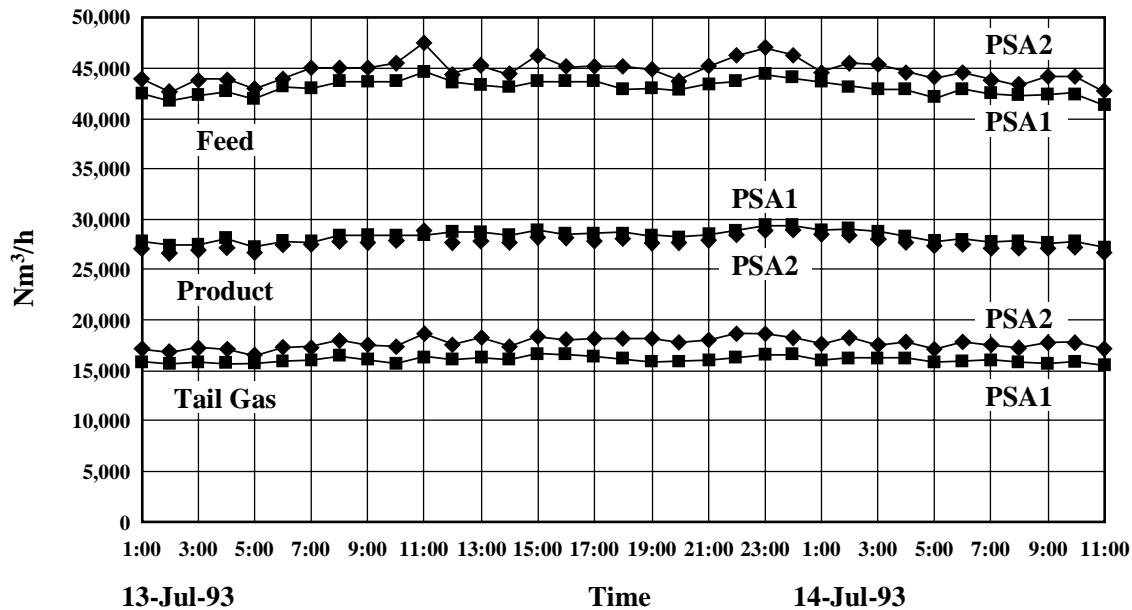
The adsorbent in the PSA originally treating the CCR off-gas was replaced with adsorbent appropriate for SMR gas. This was done in 1988 in conjunction with the first set of vessel inspections, and the PSA’s were “balanced” and optimized for the revised flow scheme. The hydrogen recovery in this one PSA increased over 6% and simultaneously resulted in an improved CO spec on the product hydrogen.

In 1992, the refiner wished to inspect the vessels of the SMR1 PSA. For the inspection, the adsorbent was vacuumed from the vessel through the top flange (manway) and then screened and replaced in its original position. About 15% of the adsorbent was “lost” during this procedure due to screening losses, interface losses and denser reloading. This presented an opportunity to replace the existing adsorbent with higher performance adsorbent to provide higher recovery and capacity.

After reloading with higher performance adsorbents, the previously identical SMR1 and SMR2 PSA trains were in operation side-by-side with advanced and original adsorbents, respectively. PSA1 demonstrated a capacity increase of 10% over the original adsorbent (still installed in PSA2) as well as a 2% increase in hydrogen recovery. (Figure 4 shows these improvements as trends recorded by the distributed control system.) By installing an on-line CO analyzer, the refiner has been able to optimize the units to ensure that they all operate at maximum efficiency.

In 1998, the plant began a project to revamp the refinery hydrogen balance to meet their future needs. A new process unit to be installed in 2001 will require additional hydrogen. The projected flow scheme for 2001 is to redesign the SMR1 and SMR2 PSA units to process the complete output of the two steam reformers. Currently, the entire load from the two reformers is processed through the three PSA units. In order to achieve this capacity increase, it will be necessary to install the same high performance adsorbents in the SMR2 PSA as have already been installed in the SMR1 PSA. The improved characteristics of the high performance adsorbents will allow both

Figure 4
Comparison of Two Otherwise Identical PSA Units



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With high performance adsorbents, PSA1 takes less feed gas to make practically the same hydrogen production. PSA2 takes more feed to make the same amount of product, therefore it makes more tail gas.

units to achieve the desired hydrogen production. UOP has already revamped the SMR1 PSA to increase feed capacity to 66 K Nm³/h (59 MMSCFD), a significant capacity increase over the original design. Although this latest increase had a recovery penalty to process the extra feed gas, the resultant hydrogen production is still 33% higher than the original design.

Increased hydrogen recovery is possible by further using an alternate process cycle. However, this new cycle would have required significant piping and instrumentation changes. The revamp option as selected by the refiner required only minor adjustments to the control valves and minimal new hardware. All of the changes were installed and the unit restarted within one week.

After the revamp is completed on both SMR PSA units, the “CCR” PSA unit will be converted to service purifying ethylene off-gas from the de-methanizer. During another vessel inspection in 1999, the unit was loaded with the optimum adsorbents for the future separation. As losses of 15% are typical during the unloading and screening process, it was decided to make-up with high performance adsorbents. This has allowed an increase in hydrogen recovery for the current operation on SMR gas and also maximizes the recovery for the future. For this unit, it has been decided to install the alternate process cycle changes for the 2001 upgrade. The net result will be

an increase both in hydrogen recovery over the original design and an increase in hydrogen production from the original 32 to 46 K Nm³/h (28.3 to 41 MMSCFD).

CASE 4

A North American ten-bed PSA unit, in operation since 1992, needed to produce hydrogen product with a significant reduction in CO content for use by a new downstream process unit. Although the changes were easy to implement, the revised operation resulted in a loss of hydrogen recovery. As the steam reformer was not able to produce extra hydrogen to compensate for the lower recovery without a major capital expenditure, it was necessary to revamp the system to re-establish the original hydrogen recovery. The revamp took one week to complete, including internal inspection of one adsorber vessel.

	Original Design	Revised Operation	Final Revamp
H ₂ Product Rate	39 K Nm ³ /hr (35 MMSCFD)	38 K Nm ³ /hr (34.2 MMSCFD)	39 K Nm ³ /hr (35 MMSCFD)
Hydrogen Spec	10 ppmv CO	1 ppmv CO	1 ppmv CO
Hydrogen Recovery	86%	84%	86%
Action	Design Basis	Shortened Adsorption Time	Partial Adsorbent Replacement

CASE 5

An Australian refiner installed a hydrogen purification unit in the 1980's designed to produce 5,700 Nm³/hr (5.1 MMSCFD) of hydrogen containing a maximum of 1 ppmv CO. A steam reformer provided the feed. The unit had operating difficulties since the initial start-up and was not meeting its design performance. There were also problems with the hardware on the valve skid. In 1994, UOP contracted with the plant to convert the unit to UOP's Polybed PSA cycle.

For the revamp, UOP installed a new charge of standard adsorbents and converted the cycle. Although the existing adsorber vessels were left intact, changes were required on nearly 50% of the control valves and associated piping. The fieldwork required four weeks to implement.

Following start-up, the unit produced hydrogen that met the specification at the design rates. This hydrogen plant was based on a conventional plant that used a CO₂ removal unit upstream of the

PSA unit. In a typical PSA-based hydrogen plant, the PSA can remove all the impurities present in the steam reformer effluent and thus the plant does not require a methanator, CO₂ removal system or low temperature shift. The PSA unit was redesigned such that the unit had the flexibility to operate with or without the CO₂ removal system. This would allow the plant to shut down the CO₂ removal system for significant savings in utilities and manpower.

In 1999, the plant needed an additional 3,800 Nm³/hr (3.4 MMSCFD) of high purity hydrogen. A gas stream containing hydrogen and hydrocarbons through C₆ was available from a nearby process unit that could serve as feed to the PSA unit. Although the PSA is capable of making virtually any separation, it is imperative that all feed impurities be identified so that the correct adsorbents can be installed in the unit. A PSA adsorber vessel typically consists of multiple layers of adsorbent, each layer dedicated to remove specific impurities. If non-design impurities are introduced, they may not be regenerated from the adsorbent and the unit will irreversibly lose its capacity to remove the design impurities.

UOP determined that the adsorbents installed for steam reformer service were not appropriate for heavier hydrocarbons, so new adsorbents were necessary. The refiner decided to reload the adsorbents with a high performance adsorbent formulation as recommended by UOP.

Cycle changes in conjunction with the new adsorbent allowed the unit to produce 9,500 Nm³/hr (8.55 MMSCFD) from either feed source – the original hydrogen plant or the new refinery off-gas. The field work, including reprogramming of the control system and the adsorbent replacement, were completed within three weeks from the start of the shutdown. The plant now has the flexibility to run a number of feed cases while maintaining a 1 ppmv CO product specification. The refiner can also optionally shutdown an operating unit (CO₂ removal) as noted earlier.

SUMMARY

Substantial improvements have been made in Polybed PSA technology over the past 30 years and the improvements continue to this day. A variety of revamps on existing PSA units are now possible without the expenditure, installation time or lead time associated with a grass roots construction. Revamps can be designed to increase hydrogen production, increase hydrogen recovery, run at alternate operating conditions, improve reliability through control system upgrades, or operate with a new feed stream. It is also possible to run at tighter product specifications to meet current refinery demands while maintaining hydrogen recovery.



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