Insert flexibility into your hydrogen network—Part 1

Advancements in refinery hydrogen management, technology and utility network can optimize existing and new systems

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A s refiners reconfigure their refineries to produce ultra-low-sulfur (ULS) clean fuels, hydrogen demand will increase, and new supply sources must be identified. Although offgas sources within refineries may provide a portion of the new hydrogen requirements, it will not be enough to address needs for ULS gasoline and diesel specifications.

Three primary technologies are available to refiners to produce "on-purpose" hydrogen: steam reforming; autothermal reforming (ATR); and partial oxidation (POX). The predominant technology used within the refining industry is steam reforming (SMR). Expansions of existing SMRs can be considered because of the potential to obtain some hydrogen at attractive incremental costs.

A refiner may also consider replacing an aging SMR with an incrementally larger, new unit to produce the combined hydrogen requirements. Several different options have been commercially proven and implemented. The optimum solution may involve constructing a new on-purpose steam reformer using either natural gas (NG) alone or a flexible combination of feeding light hydrocarbons and/or hydrogen containing offgas streams. Another solution may be connection to a multi-sourced pipeline supply for hydrogen. Each of these incremental hydrogen options will be explored.

The production of on-purpose hydrogen should be considered in combination with other utilities, particularly steam and electric power. Both can be produced economically with hydrogen production and any requirements should be addressed in parallel to the hydrogen needs. Various process configurations that are available for steam production requirements will be discussed.

OFFGAS HYDROGEN RECOVERY

Many offgas streams within the refinery and related petrochemical operations contain hydrogen. Hydrogen recovery is an increasingly important alternative. The hydrogen content of available offgases is typically 50–90%, but may be as low as 10%. This wide range of offgas hydrogen content makes choosing a recovery technology critical to obtain economically attractive hydrogen. Hydrogen-recovery technologies include membrane, adsorption and cryogenic systems. Each technology has its own unique capabilities and constraints, as summarized in Table 1.

Adsorption and membrane technology are key recovery technologies. Membranes have been used in refinery applications for many years. They provide an excellent way to recover hydrogen from many refinery streams that are available at elevated pressures. The hydrogen purity, although not as high as available from other tech-

TABLE 1. Hydrogen recovery and purification technologies

Characteristic	Membrane	Adsorption	Cryogenics
Hydrogen purity, %	< 95	99.9+	95–99
Hydrogen recovery, %	< 90	75–90	90–98
Hydrogen product pressure	<< Feed pressure	Feed pressure	Variable
Byproducts available	No	No	Yes
Feed pressure, bar g	15–125	10–50	15–35

nologies, is often adequate for a refiner's requirements. A common disadvantage of membranes is that hydrogen is produced at pressures much lower than the feed pressure and may require recompressing prior usage.

Impurities in the feed stream are also a potential concern. A detailed review of potential impurities in the feed stream, particularly during upsets, must be completed prior to selecting this technology.

Pressure swing adsorption (PSA) technology provides a hydrogen product at essentially the feed pressure and at high purity. Recoveries are typically lower than those available from the other technologies. The ability to produce the hydrogen at high purity can provide benefits to the refiner through longer catalyst life and by reducing the inerts introduced into the hydroprocessing unit.

Feed impurities are less of a problem compared to membranes. Heavy hydrocarbons, however, are a problem if they are irreversibly adsorbed. The PSA offgas is available at near atmospheric pressure and may need to be compressed to return it to the refinery fuel header. On balance, these features make PSA technology very attractive for refineries.

Cryogenic technology is the highest capital cost alternative for the refiner. Therefore , it has been limited to larger capacities when liquids recovery, such as a C_3^+ hydrocarbon cut, is required.

The refiner, working with an experienced supplier of these separation technologies, must determine which of the offgas streams can provide economical hydrogen and which separation technology will be used. Many offgas streams can be eliminated from consideration because either the available pressure or the hydrogen concentration is too low; thus, the recovered hydrogen product is uneconomical relative to other sourcing options. Without liquids recovery to offset higher capital costs, cryogenic separation generally cannot be justified over other technologies.
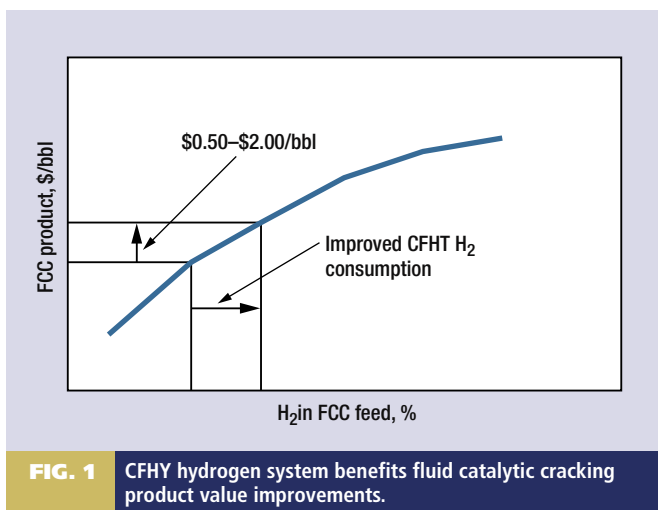
FIG. 1   CFHY hydrogen system benefits fluid catalytic cracking product value improvements.
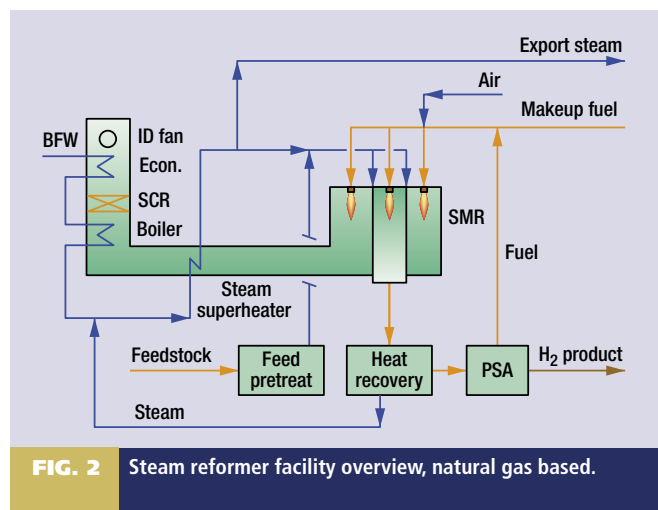
FIG. 2   Steam reformer facility overview, natural gas based.

Offgas hydrogen recovery increased significantly during the 1990s, driven by the push toward cleaner fuels. It is now estimated to total approximately 2,300+ kNm^3/h (2,100 MMscfd) in Europe and North America. Hydrogen from offgas can supplement on-purpose capacity. However, reliability must be carefully examined in the context of the total hydrogen supply balance and hydroprocessing requirements.

Refinery hydrogen management. A refinery hydrogen management program should be organized to meet some of the these objectives depending on specific refinery configuration:

• Maximize hydrogen utilization through increased recovery

• Decouple catalytic reformer operation from hydrogen production needs

• Take advantage of higher hydrogen purity fed to specific consumers.

Ultimately, the program defines recommendations that balance total costs with refinery benefits through implementing the best combination of options.

The hydrogen management program quantifies the economic benefits realized in the refinery for each recovery, purification, and production improvement option, categorized for both no/low capital and higher capital execution plans. A well-designed hydrogen management program can uncover valuable benefits for refinery operations, possibly from $1 million/year (MM/yr) to greater than $10 MM/yr. Some undertakings can be implemented within the current action plan for an immediate beneficial impact; others require capital investment for implementation in future operations.

Potential benefits that can improve current refinery operations with no/low capital investment and less than a two-year payback inlcude:

1. Decouple semi-regenerable catalytic reformer operations from hydrogen network requirements. The catalytic reformer is operated to optimize octane production. This eliminates or at least minimizes octane giveaway during winter operation while maximizing reformer catalyst cycle length. Conversely, the refinery can maintain high throughput in the hydroprocessing network regardless of a catalytic reformer hydrogen supply shortage due to its operating conditions. If hydrogen recovery can meet these objectives, it eliminates making significant capital investment to convert to continuous catalytic regeneration. Improved hydrogen utilization during the summer octane run can allow for processing less expensive, heavier and more sour crude slates.

2. Increase hydrotreater catalyst life. Hydrotreater catalyst life is a strong function of hydrogen partial pressure. Optimum hydrogen purity at the reactor inlet extends catalyst life by maintaining desulfurization kinetics at lower operating temperatures and reducing carbon laydown. Typical purity increases resulting from hydrogen purification equipment and/or increased H$_2$S removal, as well as tuning hydrogen circulation and purge rates, may extend catalyst life up to about 25%. The refinery can benefit from lower catalyst recharge costs, which can be several million dollars per charge. Reducing shutdown frequency can also decrease collateral lost production during changeout shutdowns, which add up to significant lost refinery margins. However, improved catalyst life must fit into total refinery shutdown schedules for benefits to be realized.

3. Improve hydroprocessing unit product values. Major refinery margin improvements are available when hydrogen systems are optimized in units that are directly or indirectly responsible for gasoline production—high conversion hydrocrackers and cat feed hydrotreaters (CFHT). Higher hydrogen partial pressures in the hydrocracker units result in lower operating temperatures and product quality "uplift" to higher gasoline fraction volumes. Increasing hydrocracker makeup hydrogen purity by 2–3% can increase C$_5^+$ liquid yields by several hundred barrels per day (bpd). For example, at typical uplift values, a 200 bpd C$_5^+$ yield increase translates into about $1 MM annual increased margin.

The improved CFHT operation provides value indirectly through higher gasoline selectivity from the FCC unit. When optimum hydrogen purity and hydrogen circulation rates are established in the CFHT, its product hydrogen content increases through additional aromatics saturation. Total FCC unit product value can be increased by $0.50 to $2/bbl (Fig. 1). For many FCC units, this benefit can result in over $10 MM/yr in increased revenues.

4. Improve existing hydrogen plant energy consumption costs. Implement an energy consumption program, which can help save 0.11 to 0.33 kWh/Nm^3 (10 to 30 Btu/scf) of hydrogen produced. Efficiency improvements can immediately reduce energy bills by several million dollars per year, depending on hydrogen plant operating production.

5. Maintain high refinery throughput year-round by improving existing hydrogen plant onstream reliability and debottlenecking its production when it reaches nameplate capacity.

Future hydrogen requirements may require higher capital invest-

ment to produce additional hydrogen and improve hydrotreater performance and configuration. There are potential benefits to getting the most from this necessary capital expenditure:

1. Meeting lower sulfur fuel requirements at minimum cost with hydrotreater unit reconfiguration, which can reduce future hydrogen consumption increases.

2. Defining new hydrogen generation requirements with some precision, so that future operation is not hydrogen constrained.

3. Meeting new hydrogen demands with expansion strategies for existing hydrogen plant equipment.

HYDROGEN PRODUCTION TECHNOLOGY

There are three primary hydrogen production technologies available to refiners:

Steam reforming. Over 95% of on-purpose hydrogen production for refiners is supplied by steam reforming of light hydrocarbons. The endothermic steam reforming reaction is accomplished by sending feed gas and steam through catalyst-filled tubes housed in a furnace. The resulting hydrogen and carbon oxides are processed in shift reactors to convert carbon monoxide (CO) to additional hydrogen. Many existing refinery hydrogen plants produce a medium-purity (94–97%) hydrogen product by removing the carbon dioxide (CO_2) in an absorption system and methanating any remaining carbon oxides. Since the 1980s, most SMRs use PSA technology to recover and purify the hydrogen to purities above 99.9%. These PSA-based hydrogen plants have higher efficiencies than conventional low-purity plants because of additional export steam credits.
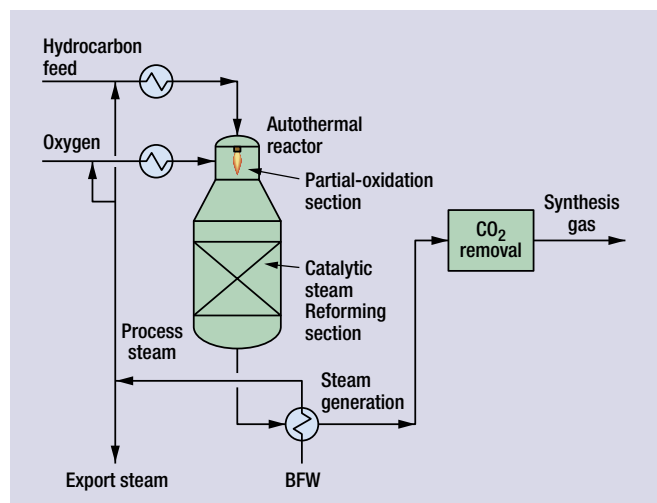
FIG. 3   Autothermal reformer facility overview.

For hydrogen manufacturing, the main processing steps are: feed compression and purification, steam reforming and shift conversion, PSA adsorption purification, product compression, and steam generation. Fig. 2 is a simplified process flow diagram of a typical methane reformer based on NG.

Autothermal reforming. An alternative to conventional steam reforming is ATR. This is a combination of partial oxidation and
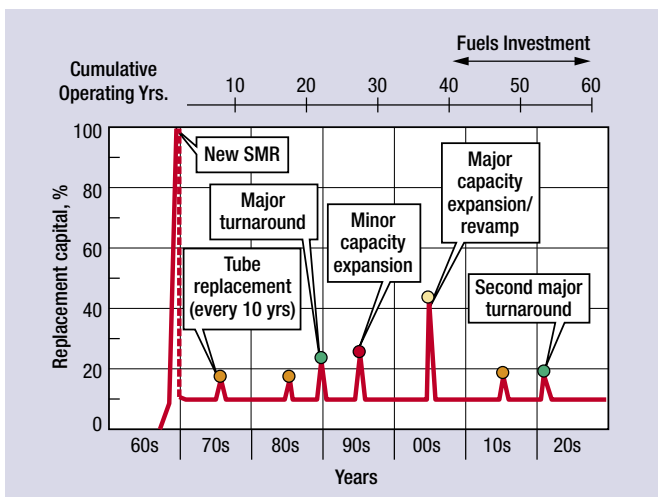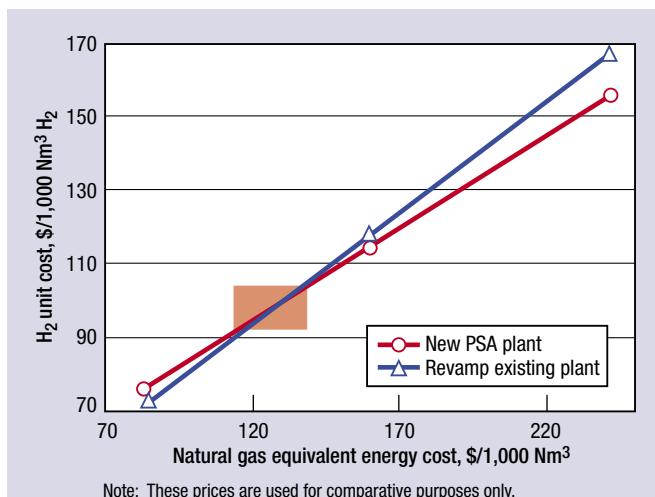
FIG. 4   Representative SMR life-cycle costs.

FIG. 5   Hydrogen unit cost comparison, basis: 50 KNm³/h SMR.

TABLE 2. Unit cost of hydrogen

Cost component	$/kNm³	%
Natural gas	44.04	59
Utilities		
Electricity	1.12	2
Water	1.12	2
Steam	(2.61)	(4)
Variable cost	43.67	59
Capital/operating charges	31.00	41
Total product cost	74.65	100

Note: Natural gas @ $83/1,000m³ ($2.75/MMBtu); steam @ $8.8/t; electricity @ $0.045/ kWh. This price is used for comparative purposes only.
Basis—50 kNm³/h, 15 tph steam (minimum steam case).

TABLE 3. Hydrogen plant performance comparison

	Traditional SMR with solvent/methanation	SMR with hydrogen PSA
Capacity, kNm³/h	50	50
Purity, %	94–97	99.9+
Steam export, tph	9–18	11–100
Efficiency, kWh/Nm³H₂	4.90–5.57	4.23–4.57

Annual savings using 0.75 kWh/Nm³
@ $125/1,000m³ = ~ $4.5 million/y
@ $83/1,000m³ = ~ $3 million/y
Note: These prices used for comparison purposes only.

steam reforming carried out in a single reactor. The endothermic heat of reaction for the steam reforming is supplied by the partial oxidation of the hydrocarbon feedstock in the first section of the reactor. Fig. 3 is a simplified flow diagram of the ATR process.

ATR is not widely used for producing hydrogen for refineries because it produces a synthesis gas with an H to CO ratio more suitable for petrochemicals feedstock. The process also requires the availability of a low-cost oxygen supply and produces a large quantity of excess steam.

Partial oxidation (gasification). Partial oxidation (POX) or gasification is the uncatalyzed reaction of hydrocarbons, coke or coal with steam and oxygen at high temperature and pressure to produce hydrogen and carbon oxides. A principal advantage of the POX process is its ability to operate on virtually any hydrocarbon feedstock. Another advantage is that it produces no SO_x or NO_x emissions.

The major disadvantage is that the process is expensive, and operating costs are high due to the high pressure and pure oxygen requirement of the process. POX is not extensively used in the refining industry for hydrogen production. However, POX is becoming more commercially acceptable as part of integrated gasification combined cycle (IGCC) power generation schemes, partially driven by the need for refinery bottoms disposal. Recovering and purifying a hydrogen stream from the synthesis gas is possible, but using gasification in refineries is primarily justified by power production rather than

hydrogen. As hydrogen production in refineries is almost exclusively sourced from steam reforming, we will focus on this technology.

Trends in economies of scale. Hydrogen production plants are highly capital intensive. For small SMRs, the capital portion of the unit cost is significant (possibly as high as 65%), with the balance comprising operating and energy costs (feed/fuel and power). It should be noted that the capital cost of a hydrogen plant is highly site-specific, dependent on size, location, feedstock considerations and degree of utility integration and reliability criteria.

As the size of the SMR increases, the capital contribution scales to a factor of approximately 0.6. Table 2 summarizes the unit cost of hydrogen from a 50 kNm³/h (45 MMscfd) SMR plant is ~60% energy and utilities and ~40% capital and operating costs. It is important to recognize that building a larger plant can reduce the unit cost of hydrogen significantly.
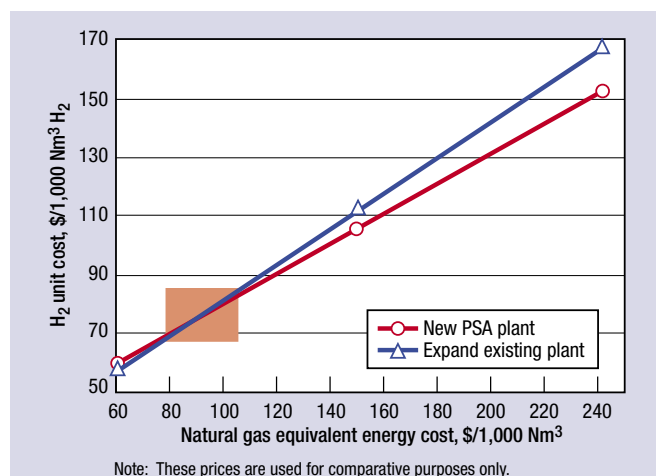
The cost savings can be passed onto the customers in the form of lower hydrogen pricing. Building a larger hydrogen plant may be justifiable by a third-party supplier in which there are additional local customers that can be connected by pipeline. Large hydrogen pipeline systems already exist in major refining centers around the world, providing significant savings to those customers.

Aging and inefficient facilities. Many refiners will have to evaluate the expansion or replacement of existing aging hydrogen plants, steam boilers and power plants because of poor efficiency and high maintenance costs. In addition, refiners will need to significantly

TABLE 4. Alternate feedstock compositions, vol%

	Feed A	Feed B	Feed C	Feed D	Feed E	LPG	Butane	Natural Gas
N_2	3.5	1.3	3.5	2.4	0.1	0.0	0.0	1.2
O_2	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
$C_5H_{12}+$	1.5	1.0	0.1	2.4	5.3	0.0	5.0	0.0
C_4H_{10}	3.0	4.0	0.4	33.4	6.9	0.1	83.0	0.0
C_3H_8	6.0	6.0	1.6	27.0	11.5	99.8	2.0	0.0
C_2H_6	7.0	15.0	15.4	0.6	17.0	0.1	0.0	1.9
CH_4	19.0	36.0	49.3	8.3	42.1	0.0	0.0	96.1
CO_2	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.0
CO	0.0	0.1	1.3	0.0	0.3	0.0	0.0	0.8
H_2	60.0	35.0	21.2	25.9	6.3	0.0	0.0	0.0
C_2H_4	0.0	1.0	4.8	0.0	2.4	0.0	0.0	0.0
C_3H_6	0.0	0.3	1.8	0.0	4.8	0.0	0.0	0.0
C_4H_8	0.0	0.1	0.5	0.0	3.2	0.0	2.0	0.0
C_5H_{10}	0.0	0.0	0.0	0.0	0.0	0.0	8.0	0.0
Total	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Note: These prices are used for comparative purposes only.

FIG. 6 Hydrogen unit cost comparison, expansion from 50 to 70 kNm³/h.

improve environmental emissions performance and/or create emissions allowances for new hydroprocessing projects in an overlapping time frame to comply with the clean fuels legislation. When a refinery is expanded, the need for additional hydrogen, steam and electrical power occurs concurrently. These situations provide an opportunity to reassess the entire hydrogen, steam and power balance to improve the refinery's total cost structure.

Since NG pricing has recently moved to new highs and energy use in SMRs is the largest cost component, improvements in energy efficiency can yield significant cost savings. Many older SMRs with a capacity of 50 kNm³/h (45 MMscfd) or greater have technologies based on solvent-CO_2 recovery and methanation. Table 3 illustrates the difference in energy consumption between traditional and new high-efficiency SMRs.

Older SMRs can consume up to 1 kWh/Nm^3 (90 Btu/scf) of hydrogen (~20%) more than the new units. Older units consume in several million dollars per year of higher energy costs at $83/1,000m^3 ($2.75/MMBtu) of NG, and even more if, for comparative purposes, energy prices stabilize at a higher level of $100 to $125/1,000m^3 ($3.30 to 4.15/MMBtu) of NG.

PSA-based hydrogen plants have many technical advantages compared to traditional SMRs with solvent extraction/methanation technology:
- Reformer can be operated at higher pressure/temperature.
- There is a lower steam to carbon ratio of 2.8:3.0 vs. 3.5:6.0.
- No low-temperature shift unit is required.
- Hydrogen is available at higher purity.
- No methane molecules are lost in the hydrogen stream.
- Greater steam export is available at 45 bar g.

At a minimum, refiners should consider benchmarking their SMR performance with an industrial gas supplier. For comparative purposes, assuming an NG price of approximately $125/1,000m^3 ($4.15/MMBtu), this translates into energy savings of $4.3 million for a 50 kNm^3/h (45 MMscfd) plant. Just a 5% saving on energy efficiency for a 50 kNm^3/h plant using a $83/1,000m^3 ($2.75/MMBtu) NG cost results in over $1 million saved in energy bills over a year. During NG price escalation periods, the savings can be even greater.

Replacement of aging facilities. In the future, with energy prices forecast to be higher and more volatile, replacement of existing SMRs due to tighter environmental regulations is an important consideration. Given that a significant number of SMRs are 25–30 years old, a refiner should carefully evaluate investments to upgrade the SMR to current environmental standards and efficiency benefits. As shown in Fig. 4, some SMR plants could be 50–60 years old by the 20th year of a hydroprocessing investment.

The first case shown in Fig. 5 illustrates the economic comparison of a refiner choosing to continue to operate a 25–30-year-old SMR and analyzing the economics of spending capital to revamp the unit vs. a replacement unit. The basis for the SMR revamp includes capital to install a selective catalytic reduction (SCR) unit (for NO$_x$ emissions), reformer tube replacement, upgrade of the syngas outlet system, and compliance with current codes and standards. The combined impact of the efficiency penalty and the required capital leads to a crossover point of $125/1,000m^3 ($4.15/MMBtu) where a new SMR becomes more cost-effective. A new SMR would also provide additional site-specific economic benefits such as:

- The new plant can be custom designed to meet the refiner's specific requirements in terms of hydrogen, steam and power production, integration with offgases and liquids, and optimization of compression and utilities.
- Higher pressure and purity hydrogen provides partial pressure benefits in downstream hydroprocessing units.
- A maximum steam case SMR could enable a refiner to shutdown an older boiler and gain energy efficiency and NO$_x$ emissions credits.
- Operation reliability will increase with all new components.
- Lower firing rate associated with a new SMR will generate fewer

tons per year of NO_x, SO_x and CO_2 emissions, even with an SCR added to the old SMR.

• Capital from the SMR revamp can be used for other projects to improve the refinery margins.

• A 4-to-6-week outage associated with revamping the SMR is saved.

Fig. 6 illustrates the second case in which a refiner needs an incremental volume of 20 kNm³/h (18 MMscfd) of hydrogen to meet ULS gasoline and diesel fuels specifications. For 20 kNm³/h of hydrogen, a refiner would need a combination of recovering hydrogen from offgas streams and expanding the existing 50 kNm³/h.

As previously discussed, a new SMR decreases unit hydrogen costs effectively when hydrogen capacity is increased. Expanding an old existing SMR does not result in the same unit cost benefit. When comparing the H_2 unit cost for this 70 kNm³/h (63 MMscfd) scenario, the crossover point moves lower, to roughly \$85/1,000m³ (\$2.82/MMBtu). In addition to its benefits, the risks associated with significant expansion of an older facility are eliminated. When additional H_2 is needed, a new SMR option is an extremely attractive option relative to expanding an older SMR. Furthermore, even if additional hydrogen is not required, there may be specific regional areas or site benefits that make a new SMR the preferred hydrogen solution.

Feedstock flexibility. An additional opportunity for integration lies with the feedstock flexibility that steam reforming offers. Whether the steam reformer is part of an over-the-fence project or a refinery owned and operated project, it can be designed to process a wide variety of refinery streams. Thus, when refinery operations change on a daily or seasonal basis, the hydrogen plant operation can be tailored to accept different feeds. For example, the refiner may have excess butane during the summer due to Rvp limitations. This butane can be used as feed to the hydrogen plant rather than export, if the economics are favorable.

Several options are available to utilize refinery gases for hydrogen generation depending on the available gas quantity, its hydrogen or hydrocarbon content, and available pressure and impurities. Streams that are hydrocarbon rich can be used as part of the reformer feedstock network after being pretreated for unacceptable levels of sulfur, olefins, chlorides, etc. Multiple feeds have been the design basis for many of our recent projects. Refinery fuel gases, coker gas, isomerization vent gas, flexi-coker gas, butane, propane and hydrorefining purge gas are some feeds that have been recently used to supplement expensive NG. Table 4 provides a range of feedstock compositions that have been utilized in recent designs.

Some refinery offgases can also be fed directly into the back-end PSA unit for hydrogen recovery. This typically is feasible when the refinery offgas has a hydrogen content of above 50% and is available at or above the PSA inlet pressure. To work, the PSA unit must have sufficient overcapacity or be capable of being revamped to increase its capacity. With this recovery method, the PSA unit typically does not require any expensive pretreatment.

Other hydrogen recovery routes that have been considered instead of or in conjunction with the PSA unit are membrane systems or cryogenic hydrocarbon recovery systems. The volatility of NG pricing, especially in the US, has made it prudent to consider designing a hydrogen plant with the flexibility to process liquid butane, liquid propane or light naphtha as alternative feedstocks to the steam reformer. Pumping liquid butane or propane can provide an additional benefit in reliability if NG is curtailed or the SMR feed compression equipment has an unexpected outage.

Next month. In Part 2, the authors discuss advanced integration methods that can be applied to existing or new SMR units. Two case histories illustrate the potential benefits by integrating hydrogen, steam and power for an existing steam methane reformer. **HP**

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