Originally appeared in:
February 2015, pgs 53-58.
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HYDROCARBON PROCESSING®

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Hydrogen perspectives for 21st century refineries—Part 2

In Part 1, the discussion focused on improving the cost-effectiveness, or unit cost of hydrogen (H_2), along with improved reliability of refinery H_2 supply through advanced H_2 network management, enhanced energy efficiency and revamping existing H_2 plants. In Part 2, other major issues will be explored including wide steam methane reformer (SMR) feedstock flexibility and composition variability, integrating H_2, steam, and power production, while lowering the total carbon footprint, and achieving carbon dioxide (CO_2) capture from SMRs, and managing problems of water quality and availability.

FEEDSTOCK USAGE FLEXIBILITY AND COMPOSITION VARIABILITY

Modern-day H_2 plants are designed with improved safety and reliability performance; these plants provide processing flexibility to handle a wide variety of refinery offgas (ROG) streams, along with captive C_3^+ hydrocarbon (HC) liquids ranging from LPG to heavy naphtha. These plants can be operated in various modes to enhance feed flexibility, including supplemental mixed feeds and alternative feeds or backup feeds based on site-specific issues.

For example, a refiner may have an excess of butane during the summer months due to gasoline Reid vapor pressure (Rvp) limits. The surplus butane, under favorable economics, can be used as part or full feed to produce required H_2 rather than exported. In addition, LPG or naphtha, as alternative feedstocks, can provide protection from any anticipated natural gas (primary feedstock) curtailments or interruptions. Typically, 800 bpd to 1,000 bpd of LPG feedstock can produce approximately 10 MMscfd of H_2.

Many H_2 generation projects have been designed to process multiple feeds. ROG, coker gas, isomerization vent gas, hydrorefining purge gas and refinery liquids, including butane, propane and pentane, are some of the HC streams used to supplement natural gas feed. **TABLE 1** lists the feedstock compositions that are used in H_2 plants.

Naphtha consists of a wide range of HCs with an initial boiling point of 80°F and a final boiling point of up to 390°F, primarily C_5 to C_{12} paraffins and cycloparaffins, with varying amounts of aromatics (typically less than 5 vol%). Although a preformer is generally beneficial for offering multiple feed flexibility, many plants operating with naphtha feedstock operate on direct reforming, i.e., without prereforming. A pre-reformer is an adiabatic reactor, containing high-activity nickel (Ni) catalyst, which converts all of the heavy HCs to an equilibrium mixture of methane (CH_4), carbon oxides and H_2 via reforming and shift reactions. Without a prereformer, the steam-to-carbon ratio for naphtha feeds must be raised and special promoted catalysts are used in the primary reformer to prevent cracking and carbon formation from heavier HCs. Naphtha is used as feedstock in many SMRs and is one of the primary feedstocks used in the Asia-Pacific (AP) region, where natural gas is not readily available or cost-effective.

Olefinic feeds. Many ROG streams contain some olefins. Unfortunately, olefinic HCs can cause operating problems in the SMR due to cracking and forming carbon in the downstream preheat circuits. However, olefinic streams can be safely and efficiently used as reformer feedstock after proper hydrogenation to saturated HCs prior to entering the reformer/prere-

TABLE 1. 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

former. The hydrogenation step is accomplished at the same time that the organic sulfur (S) compounds are hydrogenated to hydrogen sulfide (H_2S) in the feed pretreatment section. The hydrogenation reaction uses H_2 that is available in the ROG or supplied by recycling a portion of the H_2 product to the feed stream. Hydrogenation of the olefins is a highly exothermic reaction; each 1% in olefin saturation can increase the temperature of the feed stream by 35°F–45°F. The hydrogenation catalysts' maximum allowable operating temperature is approximately 750°F and requires a minimum inlet temperature. These conditions restrict the amount of olefin concentration in the ROG stream that can be processed via once-through hydrogenation. Many ROGs, however, contain higher levels of olefins. To process these streams, safe and flexible processing schemes can be used, including saturation recycle loops for temperature control.

Feeds with high S content. Natural gas and most ROG streams contain various S compounds. The typical S compounds are H_2S, mercaptans and, occasionally, carbonyl sulfide (COS). The S levels can range from a few ppm, as found in natural gas, to 1,000 ppm in some ROG streams. Typical steam reforming designs, using natural gas as the feedstock, remove the S impurities in a ZnO bed where the ZnO is converted to ZnS in the presence of H_2S. Mercaptans and carbonyl sulfide (COS) are not readily absorbed by the ZnO bed and must first be hydrogenated to H_2S in a separate catalyst bed. As the S concentration increases, the ZnO beds become larger, and are economical up to 100 ppm to 200 ppm of feed S. Higher S concentrations must be removed by using other systems such as an amine solvent.

TABLE 2. H_2 plants integrated with power facilities

	Hydrogen, MMscfd	Power, MW	Turbine configuration
Torrance, California	90	37	Gas turbine/topping
Wilmington, California	80	30	Topping/condensing
Pernis, The Netherlands	80	35	Topping/condensing
Wilmington, California	15	21	Topping/condensing
New Orleans, Louisiana	60	35	Gas turbine/topping/ condensing
Port Arthur I, Texas	105	40	Gas turbine
Port Arthur II, Texas	110	100	Gas turbine/condensing

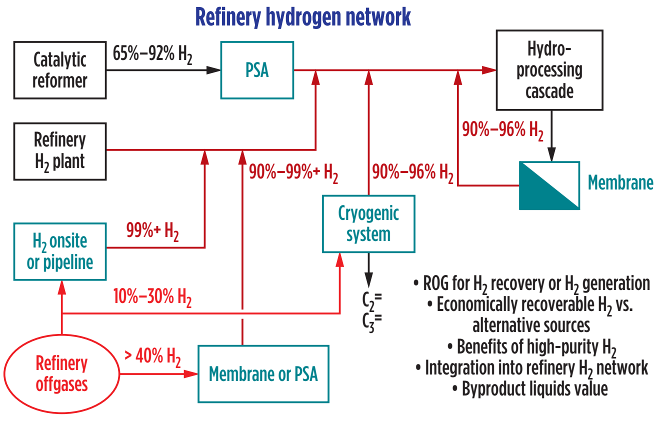

FIG. 1. Refinery hydrogen network optimization considerations.

Hydrogen-rich offgas. Many offgas streams in refineries and related petrochemical operations contain H_2. The H_2 levels can range from 5% to 90%. **Note:** Offgas with 10% H_2 is an increasingly important feedstock alternative for refiners. The wide range of H_2 content in offgas complicates selecting the recovery technology. In addition, any recovery solution should effectively utilize existing compression and minimize new compression requirements.

Commercially proven H_2 recovery technologies include membrane, adsorption and cryogenic systems. Each method has unique capabilities and constraints. **FIG. 1** illustrates a typical H_2 network optimization considering three recovery technologies.

INTEGRATING HYDROGEN WITH POWER PRODUCTION

The SMR, which is principally designed for H_2 production, can also produce steam and electric power economically. Technically, SMR is an endothermic reaction. However, for acceptable kinetics, the temperature should be above 1,550°F in the radiant section of the reformer furnace. Waste heat is usually available and is used to make export steam for process purposes.

SMR-based plants also consume power for fans, compressors and pumps. In many cases, sufficient power can be produced to meet not only the hydrogen plant's own internal needs, but also export power to the host refinery and/or the local electrical grid. This is a tremendous benefit for sites with unreliable power supply. This technology is proven and cost-effective. Often, electrical-power generation can represent a higher-value end use of the waste heat. Once H_2 and steam requirements are established, the amount of power produced can be set by incorporating the appropriate power-generation technology, which will be integrated into the total plant design.

Power integration. The SMR will normally be base-loaded and run in a near-steady-state condition for H_2 production. H_2 demands will dictate the operational "dispatch" of the plant. The ability to independently vary steam or power output is limited. Thus, the preferred operating mode of SMR operation for steam and power would be "base load," and other boilers must handle swings in steam demand.

A limited amount of steam-demand variation can be incorporated if a condensing turbine is part of the plant design. However, the incremental power produced from swings in steam demand would reduce the value, as power guarantees are not possible.

The technical viability of co-generating power in H_2 plants is well established. There are several options for power generation that can be integrated into an SMR. Ultimately, in a competitive and cost-driven marketplace, a technical concept will be adopted if it is economically attractive. **TABLE 2** lists examples of H_2 plants integrated with power facilities.

Case 1: Steam topping/condensing turbine. In a steam topping/condensing turbine scheme, the steam produced by the SMR is produced at higher than normal pressures, from 650 psig to 1,500 psig. The higher-pressure steam is then throttled back to generate power, and steam is exported at 650 psig or to a lower pressure to generate additional power, depending on the refiner's steam system requirements. If maximum power output is desired and export steam is not required for refinery operations, then the export steam can be condensed. **FIG. 2** is an example of a topping turbine integrated with a SMR.

Case 2: Steam topping/gas turbine integrated SMR. This configuration is a combination of a steam topping turbine and a gas turbine. Power production and economics are obtained through a combination of both the steam and gas turbines. **FIG. 3** is a simplified flowsheet of how the two turbines are integrated with an SMR. A key benefit of a gas turbine is the ability to use hot exhaust from a gas turbine in the radiant section of the steam reformer. At 1,000°F, the gas still contains 13% oxygen and serves as combustion air to the reformer. The high-temperature stream also reduces fuel consumption in the reformer.

The convection section takes the place of a heat-recovery steam generator (HRSG) in a cogeneration design. Once the heat is recovered, the cooled gas enters an induced draft fan and leaves via the stack. Steam raised in the convection section can be put through either a topping or condensing turbine for power generation. In this design, the steam system in the H_2 plant is upgraded above 650 psig to 1,500 psig and then sent to the topping turbine for further power recovery before export to the refinery. In this configuration, appropriate bypasses can be incorporated into the plant design to decouple H_2 and steam production from power production.

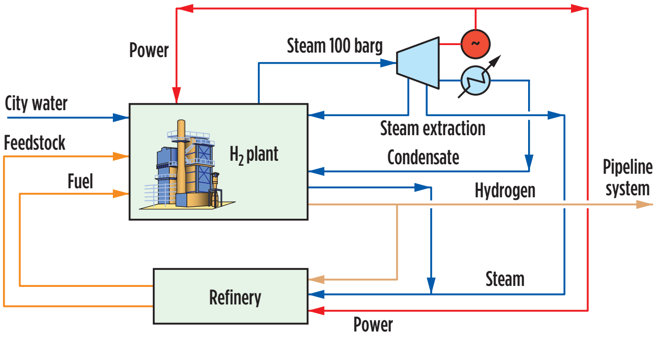

FIG. 2. An example of a topping turbine integrated with an SMR.

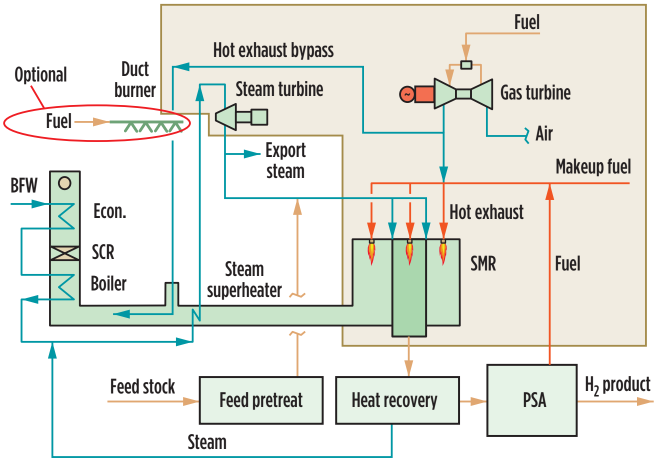

FIG. 3. Example of a totally integrated cogeneration/H_2 case: steam topping/gas turbine.

CO_2 capture from SMR for enhanced oil recovery. In addition to the need for reliable H_2, refiners may be faced with the challenge of reducing CO_2 emissions. Available and proven CO_2 removal technology can be used and integrated in new H_2 plants, as well as retrofitted into existing plants to meet CO_2 capture and management targets—and to minimize the carbon footprint, along with providing clean H_2 generation. **FIG. 4** is an overview of such an implementation on two large SMRs applied in Texas-based operations. The CO_2-removal technology was retrofitted into existing plants, which, in addition to producing H_2, also include some of the cogeneration capabilities discussed earlier in this article.[3] The captured CO_2 is used for enhanced oil recovery.

WATER MANAGEMENT: USAGE AND QUALITY

Some refiners could benefit from solutions that address water scarcity and quality problems. For example, many developing nations and regions have water-stressed areas. As reported by the World Bank, the renewable internal water resources per capita between 2009 and 2013 for Saudi Arabia, India and China were 86 m^3/yr, 1,184, m^3/yr and 2,093 m^3/yr, respectively, vs. the world average of 8,000 m^3/yr. Given that the SMR process consumes a large amount of water (40%–50% of H_2 in the SMR hydrogen product is from water), future challenges of H_2 production may be linked to water availability and cost. Additionally, SMR plants will have to use more unconventional, low-quality raw water, such as seawater, brackish water, industrial and municipal reuse/recycled water, and surface water, to address the water shortages and support conservation needs.

Seawater desalination has long been the source of industrial water in the Middle East (ME). China is facing more water challenges driven by a growing economy and population, and this nation is emerging as the next great market for seawater desalination.[4] In India, manufacturing is in competition for limited water resources with domestic and agriculture use.[5] Switching to low-quality water sources is even happening in North America (NA). For example, brackish water has become a major water

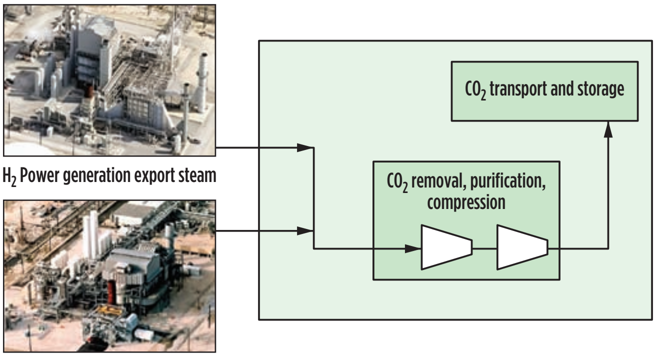

FIG. 4. CO_2 Capture Project I and II at Port Arthur, Texas.

source for industrial operations (e.g., SAGD) in Alberta, Canada. Two H_2 plants in Alberta, Canada, use raw water; one uses municipal reuse water and the other uses river water. Another SMR in Southern California has been asked to switch from municipal water to gray water by 2015.

One potential solution for low-quality water sources is to integrate the SMR process with a thermal desalination process (TDP), such as the commercial multiple-effect distillation (MED) process, multiple-stage flash (MSF) process and vapor compression (VC). TDP processes have been used in various industries around the world, especially in the ME. These plants are more robust than the reverse osmosis (RO)-based water treatment methods in handling low-quality water. This technology is well suited for many developing regions.[6] One disadvantage of the TDP process is the fuel cost to drive evaporation. As a result, TDP processes have been used mainly in areas where fuel cost is low (e.g., the ME) or when low-cost heat sources (e.g., LP steam from power plants) are available.[4]

TDP processes have never been practiced by the SMR industry as an option for water treatment. However, as shown in **FIG. 5,** there are many synergies between SMRs and TDPs. The orange blocks and dark lines in the figure represent the SMR process. The "heat recovery" block is the heat exchange network (HEN), which recovers the heat from syngas and flue gas to generate steam and preheat streams to the reformer such as air, natural gas feed and, possibly, pressure swing adsorption (PSA) purge gas. Even with heat recovery, an SMR normally still produces low-level waste heat. In contrast, the waste heat in the SMR syngas must be rejected to meet the temperature requirement when syngas enters the hydrogen PSA. The green blocks and lines represent a simple combination of SMR and TDP—using SMR syngas waste heat to generate LP steam, using the LP steam to drive TDP, and using a TDP-based water treatment system to produce boiler feedwater (BFW) for the SMR. The blue blocks and lines represent the additional optimization opportunities that SMR-TDP integration provides when export water becomes a product of the integration process. The synergies and potential benefits of the integration are:

SMR and TDP complement each other. SMRs need high-quality water and produce low-level waste heat; TDPs need low-level heat and produce high-quality water. Integration conditions of the two processes are well matched in terms of the amount of SMR water usage (approximately 3,500 m^3/d for a large SMR plant) with the commercial scale of a TDP plant, the temperature of SMR syngas waste heat (200°F) with that of the heat source for TDP, and the amount of SMR syngas waste heat with that of TDP heat usage. The SMR syngas waste heat is singled out because this stream contains a large amount of latent heat due to steam condensation and is easily piped around due to its high pressure, making it well suited for integration.

Integration provides a low-cost heat source for TDP. In the simple SMR-TDP combination, as shown by the green blocks and lines in **FIG. 5,** SMR syngas waste heat is used in an LP boiler (LPB) to generate LP steam that is used to drive a TDP process (e.g., used as the motive steam for a MED process). Since the TDP process will eventually reject all the heat as LP steam to the ambient, the LP steam generation can be viewed as part of SMR waste heat rejection. Therefore, its net cost will be low, if not fully neutralized. This creates a rare situation where the cost of a TDP heat source is low or free, mitigating a cost disadvantage of the TDP process.

Integration can produce water as a new SMR product. As shown by the blue blocks and lines in **FIG. 5,** an SMR plant can be optimized among several variables [consumption of the natural gas; capital expense (CAPEX) of the heat recovery system; and amount of export steam, export water and power generation] to maximize the total benefit. For example, if water has a good value and there is no need for export steam, the unit may be designed with zero-export steam, high export water SMR plant without suffering from poor thermal efficiency and high CAPEX than a conventional zero-export steam SMR plant would face.

Other benefits. The integration can provide additional opportunities to further reduce costs and include:

- Use the SMR syngas to directly drive a TDP process and reduce or eliminate the cost of LP steam generation. This integration requires development of a new evaporator design for the TDP process.
- Share and eliminate equipment. For example, the deaerator can be eliminated on the SMR side if deaeration is accomplished on the TDP side. Heat rejection between SMR and TDP may be integrated to reduce or eliminate total heat rejection costs.
- Use the waste heat in SMR flue gas for water production.
- Recover water in the SMR flue gas.

There are new technologies that can utilize the synergies and potential benefits of SMR-TDP integration.[7–9] A study was recently constructed with a major water technology company to demonstrate that a simple SMR-TDP combination can offer

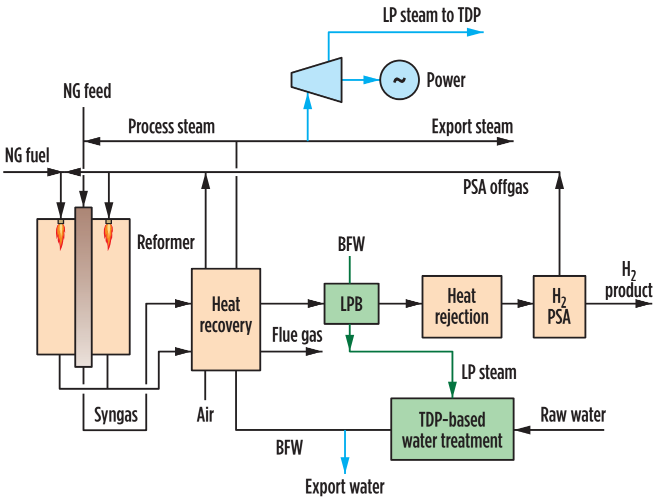

FIG. 5. SMR process and SMR-TDP integration.

more advantages than the conventional SMR process using RO-based water treatment if:

- Quality of raw water is poor, e.g., high total dissolved solids (TDS) and large composition variation
- Cost of raw water and/or waste water discharge is high
- Installation cost, e.g., labor and construction, is high.

The first two conditions are related to the higher water recovery by TDP vs. RO. The third condition is due to the smaller footprint of TDP (e.g., a MED-based system being only approximately ⅓ the footprint of a RO-based system), more modularization/less field work and no need to host TDP in a building, even in a severe climate. Adding new TDP processes into the SMR industry as another water treatment option will help overcome water challenges.

H_2 outsourcing trend. Along with increased demand for H_2 have come requests for feedstock flexibility; demand for cogeneration of H_2, steam and power; CO_2-capture requirements; and increased challenges of water quality and quantity. H_2 is a key molecule for refiners, and reliable H_2 supply is imperative. The sale-of-gas (SOG), third-party, "over-the-fence," outsourced model of H_2 supply was pioneered in the US and has become a common method of refinery H_2 supply. For example, over 70% of all SMR hydrogen awarded over the past five years in NA represents the SOG model. This is not just a North American phenomenon; globally, refiners have identified the benefits provided by outsourcing H_2, including refiners in China, India, the ME and Latin America.

Refiners and petrochemical manufacturers are well aware that efficiency, along with environmental and economic drivers, keep pushing the need for continuous improvement and innovation. These drivers make over-the-fence H_2 supply agreements attractive to manufacturers around the world.

Outlook. H_2 is the lifeblood of 21st century refineries. The application of various technological advancements and core developments has been raising the bar in the design, build, operations and maintenance of H_2 facilities. These developments will continue to reshape the industry. Such continuing advancements have especially been in the field of catalysts, materials, process diagnostics and control, automation and plant intelligence, as well as in possibilities through the use of web-based data management. Furthermore, the enormous underlying emphasis on safety, environmental compliance, efficiency and reliability will continue to define the state-of-the-art H_2 plant.

End of series. Part 1, September 2014, pp. 71–75. HP

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