Hydrocarbon Processing

Hydrogen and utility supply optimization

A third-party supply of hydrogen and other utilities can lead to substantial savings

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Several options for the third-party supply of hydrogen, other gases and utilities have been developed. These options have the potential to reduce net hydrogen cost to a refinery up to 20%. These supply options, commercially proven in a number of operating plants, can be particularly valuable to a refinery whose hydrogen requirements are large enough to justify the development of an independent, third-party supply infrastructure. By outsourcing all industrial gas and utility needs to a single supplier, a refiner can focus on its core business while taking advantage of an industrial gas producer's expertise. The key is to involve an experienced industrial gas producer early in the project development phase to take advantage of integration opportunities. Typically, a refinery needs multiple industrial gases and utilities for a variety of process needs, as shown in Table 1.

This broad spectrum of needs provides a basis for developing integrated supply options. Note that several industrial gases and utilities can be produced from a single production process. For example, hydrogen, carbon dioxide, steam and electricity can all be produced from a hydrogen plant, such as a steam reformer. Oxygen, nitrogen and compressed air can be produced from an air separation plant. Of these needs, hydrogen represents the largest value-added product or service for a typical refinery. Consequently, the entire project will typically be structured around hydrogen in terms of timing, location and economic viability. However, the other gas and utility needs should be evaluated.

Also, a refiner generally has varying amounts of hydrocarbon gases and liquids available at or below fuel value. By designing a steam reformer to process these refinery byproducts, significant refinery savings can accrue by avoiding cleanup costs and improving fuel quality. If all of these needs are developed in parallel and the appropriate design features are incorpo-

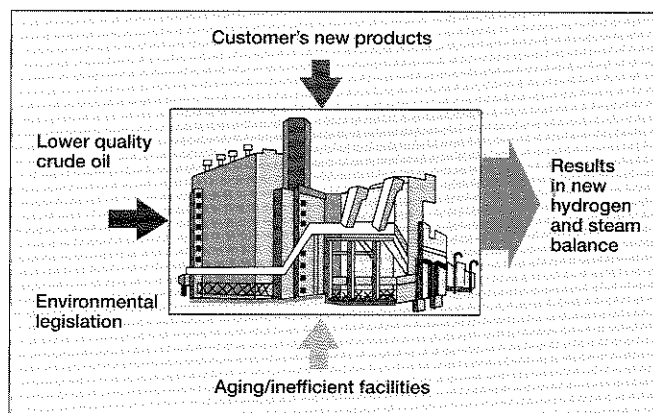| Table 1. Typical refinery needs	
Gases	Utilities
Hydrogen	Steam
Oxygen	Electricity
Nitrogen	Boiler feed water
	Cooling water
	Compressed air

Fig. 1. Forces impacting refiners.

rated at an early stage, it is possible to significantly reduce the net evaluated cost of hydrogen.

A broader supply arrangement reduces the unit cost of hydrogen by taking advantage of economies of scale in a new utility infrastructure and spreading the fixed costs over a broader range of products and services. To fully exploit these cost savings, it is important to identify the refinery's needs and the corresponding hydrogen plant design features at an early stage in the project's development.

External trends. In the last decade, several trends have increased refinery demand for hydrogen. First, in the aggregate, crude oil has been getting heavier and more sour. This has led to higher refinery hydrogen consumption for upgrading the crude oil and removing sulfur. This long-term trend is expected to continue for the foreseeable future. Second, since 1990, the refining industry has been impacted by significant environmental regulations.

In the U.S., the Federal Clean Air Act Amendments

(CAAA) and state requirements, such as the California Air Resources Board (CARB) regulations, have redefined the composition of transportation fuels, like gasoline and diesel, to reduce air emissions. These regulations include more stringent limits on aromatics, olefins and sulfur content of transportation fuels. The U.S. regulations under CAAA take effect in two separate phases in 1998 and 2000. In California, due to air quality and urban smog issues, CARB gasoline specifications (1996) are the most stringent in the world.

Initially, the first wave of environmental legislation focused on low-sulfur diesel (0.05% sulfur), which started in California in 1990, moved eastward to the entire U.S. in 1993, onward to Europe in 1996, and into several Asian countries from 1996 to 2000. More recently, gasoline has become a major focus of environmental legislation. In Europe, sweeping new regulations for both diesel and gasoline for implementation in stages during 2001 to 2005 have been proposed to the European Union (EU) parliament. To comply with these regulations, many refiners have had to adopt these practices:

• Reduce the operating severity of their catalytic reformers (the only major source of byproduct hydrogen in a refinery) to produce fewer aromatics from naphtha

• Increase hydrotreating of refinery products.

Reducing the severity of catalytic reformers *reduces byproduct hydrogen supply* at a refinery, while increasing hydrotreating *increases hydrogen demand*. These effects are depicted in Fig. 1.

Impact on refineries. The combined effect of these trends is that refineries have become significantly short of hydrogen. In the U.S., the incremental on-purpose hydrogen (defined as hydrogen that is not a byproduct of refinery processes, produced in a separate production plant, such as a steam reformer or partial oxidation unit) requirement has been greater than 600 MMscfd in the last six years, starting from a base of 2,500 MMscfd in 1991. A list of new hydrogen plants that have been constructed to rectify the supply/demand imbalance is in Table 2.

These plants are some of the largest and most sophisticated hydrogen plants ever built. In addition, pipeline systems operated by industrial gas companies have been expanded to meet the increased refiner demand by adding on-purpose and offgas hydrogen capacity. These investments require substantial capital investment and technical know-how to achieve the high degree of plant reliability that is critical to a refinery.

Response of refineries. In addition to hydrogen demand growth, refiners have also been faced with significant capital requirements to meet new environmental regulations and accommodate changes in crude oil quality. This has brought about a change in refiners' buying habits. Prior to 1991, most refiners were inclined to "make" instead of "buy" hydrogen.[1] The first large onsite hydrogen supply to Tosco Refining Co., Martinez, California, broke this paradigm. The trend of buying hydrogen instead of making it has continued through the 1990s.

Table 2. Recent hydrogen plants

Location	Capacity, MMscfd	Date on-stream
USA		
California		
Martinez	88	1995
Wilmington	80	1996
Carson	35	1995
Martinez	35	1993
Wilmington	35	1996
Rodeo	24	1997
Texas		
Pasadena	80	1997
LaPorte	65	1996
Texas City	65	1996
Louisiana		
New Orleans	55	1994
Lake Charles	70	1997
Other		
Pine Bend, Minnesota	55	1992
Ardmore, Oklahoma	35	1993
Whiting, Indiana	35	1993
Billings, Montana	22	1995
Europe		
Plock, Poland	110	1996
Rotterdam, The Netherlands	80	1994
Milazzo, Italy	50	1996
S. America		
Amuay, Venezuela	50	1997
Concepcion, Chile	8	1996
Sao Paulo, Brazil	32	1997
Asia		
Sendai, Japan	67	1996
Ulsan, Korea	65	1996
Jurong Islands, Singapore	12	1995
Melaka, Malaysia	12	1998

Refiners are increasingly outsourcing their hydrogen requirements to third-party specialists with proven project development, safety and reliability track records. This practice allows the refiner to focus its capital and human resources on its own core business. Such an approach can be particularly valuable for a large, high-conversion refinery whose hydrogen requirements are becoming large enough to justify the development of an independent, third-party supply infrastructure for supplying multiple industrial gases and utilities for a variety of process needs. These requirements can be supplied by either a hydrogen or an air separation plant, as shown in Table 3.

Of the gases and utilities listed in Table 3, hydrogen generally represents the largest value-added product or service for a typical refinery. Consequently, the entire project will usually be structured around hydrogen in terms of timing, location and economic viability. However, the other gas and utility needs should also be carefully evaluated. Additionally, a refiner generally has varying amounts of hydrocarbon gases and liquids available at or below fuel value at different times of the year. The industrial gas company can evaluate these options, select the optimum processing technology (typically steam reforming), and then analyze co-product and utility synergies with the host refinery.

By designing a flexible steam reformer to supply co-products, process refinery byproducts as feed and
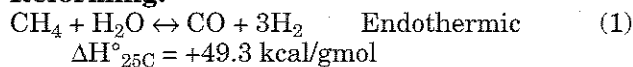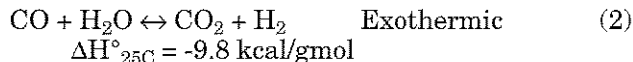
fuel during periods of excess supply, and integrating the required utilities, significant savings can accrue to the refiner. This design effort can take several months to complete. If all of these needs are evaluated in parallel and the appropriate design features are incorporated, it is possible to reduce the net cost of hydrogen up to 20%.

This broad spectrum of needs provides a basis for developing integrated supply options for industrial gases and utilities at a refinery. A broader supply arrangement has the potential to significantly reduce the unit cost of hydrogen by taking advantage of economies of scale in a new gas and utility infrastructure, minimizing capital and human resources, and spreading the fixed costs over a broader range of products and services. To fully exploit these cost savings, it is important to identify the necessary design features up front in a project's development.

TECHNOLOGY

Chemistry. Over 90% of the on-purpose hydrogen produced in refineries is by steam reforming of a hydrocarbon feedstock. When natural gas is used as the feed to a steam reformer, the basic reactions are:

Reforming:
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \text{Endothermic} \quad (1)$$
$$\Delta H°_{25C} = +49.3 \text{ kcal/gmol}$$

Shift:
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{Exothermic} \quad (2)$$
$$\Delta H°_{25C} = -9.8 \text{ kcal/gmol}$$

The reforming reaction (1) is highly endothermic and accompanied by an increase in the total number of moles. For light hydrocarbon feeds such as natural gas, a single nickel-based catalyst is used. However, for heavier feeds such as naphtha, two catalysts are usually preferred. The reforming reaction is equilibrium-limited. It is favored by high temperature (1,450°F to 1,650°F), low pressure (200 to 550 psig) and a high steam-to-carbon ratio (2.5 to 4). These conditions minimize methane slip at the reformer outlet and yield an equilibrium mixture that is rich in

hydrogen.

The shift reaction (2) is exothermic and independent of pressure. It is also equilibrium-limited and favored by low temperature (650°F to 700°F) and high steam concentration. Normally, the shift catalyst is based on iron oxide.

From this basic chemistry, it is clear that a steam reformer has the capability to also produce carbon dioxide (CO_2), carbon monoxide (CO), and synthesis gas (CO + H_2), which are valuable co-products in some geographic areas. Also, due to the high temperatures, varying amounts of steam must be generated by heat recovery from the reformer furnace. This steam can be exported to the refinery for process needs and/or converted into electricity. Byproducts such as carbon dioxide, steam and electricity have a large impact on plant design and economics. In addition, other utilities such as boiler feed water, cooling water, instrument air and nitrogen are required to support the operation of a hydrogen plant. Hence, these needs can be combined with those of the host refiner to further reduce the total system supply costs.

Process and plant design. From an engineering standpoint, the main processing steps are: feed compression and purification, steam reforming and shift conversion, pressure swing adsorption purification, product compression and steam generation. A simplified process flow diagram of a typical steam-methane reformer based on natural gas is in Fig. 2.

Feed gas at elevated pressure must be preheated and desulfurized before it can be fed to the reformer furnace. When the feed contains olefins and/or organic sulfur, hydrogenation using a Co/Mo or Ni/Mo catalyst is necessary. Hydrogenation saturates the olefins to prevent cracking and carbon formation at the reformer inlet. Likewise, it is necessary to convert the organic sulfur (mercaptans, thiophenes, etc.) to H_2S before desulfurization. Desulfurization of the feed gas, which is usually carried out with a zinc oxide bed, is needed since sulfur can poison the reformer catalyst. Hydrocarbon feedstock, with up to several hundred ppm sulfur, can be handled in a properly designed hydrogen plant. This relieves the refiner from processing sulfur-containing offgas in its fuel system.
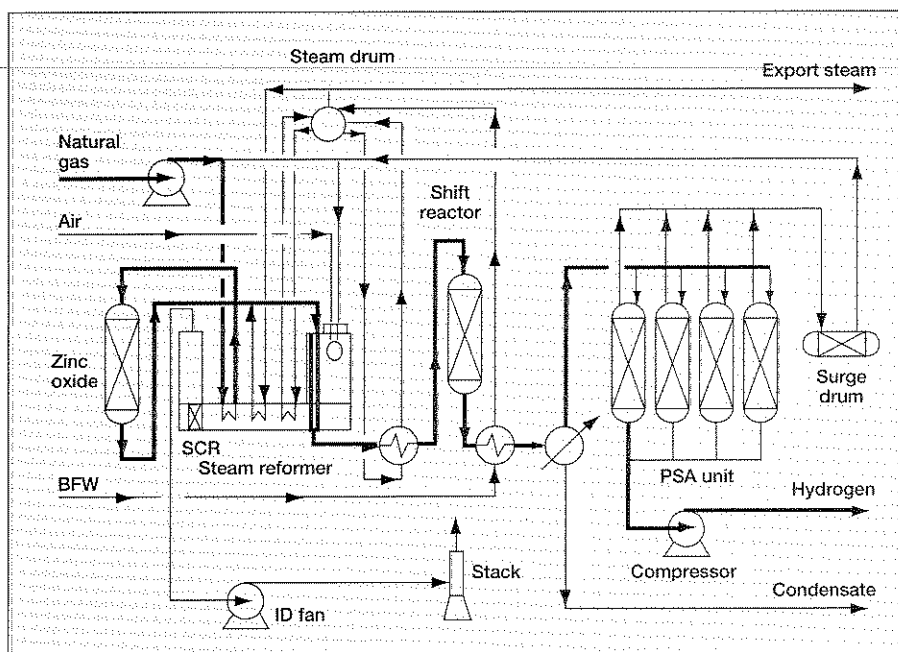
Fig. 2. Flow schematic of a steam methane reformer.

Diagram labels: Steam drum, Export steam, Natural gas, Air, Shift reactor, Zinc oxide, Surge drum, SCR, Steam reformer, BFW, PSA unit, Hydrogen, Stack, Compressor, Condensate, ID fan

close physical proximity to a refinery.

Waste heat is available from two sources in a typical steam reformer: the heat in the reformer furnace flue gases and heat in the process gases coming out of the reformer. This heat can be used to generate steam, superheat steam, preheat air and preheat the feed/steam mixture.

ECONOMICS

The economics of a large steam reformer are highly site-specific. For a specific plant size and location, capital investment is a function of the feedstock and product purity and pressure, degree of utility integration, and reliability criteria. The economics of a "generic" 50-MMscfd steam reformer based on natural gas are presented in Table 4. The total capital cost (U.S. Gulf Coast) is about $60 million, which includes about $10 million in plant offsites.

After purification, feed gas is mixed with process steam at an appropriate steam-to-carbon mole ratio. This "mixed feed" can be preheated by reformer flue gas in a mixed feed preheat coil in the reformer furnace convection section before entering the reformer. The primary reformer contains tubes filled with nickel reforming catalyst. The catalyst converts feed gas to an equilibrium mixture of hydrogen, methane and carbon oxides. Most of the carbon monoxide in the reformer product is converted to carbon dioxide and additional hydrogen in the shift reactor.

After cooling, pure hydrogen is recovered from the shift product by a pressure swing adsorption (PSA) unit. Typically, a PSA produces hydrogen at 99.9%, although the purity can be as high as 99.999%. The adsorbent, which is a mixture of activated carbon and zeolites, removes all of the contaminants from the hydrogen product in a single step. Each adsorption vessel in the PSA follows a cycle of adsorption, stepwise depressurizing, purging and stepwise repressurizing. The system maximizes hydrogen recovery by effectively using the residual hydrogen in an adsorber vessel at the end of its cycle to repressurize the other vessels and provide hydrogen for purging.

When CO_2 is desired as a co-product, it can be recovered in one of two ways depending on the desired hydrogen purity. In modern plants, CO_2 is recovered from the process gases upstream of the PSA using a solvent system. In older plants or when lower purity (96% to 97%) hydrogen is acceptable to a customer, a solvent system and methanator can be used instead of a PSA.

When CO or synthesis gas are desired as co-products, the reformer operating conditions must be altered; and CO vacuum swing adsorption (VSA), membrane or cryogenic separation must be used to recover the CO and synthesis gas. The optimal choice of adsorption, membrane and cryogenic separation will depend on the ratio of H_2, CO and synthesis gas. These products are relevant in the production of petrochemicals such as methanol and acetic acid, which are often produced in

Typically, the unit cost of hydrogen from a plant of this size is about 60% energy and utilities and 40% capital and operating costs. For larger plants, the capital portion is somewhat lower due to economies of scale. The unit cost of hydrogen from a 50-MMscfd plant is around $2.00/Mscf when natural gas is priced at $2.75/MMBtu. This is an important value to keep in mind with regard to some of the details presented below. This cost can be reduced by optimizing plant design and integrating utilities where appropriate. The most important considerations in developing an optimal plant design are:
- Hydrogen plant size
- Feed/fuel composition and cost
- Steam, electricity and carbon dioxide value
- Plant reliability and flexibility
- Project execution schedule.

Note that the hydrogen plant size is influenced by the refiner's current and future incremental hydrogen need, opportunities for replacing older reformers and potential needs of nearby customers. It is also important to understand other site-specific issues such as:

▶ Cooling water and boiler feed water cost/availability

▶ Land availability and soil conditions

▶ Flare requirements

▶ Permitting requirements, air/water discharge and noise limits.

Each of these factors can have a major impact on plant cost. To develop the most cost-effective solution for a particular customer need, it is critical to have a detailed dialog with the customer to determine the optimal process design. It is usually expensive and time-consuming to retrofit an existing plant for a different duty at a later stage.

Alternate design features. Recognizing that the price of hydrogen is often *the* single most important criteria for "buying" hydrogen instead of "making" it, we have developed several alternate design features

Table 5. Steam generation energy economics, steam methane reformer, 50 MMscfd			
	Case 1 min. steam	Case 2 "natural" steam	Case 3 max. steam
Air preheat	Yes	No	No
Pre-reformer	Yes	No	No
Mixed feed preheat	Yes	Yes	No
Relative capital	+	0	+
Export steam, lb/hr	37,500	168,500	230,000
Incremental fuel, MMBtu/hr	Base	153	224
Savings from boiler, MMBtu/hr	Base	179	263
Net energy savings $/Mscf	Base	0.035	0.051

Basis:
Natural gas @ $2.75/MMBtu
Stand-alone boiler efficiency, 80%
Steam at 1,284 Btu/lb; condensate @ 198 Btu/lb

Fig. 3. A hydrogen unit in the Los Angeles area.

to impact the net price of hydrogen.

Generate maximum steam. A steam reformer can be designed to generate varying amounts of steam by reconfiguring the heat integration or providing additional reformer firing capability. By reducing or eliminating air preheat, pre-reforming and feed preheat in the reformer design, it is possible to maximize steam production. In general, reducing heat integration can increase steam production.

During early project definition, the focus is on hydrogen, which is usually the primary driver for the project. Hence, there can be a tendency to choose minimum steam as the baseline. This may not be the optimum in terms of capital or operating costs. Increasing steam production to at least the "natural steam rate" should provide these benefits:
- Reduce investment in the steam reformer
- Enable a refiner to shut down or turn down older, less efficient boilers
- Free up environmental offsets.

Up to a point, a steam reformer has the ability to produce steam more efficiently than a conventional boiler because of improved heat recovery from the process gases, which leads to reduced stack losses. Consequently, in the overall scheme of many projects, it is usually advantageous to produce byproduct steam from a steam reformer.

For example, the greater energy efficiency of a 50-MMscfd steam reformer relative to a conventional boiler is described in Table 5. Three different options corresponding to minimum, "natural" and maximum steam are presented in this table. Case 1, representing minimum steam production is the baseline; while Case 2 is the "natural" steam rate; and Case 3 is the maximum steam that can be efficiently produced in a steam reformer.

In each case, the incremental energy is less for a steam reformer compared to a conventional boiler. This does not take into account additional savings in avoided capital and environmental offsets. The capital of a steam reformer is 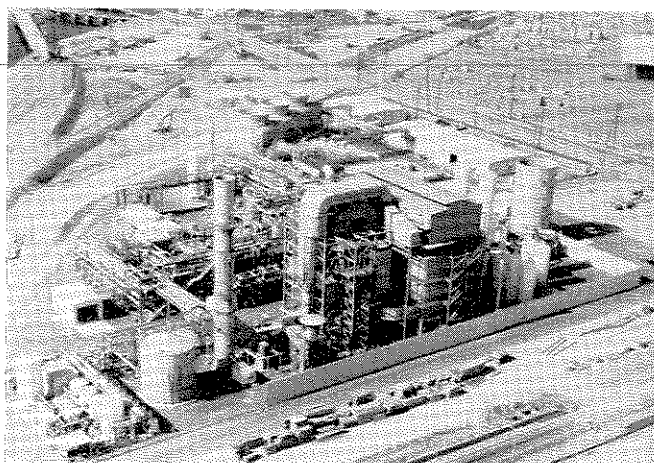reduced when steam production is optimized. Also, capital is avoided in not having to invest in a stand-alone boiler to produce steam. The net energy savings translates into $0.03 to $0.05/Mscf of hydrogen (at $2.75/MMBtu for natural gas). In summary, such an arrangement has the potential of reducing the net hydrogen cost by 1.5% to 2.5%.

Cogenerate electricity. Electricity can be generated from the steam produced in a steam reformer. To do this most efficiently, the steam system in the reformer must be upgraded. Also, the boiler feed water must be demineralized by both reverse osmosis and ion exchange. There are three possible levels of power cogeneration:
- Topping turbine
- Condensing turbine
- Integrated gas turbine.

A topping turbine can produce around 5 MW of power, which is usually adequate for the captive hydrogen plant needs. A condensing steam turbine can produce up to 30 MW of electricity for export, when steam export is minimized. Incorporating a gas turbine can further increase power generation. Assuming $0.045/KWh as the cost of power, such an arrangement has the potential of reducing the net hydrogen cost by 5% to 10%.

Use low-value refinery offgas as feedstock. Most refineries have varying amounts of low-value offgas that may be evaluated at less than fuel value, depending on the impurities. By using these gases as feed and fuel to the reformer, significant operating cost savings can accrue to the refiner, such as lower gas treatment costs, improved fuel quality and reduced flaring of excess fuel. In addition, hydrogen in the refinery offgases can be recovered in the PSA instead of being burned in the refinery. These benefits can be passed on to the refiner. From prior experience, such an arrangement has the potential of reducing the net hydrogen cost by 1.5% to 2.5%.

Use refinery liquids as feedstocks. Sometimes naphtha, butane and/or pentane is available at fuel value in a refinery. Typically, this happens in the summer months. Supplementing some of the feed and fuel with refinery liquids provides flexibility to the refiner when refinery inventory is high. Adding liquid feed capability will require some additional equipment for feed vaporization. However, this option provides sig-

nificant cost savings and flexibility, if the refinery liquids are evaluated at less than fuel value. These savings can be passed on to the refiner. When offgas or natural gas is the primary feed, providing liquid feed capability leads to enhanced reliability without the investment in redundant feed compressors. From prior experience, such an arrangement has the potential of reducing the net hydrogen cost by 1% to 1.5%.

Recover byproduct carbon dioxide. Process gas exiting the shift reactor contains 15% to 18% CO_2, which can be recovered and used. As noted previously, an amine-based solvent system is normally used upstream of the PSA. If low-purity hydrogen is adequate, an amine solvent system coupled with a methanator can be used. The CO_2 can be liquefied and sold on the merchant market. Alternatively, the CO_2 can be used in a refinery for inerting and blanketing. Such an arrangement has the potential of reducing the net hydrogen cost by 1.5% to 2.5%.

Co-produce carbon monoxide and/or synthesis gas. A steam reformer can be operated to produce CO and/or synthesis gas. This requires altering the operating conditions of the steam reformer and using a combination of VSA, H_2 PSA, H_2S removal and cryogenics to recover the CO and synthesis gas. Typically, the CO and synthesis gas are used in the production of petrochemicals, such as methanol and acetic acid. In geographic areas where the petrochemical producer is situated close to the refinery, such an arrangement can greatly enhance project economics.

Supply boiler feed water and cooling water. Many refiners expect a gas supplier to be self-sufficient. This entails having to install boiler feed water (BFW) makeup treatment and cooling water systems. The BFW makeup system will include filtration, ion exchange and reverse osmosis. Given that the necessary operating staff will have to be dedicated to these utility systems, it may be desirable to build a larger water treatment system to also serve the refiner's other needs. It is also possible to minimize process wastewater by introducing it into the cooling water system. Such an arrangement has the potential to reduce the refiner's overall water treatment costs.

Build a larger flare system. To be self-sufficient, it is often necessary to install a separate flare system. Due to environmental regulations, it is necessary to install either a ground-level or elevated flare system. A ground-level flare system, while environmentally desirable and aesthetically pleasing, is very expensive. Building a larger flare system that is shared with the refinery can reduce the refiner's overall flare system cost.

These options are meant to be a sample of the types of alternatives that can be developed to increase overall value to a refiner. Incorporating these concepts into a hydrogen plant can reduce the net hydrogen price by 10% to 20%, as well as provide overall utility system savings to the refiner. This is equivalent to $0.20 to $0.40/Mscf of hydrogen.

A picture of an operating facility in the Los Angeles basin, which was commissioned in 1996, is in Fig. 3. This facility, which represents an investment of over $80 million, provides hydrogen to Ultramar Diamond Shamrock and other area refiners. The facility also generates steam and power and is self-sufficient with respect to other utilities. Some of the value added features incorporated into this facility include: dual compression for enhanced reliability, steam turbine for power generation, and the ability to use refinery offgas for feedstock flexibility.

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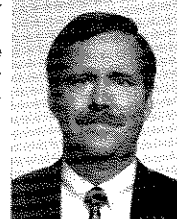
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