# Selection and Revamp of Hydrogen Purification Processes

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# ABSTRACT

Increased demand for lighter fuels and products, a desire for higher-performance products, and an insistence on more environmentally acceptable products require refiners to alter processing conditions and technologies so that they can successfully meet the demands of today's society. Although all of these demands relate to product slate or quality, they also have a significant impact on a valuable but often overlooked refinery by-product: hydrogen, which is important as both a commodity and a reactant in the total refinery.

The hydrogen balance in a typical refinery is straightforward: hydrogen supplied by the feedstock leaves in the products, by-products, and wastes. In the 1950s, catalytic reforming provided refiners with a relatively pure hydrogen stream as a by-product of normal refining practice. Refiners had a ready-made source of hydrogen, which could be used as a reagent in the chemistry of their refining schemes. In the 1990s, increasingly demanding product specifications require more hydrogen content in the products as well as removal of contaminants.

To avoid investing in a new hydrogen-producing plant, a refiner with a tight hydrogen balance needs to consider three main issues:
- Maximizing the hydrogen yield from the refinery with particular attention to the primary source: the catalytic reformer.
- Determining the hydrogen required to produce increasing amounts of high-performance products.
- Considering the hydrogen management technologies required to convey hydrogen from the source to the user under the most-appropriate conditions.

This paper compares the three processes for the recovery and purification of hydrogen: adsorption using pressure swing adsorption, permeation using semi-permeable membranes and cryogenics.

The paper then addresses improvements that have been made to existing equipment to increase hydrogen production by either debottlenecking units to increase throughput or increasing hydrogen recovery to improve the hydrogen balance in refineries.

# INTRODUCTION

Although the balance of the hydrogen content in a refinery's feed and products is fundamental to the ultimate product slate that can be achieved, refiners are not entirely left to the whims of Mother Nature to restrict their product slates. In today's refinery, the desired hydrogen content of the products is achieved almost exclusively by reaction. The modern oil refinery consists of several processing operations that either produce or consume molecular hydrogen. Thus, in a practical sense, hydrogen management is the collection of hydrogen from the producers and the distribution of that hydrogen to the consumers. The distribution of the hydrogen often involves purification to ensure the efficient operation of the consuming operations.

Selection of an appropriate hydrogen management technology is crucial to fully utilizing hydrogen sources and hydrogen-rich off-gas streams. The selection of this technology is especially true when the primary source of hydrogen is a catalytic reformer and the continuing drive to greater yields of high-quality products makes the refinery hydrogen balance tight.

When a catalytic reformer is the primary source of hydrogen in a refinery, the technology used to purify the hydrogen source as well as recover hydrogen from off-gas streams for redistribution to consumers clearly plays a crucial role in the refinery material balance. The selection of the appropriate hydrogen purification technology is intimately related to the hydrogen source and the final use of the hydrogen.

# HYDROGEN PURIFICATION TECHNOLOGIES

The purity of the hydrogen available to consumers can have a significant effect on the design and operation of the consuming units which is generally a hydro-processing unit. The three main hydrogen purification technologies used in refineries are pressure swing adsorption (PSA), selective permeation using polymer membranes, and cryogenic separation. Each of these processes is based on a different separation principle, and consequently, the process characteristics differ significantly. Selecting the appropriate hydrogen purification technology depends not only on the economics, but also on such project considerations as process flexibility, reliability, and ease of future expansion. This paper reviews the purification process characteristics and equipment as well as other project considerations for these technologies. General selection guidelines are presented along with process integration that takes advantage of the complementary characteristics of the three processes.

## PSA Process

POLYBED™ PSA units for hydrogen purification are based on the ability of adsorbents to adsorb more impurities at high gas-phase partial pressure than at low partial pressure. This UOP process has been in commercial operation since 1966 for various refinery and petrochemical applications Nearly 600 units are on-stream worldwide. Impurities are adsorbed in an adsorber at high partial pressure and then desorbed at low

partial pressure. The impurity partial pressure is lowered by swinging the adsorber pressure from the feed pressure to the tail gas pressure and by using a high-purity purge gas. Hydrogen is recovered at high pressure and purity. Although cyclic, multiple absorbers are used to provide constant product and tail-gas flows. Commercial units normally use between 4 and 12 absorbers. More absorbers are used to provide higher hydrogen recovery or to increase capacity.

The driving force for the separation is the difference in impurity partial pressure between the feed and tail gas. A minimum pressure ratio of approximately 4:1 between the feed and tail-gas pressure is usually required for hydrogen purification. However, the absolute pressure of the feed and tail-gas is also important, particularly for hydrogen recovery. In refinery applications, the feed pressure is usually in the range of 200 to 500 psig, but more important than the feed pressure is the tail-gas pressure. The optimum tail-gas pressure is as low as possible. Because vacuum is normally avoided, tail-gas pressures of 5 to 10 psig are typically used when high hydrogen recovery is desired. For refinery feed, the PSA tail-gas is frequently compressed from this low pressure to fuel-gas pressure. For steam reformer operation, the PSA tail-gas is normally used at a pressure of 5 psig in low-pressure burners.

Hydrogen is essentially not adsorbed in the PSA process and is available at close to feed pressure: the typical pressure drop between the feed and product battery limits is less than 10 psi. The two key advantages of the PSA process are its ability to remove impurities to any level and to produce a high-purity high-pressure hydrogen product. The purity of the hydrogen product from a PSA unit is typically in excess of 99 vol-% and frequently 99.999 vol-%. Removal of CO and $CO_2$ to a volume level of 0.1 to 10 ppm is common and readily achieved.

**Membrane Process**

POLYSEP$^{TM}$ membrane systems are based on the difference in permeation rates between hydrogen and impurities across a gas-permeable polymer membrane. Permeation involves two sequential mechanisms: the gas-phase component must first dissolve into the membrane and then diffuse through it to the permeate side. Different components have different solubility and permeation rates. Solubility depends primarily on the chemical composition of the membrane and diffusion on the structure of the membrane. Gases can have high permeation rates as a result of high solubility, high diffusivity, or both. The driving force for both solution and diffusion is the partial pressure difference across the membrane between the feed and permeate sides. Gases with higher permeability, such as hydrogen, enrich on the permeate side of the membrane, and gases with lower permeability enrich on the non-permeate side of the membrane because of the depletion of components with high permeability.

The first fraction of the gas to permeate through the membrane consists primarily of the components with the highest permeability. As a larger fraction of the feed gas is allowed to permeate, the relative amount of the components with lower permeability increases in the permeate stream.

In hydrogen separations, higher purity hydrogen is associated with lower recovery, and lower purity hydrogen is associated with higher recovery. The effect of hydrogen purity on recovery is much more dramatic with membrane systems than with PSA or cryogenics units. A fairly small change in hydrogen purity can change the recovery significantly. (Figure 1)

**Figure 1**
**Hydrogen Recovery vs Product Purity**
**Membrane Systems**
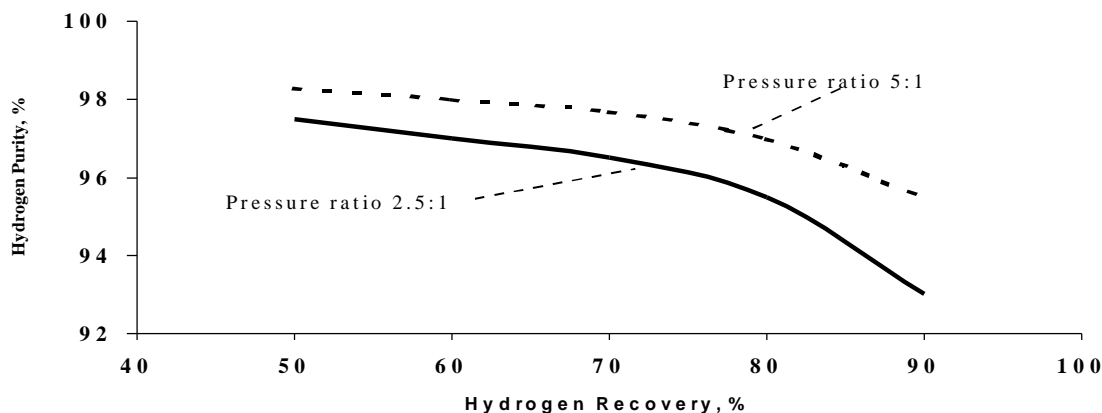


Higher hydrogen recovery also requires that more membrane area be provided. The membrane area required when feed composition and system pressure levels are fixed increases exponentially at high hydrogen recovery. The performance of a specific membrane system, that is, the recovery versus the product purity for a given feedstock, is primarily dependent on the ratio of feed to permeate pressure and is largely independent of the absolute pressure level. However, the area requirement is inversely proportional to the feed pressure. Hence, compressing the feed gas rather than the permeate, even though the permeate flow is smaller, is often preferable when the objective is to achieve the required pressure ratio.

**Cryogenic Process**

Cryogenic units are based on the difference in boiling temperatures (relative volatility) of the feed components. Hydrogen has a high relative volatility compared with hydrocarbons. The process condenses the required amount of feed impurities by cooling the feed stream against the warming product and tail-gas streams in brazed aluminum multi-pass heat exchangers. The refrigeration required for the process is obtained by Joule-Thomson refrigeration, which is derived from throttling the condensed liquid hydrocarbons. Additional refrigeration, if required, can be obtained by external refrigeration packages or by turbo expansion of the hydrogen product.

The partial condensation process is normally applied to hydrogen-hydrocarbon separations. The feed needs to be pretreated to remove water and other components that could freeze in the system. The pretreated feed at high pressure, 300 to 1,200 psig, is cooled against a stream leaving the cryogenic unit to a temperature at which the majority of the $C_2^+$ hydrocarbons condense. The two-phase stream is sent to a separator where the hydrogen-methane vapor stream is taken overhead and further cooled to a temperature low enough to give the desired hydrogen purity. The cooled stream is fed to another separator, and the hydrogen product is taken overhead. Before leaving the cryogenic unit, the hydrogen is heated by heat exchange against the hydrogen-methane from the first separator and the feed. The liquid methane from the second separator is expanded to a suitable pressure so that it will vaporize against the hydrogen-methane stream from the first separator. Additional cooling is provided by expanding part of the $C_2^+$ hydrocarbons product, if necessary.

Thus, the cryogenic unit typically splits the feed into three products: a high purity hydrogen stream, a methane-rich stream at fuel gas pressure, and a $C_2^+$ hydrocarbons product, which may be two phase. By using additional separators, additional products, such as ethane-propane and LPG streams, can also be produced. If the feed stream does not contain sufficient hydrocarbons to achieve the necessary cooling by the Joule-Thomson effect alone, then additional refrigeration can be provided by expansion of the hydrogen product or a package refrigeration system, normally at 5 to -40°F.

## TECHNOLOGY SELECTION CRITERIA

The most-appropriate choice of hydrogen purification technology depends on both performance criteria (hydrogen recovery and feed and product conditions) and operational requirements (flexibility, reliability, feed pretreatment and by-product recovery). These factors are summarized for each of the three technologies previously discussed in Tables 1 and 2. The PSA process requires relatively high hydrogen purity feeds

**Table 1**
**Process Considerations for Hydrogen Purification Technology**

| Factors | PSA | Membrane | Cryogenic |
|---|---|---|---|
| Minimum feed $H_2$, % | 50 | 15 | 15 |
| Feed pressure, psig | 150 - 1,000 | 200 - 2,000 | 200 - 1,200 |
| $H_2$ purity, % | 99.9+ | 98 max. | 97 max. |
| $H_2$ recovery, % | up to 90 | up to 97 | up to 98 |
| CO + $CO_2$ removal | Yes | No | No |
| $H_2$ product pressure | Approximately feed | Much less than feed | Approximately feed |

**Table 2**
**Operational Considerations for Hydrogen Purification Technology**

| Factors | PSA | Membrane | Cryogenic |
|---|---|---|---|
| Feed pretreatment | No | Yes | Yes |
| Flexibility | Very high | High | Average |
| Reliability | High | High | Average |
| By-product recovery | No | Possible | Yes |
| Ease of expansion | Average | High | Low |

(typically above 50 vol-%) at moderate pressures but delivers a high-purity product with little pressure drop and good hydrogen recovery from the feed. PSA units are particularly well suited for purifying catalytic reformer hydrogen for use in hydro-processing units. The high purity of the hydrogen from a PSA unit helps maintain a high recycle gas purity in the hydro-processing unit and the small pressure drop across the PSA avoids excessive recompression duties.

Membrane systems need to operate under sizeable pressure drop to deliver moderately pure hydrogen (typically 90 to 95 vol-%) at low pressure but with high recovery. Such systems are more suited to recovering hydrogen from high-pressure purge gases.

The performance of cryogenic units is similar to that of membrane systems except that the hydrogen pressure loss is much less. The cryogenic process is most attractive when the hydrogen content of the feed is low (30 to 50 vol-%), when the expansion of hydrocarbons provides the necessary cooling without external refrigeration.

Cryogenic units allow the simultaneous recovery of by-products, such as ethane and methane. However, they are handicapped by poorer reliability and flexibility and require significant feed pretreatment.

Although the cryogenic process is thermodynamically the most-efficient hydrogen purification processes, the PSA process is the most commonly selected hydrogen purification technology, despite its lower hydrogen recovery. This lower hydrogen recovery is more than compensated for by the flexibility of operation, the high reliability, and the ability of the adsorption process to produce high-purity, high-pressure hydrogen. If higher hydrogen combined with by-product recovery is needed the integration of a PSA unit with a cryogenic unit can provide the required high-purity hydrogen at high overall recovery. This subject is described in the paper by Pacalowska, Whysall and Narasimhan.

# PSA Revamps

Recently, many refineries and chemical plants have faced a hydrogen shortage. Revamping existing PSA units for additional hydrogen capacity is an option that offers attractive economics. Many PSA units continue to operate today at original design capacities and performance. Since their original design, a number of developments have increased both capacity and performance. Cycle modifications have demonstrated increases in capacity in excess of 15%, and new adsorbents offer better performance.

To increase the recovery of hydrogen in a PSA unit several co-current depressurization steps are made to transfer the hydrogen that is present in the voids to another adsorber, which is at a lower pressure, either on the purge step or during repressurization back to feed pressure. Adding to the number of depressurization and repressurization (equalization) steps increases the hydrogen recovery, but the amount of adsorbent required to keep the impurities trapped also increases (Figure 2).

**Figure 2**
**Relationship between Hydrogen Recovery and Adsorbent Quantity**
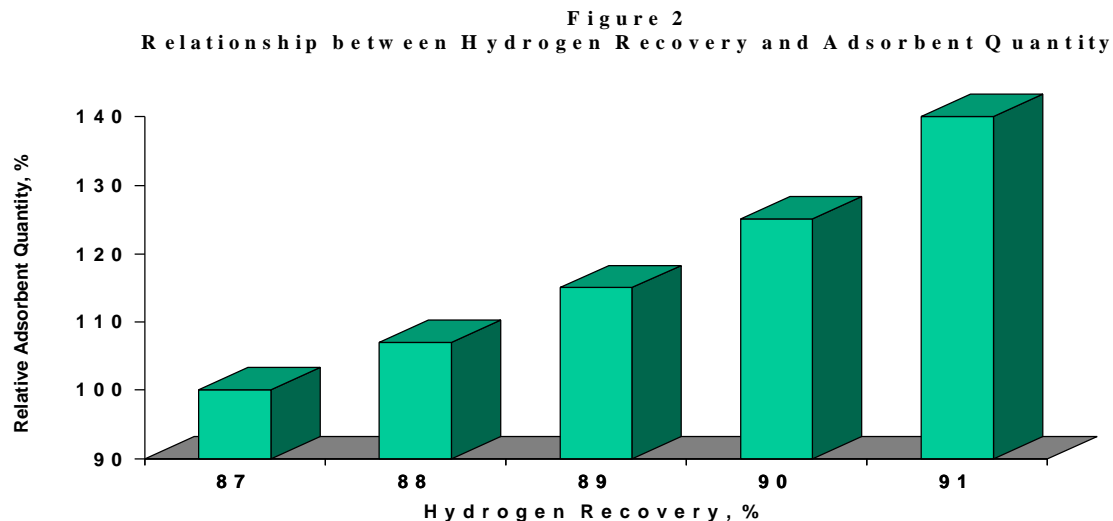


In an existing unit, the quantity of adsorbent is fixed, but reducing the number of co-current depressurization steps, which effectively frees up adsorbent capacity, allows significant increases in the feed rate to the PSA unit and only a small decrease in hydrogen recovery. Capacity increases of up to 40% have been achieved by this type of revamp. The maximum capacity increase is normally set by hydraulics limitations: frequently by the pressure drop over the hydrogen product valves. Development in the last 10 years has resulted in a new generation of adsorbents with superior mass transfer characteristics. Using these adsorbents can give either an increase in capacity or hydrogen recovery. In some cases the loss in hydrogen recovery as a result of reducing the co-current depressurization steps can be largely compensated for by replacing part of the original adsorbent charge.

# PSA AND MEMBRANE INTEGRATION FOR DEBOTTLENECKING

In 1983, a large atmospheric residuum desulfurization (ARDS) unit was commissioned. The hydrogen make-up for this plant came from a steam reformer with a product flow of 55 MM SCFD; the purification of the steam reformer effluent used a 10-adsorber PSA unit. As designed, the feed gas to the steam reformer was mainly natural gas supplemented with the high-pressure vent and the low-pressure flash gases from the ARDS unit. The flow scheme is shown in Figure 3.

**Figure 3**
**Original Refinery Flow Balance**
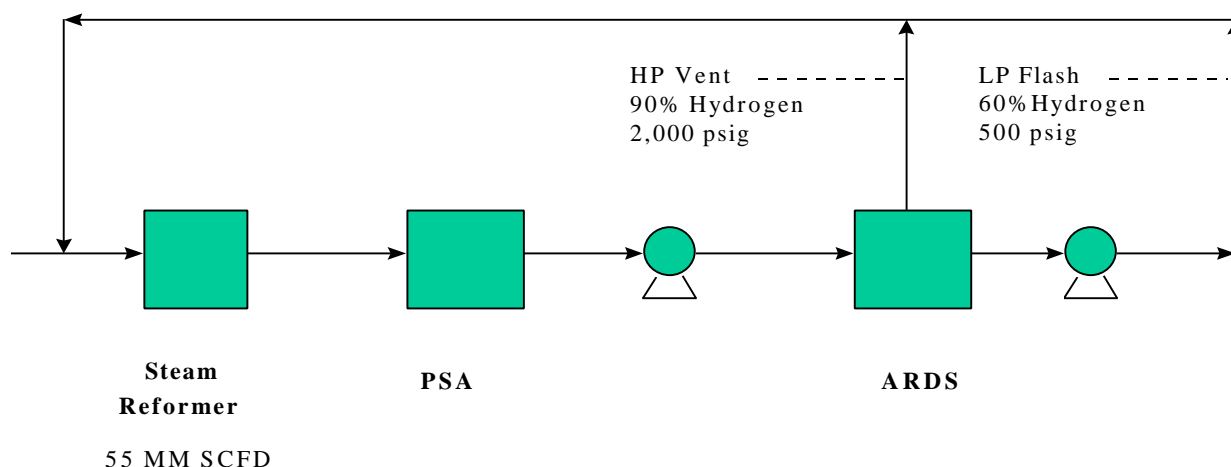


In 1987, a plant expansion was undertaken, and the target hydrogen capacity was increased from 55 to 80 MM SCFD. The first capacity increase was achieved by debottlenecking the steam reformer and its associated PSA unit to increase the capacity by 18%, from 55 to 65 MM SCFD. This increase was achieved through a process redesign, required reprogramming of the control software and essentially no hardware changes.

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 a further 5 MM SCFD of hydrogen to the refinery balance.

A second PSA unit was proposed to purify the low-pressure flash gas from the ARDS unit combined with the non-permeate from the membrane unit and to deliver the product to the suction of the make-up compressor. This change would have increased the amount of available hydrogen to the desired 80 MM SCFD. Implementation of this change is still pending. The revamped scheme is shown in Figure 4.

**Figure 4**
**Revamped Refinery Flow Balance**
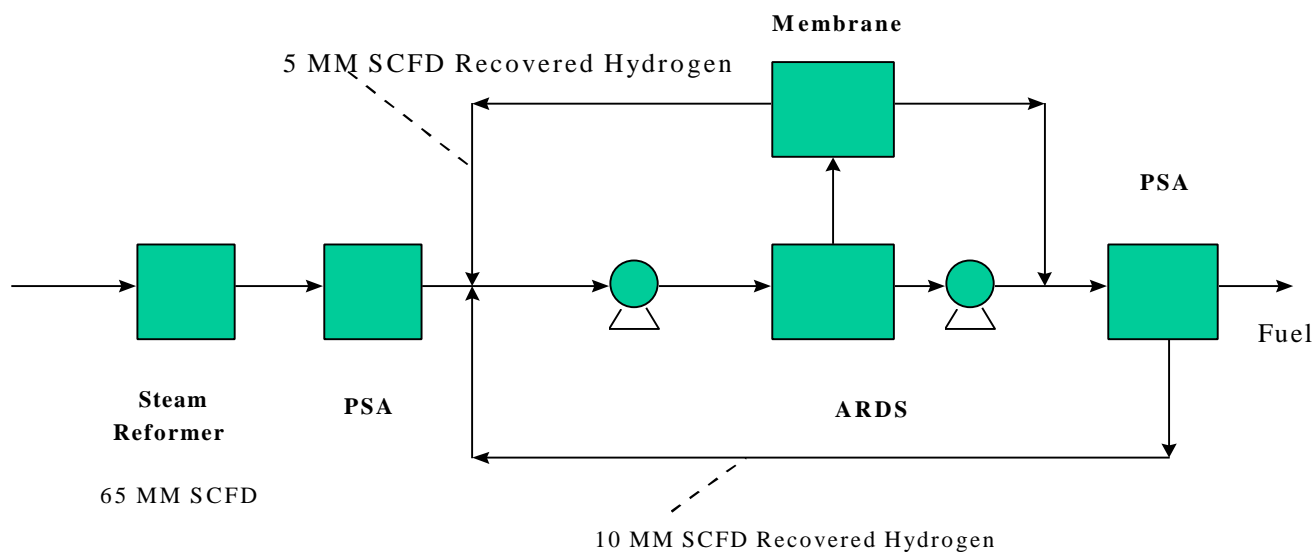


## SUMMARY

As the product slate of refineries shifts further toward lighter products with enhanced performance and cleaner properties to meet environmental considerations, the more important effective hydrogen management becomes. Careful consideration should be given to the purification and utilization of the hydrogen produced from existing units before the additional investment in a steam reforming hydrogen plant is considered.

Catalytic reforming is still often the main supplier of hydrogen in a refinery. The technology is continually evolving to produce increasingly higher yields of hydrogen, although for the low-pressure CCR Platforming™ process, the hydrogen yield is approaching the theoretical maximum. By applying hydrogen management technologies and by carefully selecting the appropriate hydrogen purification technology, refiners can make efficient use of the hydrogen contained in the crude.

## REFERENCE

Pacalowska, B., Whysall, M., and Narasimhan, M. V. "Improve Hydrogen Recovery from Refinery Offgases", *Hydrocarbon Processing*, Nov. 1996.