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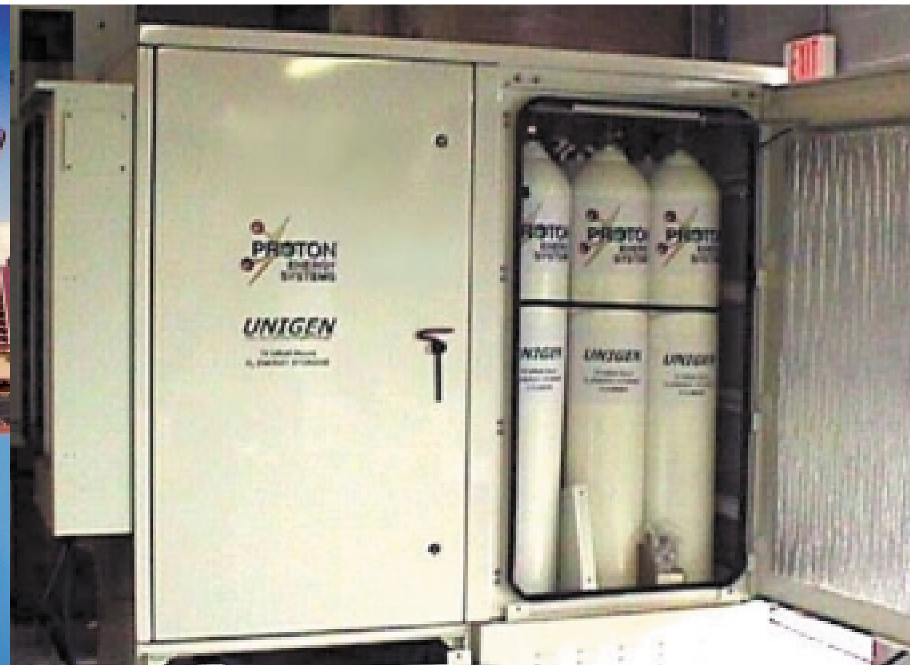


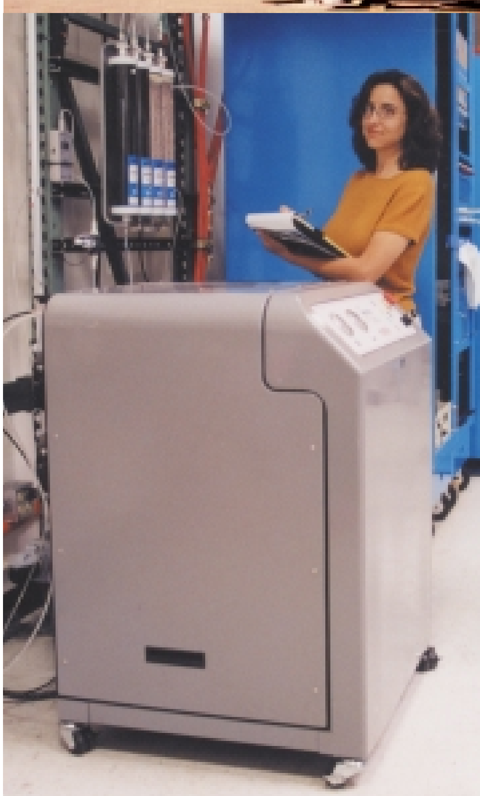

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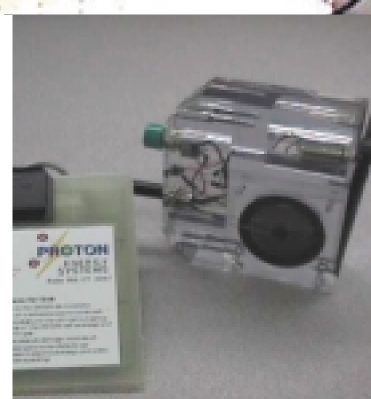


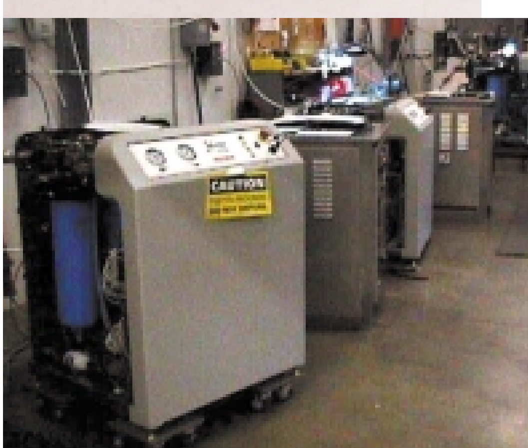


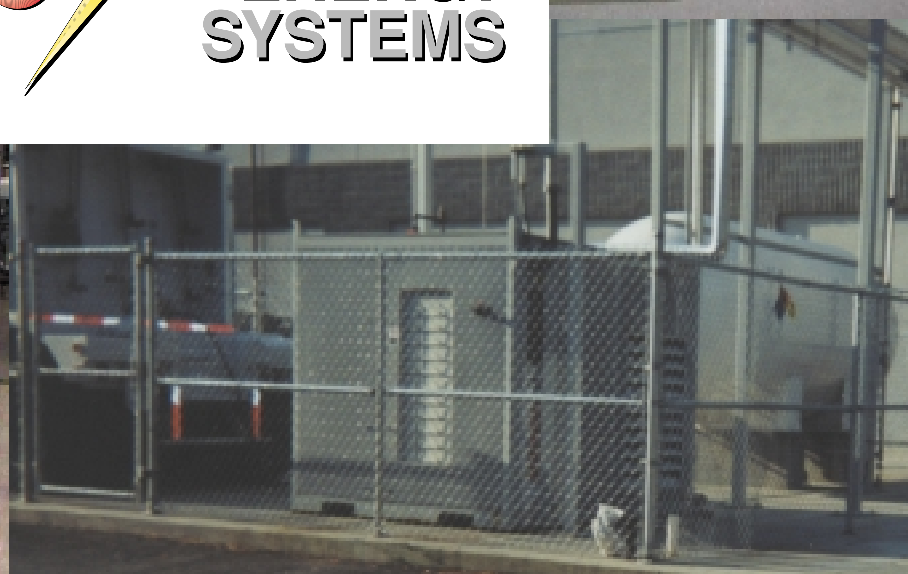

# Producing Hydrogen On-site

## New technologies offer options to the chemical industry

By David Wolff

Hydrogen gas is crucial to many chemical and industrial processes — oil processing and other hydrogenation processes, chemical reduction processes, heat treatment, powder metallurgy applications, nanomaterials production, electric generator cooling and glass manufacturing.

Like other industrial gases such as oxygen and nitrogen, hydrogen can be supplied by industrial gas producers. Unlike other industrial gases, however, hydrogen is not produced from air distillation, and historically it has been more difficult and expensive to supply in small quantities than the air-derived gases. Large-volume users can supply hydrogen relatively inexpensively from large on-site generation plants.

United States-based users too small to justify a traditional large on-site generation plant may be able to afford the delivery of liquid hydrogen, a convenient and relatively inexpensive form. Outside the United States, liquid hydrogen is generally unavailable, and hydrogen usually is supplied to most users in the form of pressurized gas, which is expensive and difficult to supply on a reliable basis.

### Hydrogen supply mechanisms

Until recently, hydrogen gas was available in on-site production form to only the major users — most other users purchased it in compressed gas form in cylinders or tube trailers, or in liquefied form. These types of product deliveries were used in the early 1900s for oxygen and nitrogen. On-site nitrogen and oxygen technologies introduced over the past several decades have expanded the use of these gases in the chemical processing industries dramatically by offering improved flexibility, economics, supply options and safety over liquid or compressed gas deliveries.

New on-site hydrogen production technologies promise to ease the hydrogen-supply problems of small industrial applications by reducing the scale, cost, complexity and manpower required to produce the gas on-site.

Increased interest in a new generation of hydrogen-fueled vehicles has fueled hydrogen-producing technologies. The commercialization of these technologies has led to new supply options for on-site hydrogen production applicable to smaller-volume users. These technologies include advanced electrolytic technologies, which use electricity to make hydrogen; small-scale reforming technologies, which crack hydrocarbons to produce hydrogen; and chemically derived hydrogen supply systems, which use chemical hydrides as hydrogen carriers.

### Hydrogen supply costs

Hydrogen delivered to a customer's site, whether in liquefied or compressed form, first must be:

- Produced.
- Purified.
- Compressed (and optionally liquefied).
- Packaged.
- Loaded.
- Transported.
- Delivered to the customer.
- Metered or counted.
- Billed.

Each of these steps adds to the supplier's hydrogen cost and, therefore, to the customer's price. Many of the cost factors are rising faster than expected because they depend directly on the cost of natural gas, motor fuel, labor and hazardous material compliance, all of which are rising rapidly.

### Compressed hydrogen

For hydrogen customers, buying gas in cylinders or tube trailers is an excellent method to start out or to pilot new applications. The cost structure in the industrial gas industry means these hydrogen supply methods come with a highly variable cost. If there is little demand, then the cost is relatively low. Conversely, the cost rises in a linear fashion as demand picks up. If the demand disappears, it is relatively inexpensive to shed the hydrogen supply mechanism, and costs go down to zero. Thus, delivered hydrogen may be the best solution for intermittent, variable or unpredictable demand and growing or shrinking hydrogen requirements. Because on-site hydrogen cannot provide very high pressures without an additional compressor, delivered hydrogen also may be the best solution for very high-pressure or portable applications.

A structural disadvantage to buying hydrogen gas in compressed or liquefied form is realized as a customer uses more hydrogen on a regular basis. Because the customer pays for every volume of gas delivered, there is little economy-of-scale benefit. In fact, because every increment of gas must be produced, purified, compressed (and optionally liquefied), packaged, loaded, transported, delivered to the customer, metered or counted, and billed, little actual savings occurs through additional usage. The cost of delivered hydrogen, and therefore the price, is affected by many factors — electrical and energy cost changes, rising costs for labor, fuel and delivery costs, capital charges for cost-intensive facilities, storage equipment rental fees, and hazardous material and delivery fees.

### On-site hydrogen generation

On-site gas production for oxygen and nitrogen can reduce customer costs by eliminating some of the most volatile cost factors from the supply chain — packaging, transportation and delivery. The gas supply process is simplified to producing, purifying and billing.

This simplification is yielding significant savings for some customers, as illustrated in the sidebar below.

On-site generation also can be used to provide the baseline hydrogen supply for a varying requirement. In this case, the on-site generator is sized to provide the lowest-cost baseline requirement, and the supply is supplemented as necessary with gas drawn from a delivered merchant gas supply to meet peak demands.

On-site manufactured gases are manufactured by a purchased or leased generation system placed at a customer's location. The system can reduce customer costs because the generator is a fixed cost. The harder the customer drives it, the more volume over which the fixed cost is allocated — and the less expensive the gas per volume. In addition, compression, packaging, loading, transportation, delivery and metering are eliminated, removing many of the rapidly escalating cost categories.

On-site hydrogen generators also represent a fixed or semifixed cost. This can translate into cost savings when the usage is predictable, the hydrogen volume requirements are long-term and steady, and the pressure requirements are within the range offered (generally a maximum of 200 psig). On-site hydrogen has one additional, and potentially significant, advantage — it reduces or eliminates flammable gas inventory. With delivered hydrogen, as customers' hydrogen usage rises, their inventory of flammable hydrogen gas also goes up. This can cause appreciable problems for customers located in urban, residential or seismically active areas.

## On-site options

For decades, customers using large amounts of hydrogen have employed steam methane reformers and other hydrocarbon reforming technologies to supply hydrogen in enormous quantities. These units are very efficient at converting hydrocarbons to hydrogen, but only on a huge scale, making their use unwieldy for most smaller-volume users.

Small-scale hydrogen users at one time had only one practical choice in on-site hydrogen generation — liquid-phase water electrolysis units. These units, long used commercially, have provided good service but traditionally have been relatively expensive, requiring intensive manpower to operate and maintain. Over time, these units have become relegated primarily to geographically remote sites where hydrogen is necessary and cost is secondary.

*New on-site supply technologies.* A number of organizations, expecting hydrogen-fueled vehicles to be commercialized over the next decade, are introducing innovative technologies to produce hydrogen on a small scale for vehicle refueling. Technologies include advanced water electrolysis systems, small-scale hydrocarbon reforming methods and several chemical-based hydrogen extraction systems. Various systems offer unique characteristics, advantages and disadvantages, and are at different stages of technical maturity, so it is imperative to investigate and fully understand an option before selecting it.

### Economics — Delivered Hydrogen vs. On-site Generation via a Packaged Water Electrolysis System

This example assumes the user employs two cylinders per day of high-purity hydrogen (99.99 percent assay). The cylinders have a 250-scf nominal capacity — most users get approximately 200 scf out of each cylinder before returning them as empties. This customer receives two deliveries per month, totaling 60 cylinders, and keeps an average of 40 cylinders on hand (see Table A).

Table A. Delivered Hydrogen

| Cost category | Charge per unit | Charge per month | Annual cost | Cost per 100 scf used |
|---|---|---|---|---|
| Gas used | $30 per cylinder | $1,800 | $21,600 | $15 |
| Cylinder rental | $3 per cylinder per month | $120 | $1,440 | $1.00 |
| Delivery fee | $25 per delivery | $50 | $600 | $0.42 |
| Hazardous material fee | $15 per delivery | $30 | $360 | $0.25 |
| Total | | | $24,000 | $16.67 |

If the same customer were to use on-site generation via a packaged water electrolysis system, he or she would own (or lease) a generator and keep 12 cylinders on hand for backup (see Table B).

Table B. On-site Generation via a Packaged Water Electrolysis System

| Cost category | Charge per unit | Charge per month | Annual cost | Cost per 100 scf used |
|---|---|---|---|---|
| Generator cost | $40,000 | $1,100 | $13,200 | $9.04 |
| Electricity | $0.06/kwh | $144 | $1,728 | $1.20 |
| Maintenance | $0 | $0 | $1,000 | $0.69 |
| Cylinder backup | $3 per cylinder per month | $36 | $432 | $0.30 |
| Delivery fee | $25 per delivery | $0 | $25 | $0.02 |
| Hazardous material fee | $15 per delivery | $0 | $15 | $0.01 |
| Total | | | $16,400 | $11.26 |

It also is critical to ensure the hydrogen supply needs are relatively permanent and ongoing because on-site supply systems, whether owned or leased, invariably will require a long-term commitment for a supply strategy to pay off.

*Advanced water electrolysis systems.* Although water electrolysis has been used for decades in remote areas for small- and medium-scale hydrogen supply, the systems generally were expensive, custom-engineered, field-erected units designed for hydrogen supply to glass-making, oil hydrogenation and electrical generator cooling applications in developing countries where hydrogen from customary sources was unavailable. The design and construction of these systems have made them costly from a capital standpoint, as well as highly labor-intensive to operate and maintain.

Today, several manufacturers have introduced advanced water electrolysis systems that are standardized, compact in size, need minimal operator intervention and require little maintenance. The basic electrolysis reaction has not changed, but new cell designs, materials of construction, standardized designs and manufacture techniques have enabled manufacturers to decrease the fixed costs of electrolysis technology dramatically per unit of capacity. Additionally, these new systems operate automatically and require very little maintenance, reducing personnel costs.

Electrolytic hydrogen production has many advantages. It yields the highest-purity hydrogen, benefits from widespread raw materials availability (electricity and water), boasts simple system architecture, and can be scaled economically to serve applications ranging from the smallest hydrogen uses to the larger-volume uses. Electrolysis systems have a very simple, largely solid-state architecture. Some can produce hydrogen at a substantial delivery pressure without a compressor. Electrolysis systems are capable of producing hydrogen of ultra-high-purity grade (99.999 percent) or better with minimal purification. The main disadvantage to using water electrolysis to produce hydrogen is that electricity is an expensive "fuel," so the technology generally is practical only for systems with hydrogen requirements of approximately 2,000 standard cubic feet/hour (scf/hr) and less.

*Small-scale hydrocarbon reforming technologies.* Many hydrocarbons, including methane (natural gas), propane, methanol, gasoline, naphtha and others, can be reformed to produce synthesis gas — a mixture of hydrogen, water, carbon monoxide and carbon dioxide with a small amount of unreacted hydrocarbon feedstock (called "slip"). This synthesis gas (often called "syngas") then can be purified to produce hydrogen gas at a range of purities, depending on the severity of the purification employed. In general, the more severe the purification, the higher the hydrogen cost in terms of waste gas venting or in terms of pressure drop through the purifier.

Small-scale reforming systems are being pursued by a number of companies developing fuel cell electrical generating systems for home and automotive fuel cell applications. Long before these systems become affordable and simple enough to be used as home electrical system components, they may be cost-effective for industrial hydrogen supply systems.

Small-scale reforming systems are relatively complex because they need fuel and air-feed systems, the reformer, a hydrogen purification system and various cooling and water processing ancillary systems to make it all work. Additionally, the systems employ a specific hydrocarbon (for example, natural gas or propane) that is available at a reasonable cost at a customer's location. These systems probably work best for customers with hydrogen consumption rates in the 1,500-scf/hr-to-10,000-scf/hr range, and they are most cost-effective when employed to produce hydrogen of a 99.9 percent or lower assay.

Currently, small-scale reforming systems are not commercial — they are in the advanced development stage. In spite of these limitations, small-scale reformers show promise for becoming a highly cost-effective solution for medium-volume and larger-volume hydrogen users.

*Chemical-based hydrogen extraction systems.* Several companies have introduced chemical-based hydrogen supply mechanisms that can manufacture hydrogen on demand using chemical feedstocks. These technologies show particular promise for situations in which portability, rapid response and minimal infrastructure are necessary. The two technologies farthest along in development are:

- Sodium borohydride technology. Sodium borohydride is a powder that can be dissolved in water to make a liquid solution that emits hydrogen gas when contacted with a catalyst in an engineered system.
- Polymer-coated sodium hydride balls. These will emit large volumes of hydrogen gas when contacted with water.

Other suppliers are working with technologies that may approach market readiness during the next several years.

## Calculating costs

*Can on-site hydrogen save your plant money?* The best approach to answering this question is to determine how well your present supply mode serves your facility. Ask:

- Is the plant a long-term hydrogen user?
- Are the problems the facility is experiencing with its current hydrogen supply mode going to be solved by on-site generation?
- Can plant hydrogen quality and quantity requirements be met by an available on-site technology?
- Do you have a complete accounting of the plant's total hydrogen costs, including product, rental, labor, billing, price volatility and contract negotiations?

The sidebar provides a sample cost comparison scenario for delivered hydrogen and on-site generation via a packaged water electrolysis system. Once the total costs are understood, it is possible to analyze the alternatives to determine their potential to provide cost savings.

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