

Recovering Hydrogen — and Profits — from Hydrogen-Rich Offgas

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As demand for industrial-grade hydrogen increases, more facilities are recovering H₂ from offgas and selling it. Several recovery technologies are available, each with its own strengths and limitations.

Hydrogen is an integral part of many industrial processes, and its consumption is expected to increase as government mandates and consumer preferences drive demand for cleaner fuels. Although most industrial-grade hydrogen is produced intentionally, hydrogen can also be recovered from chemical-, olefin-, and gas-processing streams. In some cases, combustion is used to recover hydrogen's fuel value, downgrading the value of the hydrogen off-gas stream. However, this approach is not always economical, because the thermal energy supplied by hydrogen can cost about 11 to 15 times more than the equivalent amount delivered by natural gas.

A more profitable and efficient way to capture hydrogen's full value is by capturing and purifying hydrogen from offgas and repurposing it for industrial use. Several recovery technologies are available to do this.

Growing demand makes hydrogen recovery a more attractive option. Industry trends, including fuel desulfurization, lower quality crude sources, and projected growth in the use of fuel-cell-powered vehicles, will increase the need for hydrogen and for more profitable sources of the gas.

Today, many industrial warehouses use hydrogen for fuel-cell-powered forklifts, which take less time to charge and run longer than traditional combustion- or battery-powered vehicles. Also contributing to increased hydrogen demand is growth in important chemical manufacturing and industrial markets, such as electronics chemicals, glass manufacturing, and annealing atmospheres for metals processing. All of these markets can be served by sources of merchant hydrogen that are either deliberately produced or recovered as a byproduct of other processes.

Various processes generate hydrogen-rich offgases, among them ethane steam cracking, propane and butane dehydrogenation, chlor-alkali processing, and catalytic reforming. This article examines different techniques that are available for recovering and purifying hydrogen from these streams and reviews the economic drivers behind these techniques. It also examines two cases of hydrogen recovery and identifies feasible technologies based on criteria that include hydrogen purity, volume, geography, demand, and supply mode.

The true value of hydrogen

To quantify the value lost by burning hydrogen as fuel, consider the cost of natural gas and hydrogen relative to the lower heating value (LHV), or net calorific value, of each. For example, a pipeline-supplied hydrogen consumer on the U.S. Gulf Coast can pay three to four times more for hydrogen, on a volumetric basis, than for natural gas. However, the LHV of hydrogen, at 274 Btu/scf, is roughly one-third that of natural gas. This disparity puts the real cost of hydrogen used as fuel gas at 11–15 times that of natural gas used for the same purpose.

Depending on the quantity and purity of hydrogen offgas streams, recovered hydrogen can be recycled to the front end of the process or, in some cases, sold to a third party. Significant cost savings and productivity improvements can be realized by installing a hydrogen-recovery system.

Purification techniques

To maximize their value, hydrogen-rich offgas streams must first be cleaned of process-specific impurities. Membrane separation, pressure swing adsorption (PSA), and

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Table 1. Hydrogen-purification techniques are available to meet a wide range of process conditions.

Parameter	Membrane Separation	Pressure-Swing Adsorption	Cryogenic Distillation
H ₂ Purity	90%–98%	99.9+%	95%–99%
H ₂ Recovery	85%–95%	75%–92%	90%–98%
H ₂ Product Pressure	< Feed pressure	Feed pressure	Feed/Low pressure
Feed Pressure	300–2,300 psig	150–600 psig	>75–1,100 psig
H ₂ Feed Content	>25–50%	>40%	>10%
Byproduct Capability	Poor	Poor	Excellent
H ₂ Capacity	1–50+ MM scfd	1–200 MM scfd	10–75+ MM scfd
Pretreatment Requirements	Minimum	None	CO ₂ , H ₂ O removal
Capital Cost	Low	Medium	Higher
Scale Economics	Modular	Moderate	Good
Startup Time	Minutes	Minutes	Hours

cryogenic distillation are the predominant technologies available to clean offgas hydrogen streams and likely to be the most financially beneficial (Table 1).

Membrane separation with polymeric membranes

Membrane separation exploits differences in gas permeability through a polymer membrane (Figure 1). The gas first dissolves into the polymeric membrane, then diffuses through the thickness before again dissolving into the bulk on the opposite side. Polymer structure and composition dictate the solubility of different gases in the polymer, and the rate of permeation is tied to pressure differential (*I*). Thus, designs that employ high feed pressures (>300 psig) are more economical.

The purified hydrogen stream exits the membrane as permeate, but incurs a pressure drop of at least several hundred psi. Impurities, which have lower relative rates of

permeation, remain largely in the retentate, exiting the membrane at essentially the feed pressure.

Since membranes are typically arranged in modules of parallel banks, they are not subject to economies of scale and are well suited for small- to medium-size operations. A membrane system is very simple to start up and operate, and allows for improved control of product purity. The desired level of hydrogen purity can be reached within minutes of startup, which consists of opening the feed and product valves. Hydrogen membrane separation is most commonly used to adjust the hydrogen-to-carbon-monoxide ratio of a synthesis gas (syngas) stream (*I*).

Hydrogen membrane separation systems have some limitations, however. They

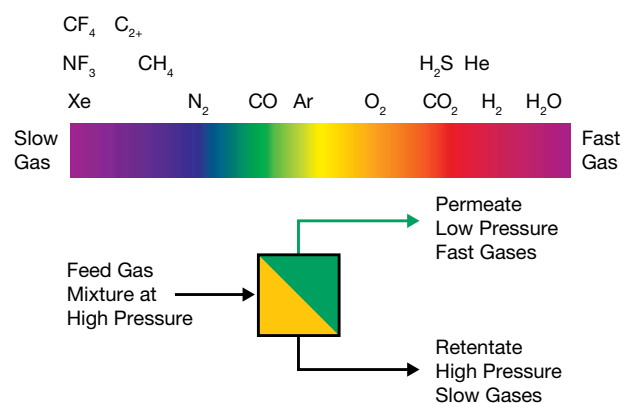
may be capable of separating hydrogen from a bulk impurity, but they are not suitable for producing a high-purity product stream. Consequently, membranes are used primarily when high purity is not required, and their use depends highly on the feed pressure and the major impurity involved. While it is possible to use membrane separation to generate hydrogen of up to 98% purity, 95% purity levels are more typical of membrane separation (*I*).

In addition, corrosive or highly acidic compounds, such as hydrogen sulfide, can degrade the membrane bundles, which may not be fit for use in process environments where these chemicals are found. Membranes are also vulnerable, and may be permanently damaged by liquids and saturated feeds. As the permeate is separated, the concentration of the retentate impurities increases, causing condensation in saturated feeds. Therefore, saturated feeds must be heated well above the dew point of the offgas if this separation method is to be used.

Pressure-swing adsorption

PSA systems can produce ultrahigh-purity (up to 99.999% pure) hydrogen. They can operate at high or low pressure, but they require complex control schemes and have higher capital and operational costs. PSA unit operation has become widely popular in the chemical and refining industries due to its versatility and ability to be tailored to specific applications. For example, refinery offgas can be purified in a PSA system, which provides refineries a way to recover pure hydrogen from streams that contain light hydrocarbons.

Recovering pure hydrogen from an offgas stream is more valuable than sending the entire stream to fuel for use in power production. PSA's key strength in this application is its ability to adsorb compounds such as hydrogen sulfide, hydrocarbons, carbon oxides, and water. PSAs can also



▲ **Figure 1.** Gases diffuse through polymeric membranes at different rates.

deliver purified product at nearly the same pressure as the feed. In addition, the pressure drop over a PSA's adsorbent bed is negligible compared to that of a membrane system.

PSA works on the principle that, at elevated partial pressure, molecular sieve adsorbents can retain a larger volume of gaseous components, some stronger than others. Adsorption strength typically increases with the molecular weight of each component, and hydrogen has the weakest strength of adsorption of these components (Figure 2). This allows heavier components to be adsorbed while the purified hydrogen passes through.

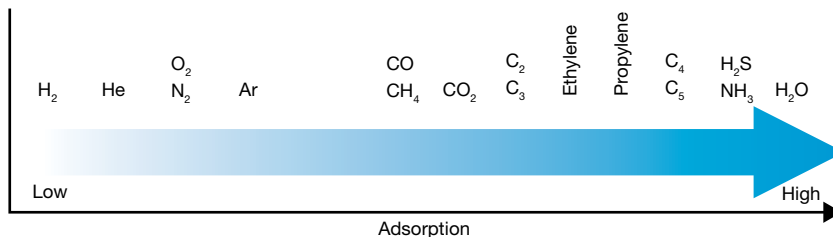
In a typical PSA cycle (Figure 3), the feed passes over an adsorber bed at high pressure, where the heavier components adsorb, leaving behind a pure hydrogen stream at the end of the bed. The bed slowly becomes saturated with impurities and eventually these impurities start to leak through. The feed then switches to a fresh bed, and the saturated bed depressurizes to regenerate, desorbing all of the heavier components into the tail gas stream.

Typically, a PSA system contains two trains of adsorbers, each with four to six adsorber beds. The purified hydrogen comes off at near feed pressure, while the tail gas is at very low pressure (~5 psig) to maximize recovery. To maximize product recovery, these functions occur during four to 12 discrete processing steps.

A pressure-swing adsorber may be complex to control, but it is relatively simple for an operator to handle. Control is typically by a programmable logic controller (PLC) and involves precise depressurization and repressurization steps between beds. Bed cycle time must be closely controlled to prevent oversaturation of the bed, which can result in off-spec hydrogen.

Temperature is a critical factor in PSA operation, because high temperature reduces the adsorption capacity and increases the capital cost of recovery. The unit's operating temperature should normally be kept in the range of 70–150°F. In addition, the feed stream should be brought to ambient temperature to condense and separate water and organics before they can enter the adsorbent beds.

High or highly variable concentrations of heavily adsorbing components can adversely affect the operation of PSA, precluding its use in such applications. In addition, PSA systems have lower turndown capabilities than membrane units. However, if dual trains are installed, it is possible to improve the turndown capability by running a single train.



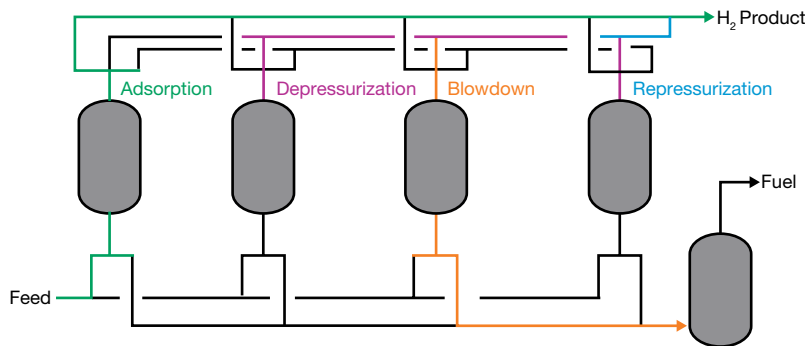
▲ **Figure 2.** The suitability of pressure-swing adsorption depends on the adsorption strength of the gas, which typically increases with molecular weight.

Cryogenic separation

Cryogenic distillation (Figure 4) is much more capital- and energy-intensive than membrane separation and pressure swing adsorption, as well as operationally challenging. For these reasons, using cryogenics to purify hydrogen offgas is less common. Cryogenic separation is typically employed to purify and separate a syngas stream with significant hydrocarbon impurities or when a syngas or carbon monoxide product is desired. Because the adsorption and permeation rates are very similar for carbon monoxide and methane, separating these components is difficult and inefficient by any means other than cryogenics. Although membrane and adsorption systems have been designed to separate these components, cryogenic separation remains the primary technology used for this purpose.

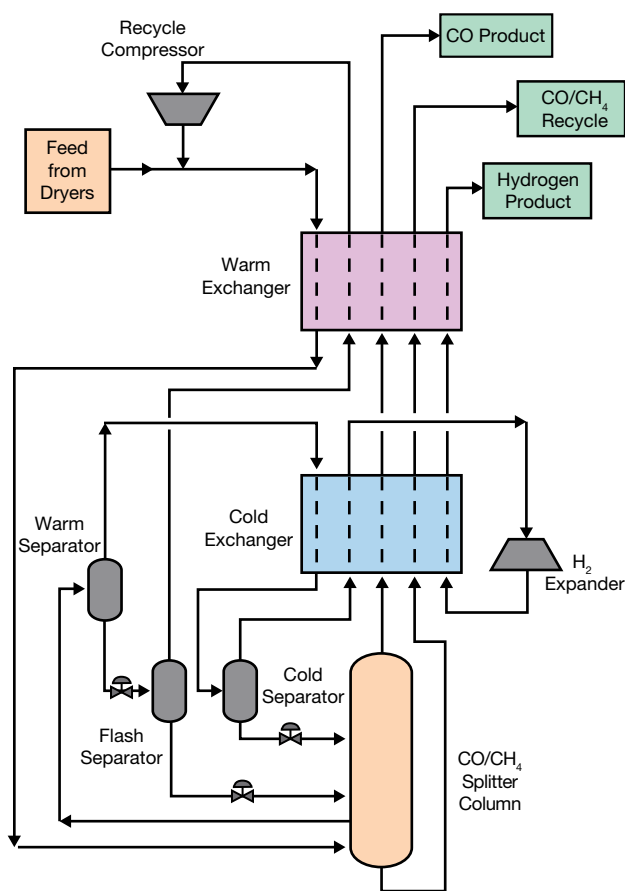
Various cryogenic solutions have been optimized for hydrogen recovery. Selecting the best option depends on syngas quality and overall product specifications. The two main process schemes for cryogenic purification of a syngas that contains methane are partial condensation and methane wash (1). Both approaches require the offgas stream to be dried of compounds that would freeze at cryogenic temperatures and affect plant operation — specifically water, carbon dioxide, and heavier hydrocarbons.

Partial condensation separates hydrogen from carbon dioxide in a series of flash separators followed by a carbon monoxide/methane splitter column to produce a moderate-



▲ **Figure 3.** A typical PSA installation involves several operations: adsorption, depressurization, blowdown, and repressurization.

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▲ **Figure 4.** Cryogenic distillation is the most capital-intensive hydrogen recovery process, but it is highly effective for streams that contain methane.

purity carbon monoxide product. With modifications, the process can achieve higher purities at the expense of efficiency (1).

In the methane wash process, liquid methane absorbs carbon monoxide and methane, leaving a higher-purity hydrogen product stream. The carbon monoxide/methane liquid is then fed to a flash column that removes dissolved hydrogen followed by a carbon monoxide/methane splitter. The splitter column uses a liquid carbon monoxide recycle to achieve higher purity than the standard partial condensation scheme (1).

The level of methane and hydrocarbon impurities is the driving factor for syngas separation by cryogenic distillation. Without those impurities, membranes can be more efficient in adjusting the syngas ratio.

Selling hydrogen-rich offgas

Logistics and profitability for the purchaser are major factors that can help determine whether or not to recover and sell hydrogen. Selling hydrogen-rich offgas is feasible

when the source is located within the immediate vicinity of a hydrogen pipeline or end-user plant. Catalytic reforming is one example of a process with profitable location synergies for hydrogen, since the gas recovered from this process can easily be used within a refinery's hydrogen network for hydrocracking, hydrotreating and other petrochemical processes in close proximity (2).

If hydrogen is not fed by pipeline or over-the-fence piping, it must be transported either as a high-pressure gas or as a cryogenic liquid. This requires a cryogenic hydrogen compressor system, which can be easy to install, is reliable, and with load-following improves efficiency.

However, high-pressure compression or liquefaction adds capital and operating costs that must be minimized through local market demand for hydrogen use in chemical synthesis or for fuel cells. Hydrogen fuel cells are a growing market for compressed and liquefied hydrogen, which is used by hydrogen energy stations for power generation and by hydrogen fueling stations to power forklifts, automobiles, buses, and other vehicles.

Case 1: Ethane steam cracking offgas in the Marcellus Shale Region

Ethane steam crackers produce ethylene and propylene, which are the basic building blocks in the production of many organic chemicals, plastics, and synthetic fibers. Large quantities of hydrogen-rich offgas are also produced as a byproduct of the high-temperature cracking reaction. The cracked gas is quenched, compressed, and then separated to remove the light hydrogen-rich offgas from the olefins.

Developments in hydraulic fracturing and horizontal drilling of shale deposits in North America have spurred growth in the production of ethylene from natural gas liquids (ethane and liquefied petroleum gas). This abundant supply and growing capacity have reduced the price of natural gas liquids and increased the profitability of ethylene and propylene production. Thus, an ethylene plant is in a good position to purify and sell its offgas stream, which can contain more than 80% hydrogen, with the major impurity being methane (3).

As previously discussed, separating impurities from a hydrogen-rich offgas stream can be easily accomplished with a PSA or membrane system, depending largely on the required purity. Assuming that a high purity is required to allow the most versatility in marketing the byproduct, PSA is a viable option. A hydrogen stream of this size requires a dedicated plant on the customer's site or pipeline access to accommodate the large supply of hydrogen.

With no pipeline availability in eastern Ohio or western Pennsylvania, a dedicated customer plant is the preferred option for offloading a large quantity of hydrogen-rich off-

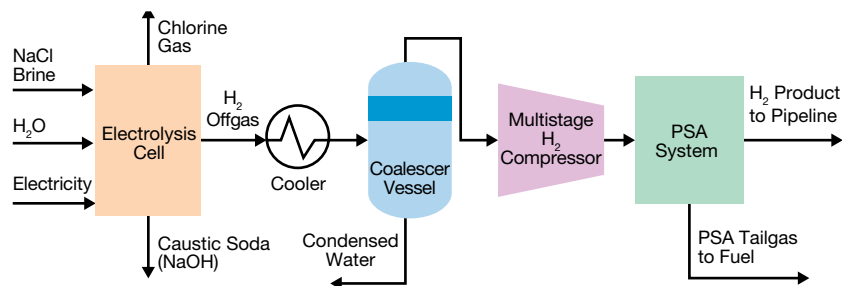
gas. An ethylene producer may also decide to consume the hydrogen internally in a process such as large-scale hydrogenation or hydrotreatment. Many petrochemical processes use hydrogenation to react hydrogen with organic compounds, while refineries use hydrotreatment to reduce sulfur, nitrogen, and aromatics content.

Case 2: Chlor-alkali offgas in the Gulf Coast

The chlor-alkali process is the most common method of producing chlorine gas and sodium hydroxide (caustic soda) for use in basic chemicals. An electrochemical cell with either a diaphragm or a membrane electrolyzes a solution of water and sodium chloride into hydrogen, chlorine gas, and sodium hydroxide (Figure 5) (4). The byproduct of this reaction is hydrogen, which can be recovered for use in manufacturing industrial chemicals. Hydrogen generated during the chlor-alkali process is relatively pure at 90–95%; depending on the process used, the major impurities are water (with a membrane cell), or water and oxygen (with a diaphragm cell) (4). The case illustrated here uses a membrane cell, with water as the only impurity.

The producer in this example is located in the U.S. Gulf Coast region and is adjacent to a hydrogen pipeline that supplies high-purity hydrogen at 99.999%. Because high purity is required, the offgas must be processed in a PSA system. The relative permeation rates of hydrogen and water are too close for a membrane system to separate these components; even if the permeation rates were dissimilar, a membrane system would not be able to achieve the desired purity. The hydrogen that exits the PSA is very pure and can be fed into a hydrogen pipeline or bulk gas container following compression. Capital equipment needed includes the PSA system, a multistage reciprocating feed compressor, and associated process control equipment.

Because a pipeline is located in the immediate vicinity, this opportunity has very low operating costs. At this volume, hydrogen recovery for merchant gas sale would



▲ Figure 5. Relatively pure hydrogen can be recovered from the chlor-alkali process.

be less profitable, however, because the capital and operating costs of a high-pressure or bulk liquid terminal are high.

The financial benefit of recovering hydrogen from a chlor-alkali process can be significant. Therefore, some chlor-alkali producers have incorporated this process as part of their business plan and standard plant operations.

Closing thoughts

Hydrogen recovery from industrial processes is becoming an increasingly important source of hydrogen. The revenue potential of capturing and purifying an offgas stream for use in other industrial applications can be significant. When hydrogen offgas is burned for fuel or vented to the atmosphere, some or all of its value is lost. Technologies such as membrane separation, pressure-swing adsorption, and cryogenic distillation enable this byproduct to be captured, purified, and recycled. Choosing the right technology for hydrogen recovery is critical to achieving maximum profitability, reliability, and market potential. The location of hydrogen-rich offgas generation plants and proximity to key markets are also key factors in maximizing the value of recovered hydrogen. ◆

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