

A decorative background element consisting of two curved lines. One is a solid yellow line that starts from the left edge and curves upwards and then slightly downwards towards the right. The other is a dotted blue line that starts from the top edge and curves downwards and then slightly upwards towards the right. They intersect in the upper-middle part of the page.

Creating Value Through Refinery Hydrogen Management

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Nitin Patel, Bill Baade - Air Products, USA, Leong Wah Fong - Air Products, Asia And Vinay Khurana – Technip – Coflexip, USA

(Paper presented at the ARTC in Singapore in 2006)

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A critical issue facing the world's refiners today is the changing landscape in processing petroleum crude into refined transportation fuels under an environment of increasingly more stringent clean fuel regulations, decreasing heavy fuel oil demand and increasingly heavy, more sour crude supply. Hydrogen network optimization is at the forefront of world refineries options to address clean fuel trends, to meet growing transportation fuel demands and to continue to make a profit from their crudes. A key element of a refiner's hydrogen network analysis in the U.S. and Europe involves unlocking the value of hydrogen in its fuel streams and extending its flexibility and processing options through new onsite hydrogen capacity or multi-customer hydrogen pipeline systems. Overall, innovative hydrogen network optimization will be a critical factor influencing refiners future operating flexibility and profitability in a shifting world of crude feedstock supplies and ultra low- sulfur (ULS) gasoline and diesel fuels.

Refining trends

In the last decade, the worldwide refining industry has been impacted by several trends that have increased hydrogen demand significantly. First, in aggregate, crude oil has been getting heavier and contains more sulfur and nitrogen; second, decreasing heavy fuel oil demand requires more "bottoms" upgrading; and third, increasingly stringent environmental regulations require cleaner transportation fuels production. These factors have led to higher hydrogen consumption for upgrading crude oil into light transportation fuels and removing sulphur and nitrogen compounds. This long-term trend is expected to continue through 2012 as heavier crude oil production is sold into the marketplace and the next wave of clean fuels specifications are progressively tightened. The World Fuel Charter, crafted by the eight major automobile manufacturers, sets the long-term goal of <10 ppm S for both gasoline and diesel fuels in the U.S. and Europe by 2010⁽¹⁾.

In the U.S., the Federal EPA Clean Air Act Amendments (CAAA) and the California Air Resources Board (CARB) regulations have redefined the composition of transportation fuels, such as gasoline and diesel, to reduce pollutant emissions from automobile and truck exhausts. Environment Canada has implemented tighter sulfur specifications paralleling the U.S. implementation. In Europe, the Auto Oil I legislation (2000) introduced a number of stringent product specifications, with a further reduction to 50 ppm S in 2005 (Auto Oil II).

As product specifications tighten globally, refiners in other regions will face similar constraints. Clean fuels regulations are being considered in Mexico, South America and in selected Asian cities, where air pollution is particularly acute. Several Asian countries are anticipated to target 50 ppm S fuels similar to European Auto Oil II standards by 2010 ^{(2), (3)}.

The push to cleaner fuels is not limited to highway transportation fuels. The next environmental wave in the U.S. and Europe includes proposals to mandate ULS diesel for “off-road” applications such as construction, agricultural and trains. Marine fuels are also coming under greater scrutiny to reduce the sulfur and control nitrogen oxide emissions and fall into two categories: (1) inland waterways; and (2) bunker “C” fuel for ships at sea.

As higher quality fuels are mandated, the processing intensity within the refinery must increase. In North America and Europe, the majority of refinery hydrogen supply/demand balances are no longer matched. For refineries to maintain a balance, they must either move to a sweeter crude slate (higher crude differential cost) and/or secure additional hydrogen capacity (generally on-purpose SMR H₂ plants) to remain profitable. In addition, it is expected that no new refineries will be built in the U.S. or Europe ⁽⁴⁾. Future growth in product demand will need to be addressed by a combination of existing refiner’s creep capacity, investment in more conversion capacity and continued high utilization rates within these refining regions. In Europe, a number of refiners are now reviewing the option of hydrocracking to meet fuel quality requirements and the shifting product demand barrel towards diesel. In the U.S., refiners have built new hydrocracking units or new coking units or have expanded their hydroprocessing capacity ⁽⁵⁾. **Figure 1** illustrates the hydrogen intensity of refineries as they progress from low conversion through high conversion in today’s era of ULS transportation fuels.

Figure 1: Hydrogen Production Increases with Refinery Conversion Levels and Clean Fuels

On-Purpose Hydrogen Growth--
It's More than Clean Fuels . . .

U.S. and Europe Refining Market

- More heavy, sour crude
- More high-value products
- Meeting clean fuels specs

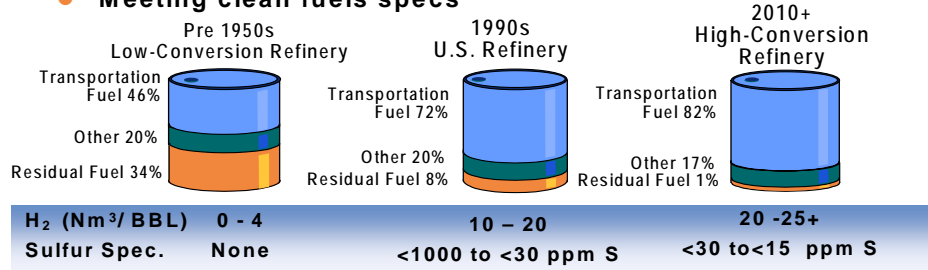


Table 2 provides a comparative overview of the U.S., W. European and Asian regional refining capacities and process configurations. In the U.S., refineries are geared towards high conversion to produce a high volume of transportation fuels (gasoline, diesel and jet fuel) from a barrel of crude oil processed. European and Asian refineries are more heavily weighted towards diesel production as the major transportation fuel and significant quantities of residual fuel for power generation and marine fuel oil markets ⁽⁶⁾.

Table 2. Comparison of Regional Refining Processing Capabilities

Basis: 2002 O&G Journal Statistics

| | Crude (MM bpd) | Avg. Size (K bpd) | FCC (% Crude) | HDC (% Crude) | Coking (% Crude) | Sulfur (MT/ 100 K bpd) | On-Purpose H2 (Nm ³ /bbl) |
|-----------------------|----------------|-------------------|---------------|---------------|------------------|------------------------|--------------------------------------|
| North America | 18.4 | | | | | | |
| US | 16.5 | 115 | 34% | 8.9% | 13.0% | 150 | 5.8 |
| Canada | 1.9 | 100 | 25% | 13.5% | 2.0% | 70 | 4.5 |
| Western Europe | 14.5 | 145 | 15% | 6.1% | 2.1% | 70 | 2.6 |
| Asia-Pacific | 20.2 | | | | | | |
| Japan | 4.8 | 145 | 17% | 3.1% | 1.8% | 173 | 6.0 |
| China | 4.5 | 50 | 20% | 2.7% | 6.8% | 7 | 0 |
| Other Asia Pacific | 10.9 | 150 | 9% | 4.1% | 1.2% | 56 | 2.2 |

Clean fuels investments

Refineries will require new or revamped production facilities, which in turn will require expensive capital investments coupled with significant operating costs. Refiners are facing the dual pressures of regulatory change and limited capital. Profitability has varied but historically has been low enough to discourage reinvestment, with the exception of regulated clean fuels investments or heavy crude refinery netback investment projects. Refiners are therefore focused on asset optimization and capital avoidance as they adjust to high quality product requirements and generally lower quality heavy, sour crude. Third party supplied hydrogen (outsourcing) can assist refiners with flexibility in operations and improvements in the important financial measure of return on capital employed or ROCE.

In the 1980s, Air Products operated hydrogen pipeline systems in the U.S. Gulf Coast and Europe for the supply of dedicated and backup hydrogen to refiners and chemical facilities. In 1992, Air Products approached the California refiners with an “outsourcing” business model to address their hydrogen requirements for producing CARB transportation fuels. Air Products and KTI Corporation (now Technip-Coflexip) designed and constructed the world’s first large third party outsourced hydrogen plant for the Tosco refinery in Martinez, near San Francisco, California (at press time, this facility is owned by Tesoro Petroleum). The 39 thousand Nm³/hr (or 35 MM scfd) hydrogen plant is owned, operated and maintained by Air Products to supply high purity hydrogen and steam to Tesoro, and is in its tenth year of operation.

Refiners have embraced outsourcing of hydrogen (see **Table 2**) as a means to leverage their limited capital resources and take advantage of the design and operating expertise of certain industrial gas suppliers. In 2003, Air Products will have 1 million Nm³/hr (or 900 MM scfd) of hydrogen capacity serving 24 refiners in the U.S., Europe and Asia.

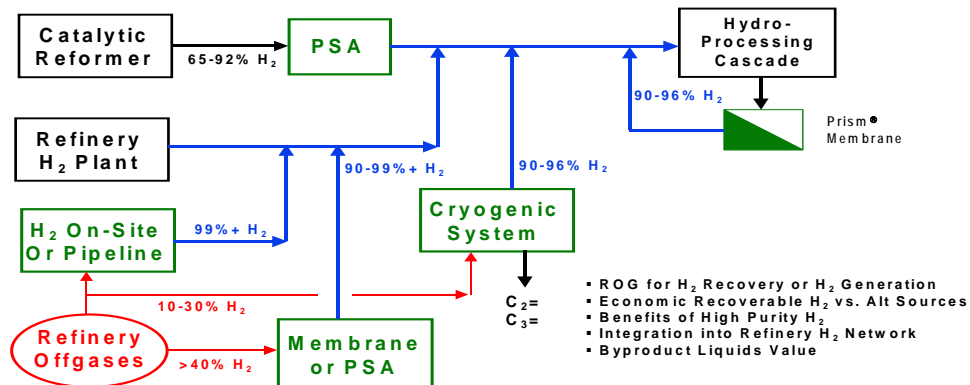
**Table 2 – Refiners Embrace Outsourcing of Hydrogen--
Growth in Industrial Gas Supplied Hydrogen to US and European Refiners**

| | Year | “Make” Hydrogen | “Buy” Hydrogen | Total On- Purpose Hydrogen | Outsourced Hydrogen |
|---|------|--------------------|-------------------|----------------------------------|------------------------|
| US Refiners (Thousand Nm ³ /hr) | 1991 | 2780 | 80 | 2860 | ~ 3% |
| | 2003 | 3040 | 1325 | 4365 | ~30% |
| European Refiners (Thousand Nm ³ /hr) | 1991 | 730 | -- | 730 | 0% |
| | 2003 | 1520 | 455 | 1975 | ~23% |

Hydrogen network optimization

Hydrogen network optimization is at the forefront of options to address clean fuel trends, meet growing transportation fuel demands and help maintain profitability from refining crude oils. A typical refinery hydrogen network is illustrated in **Figure 2**. The majority of hydrogen consumed in today's refinery is produced from the catalytic reformer system and may be supplemented by an on-purpose hydrogen facility and/or pipeline hydrogen supply. The refinery hydrogen distribution system is cascaded through multiple hydroprocessing units, where higher H₂ purity and higher-pressure consumers send their purge gases to lower H₂ purity and lower pressure consumers. Ultimately, purge gases containing residual hydrogen are sent to fuel.

Figure 2: Refinery Hydrogen Network Optimization Consideration



Many makeup and recycle compressors drive the hydrogen through this complex network of hydrotreater and hydrocracker units. The various hydroprocessing units consume hydrogen to remove sulfur and nitrogen, reduce boiling point, and/or saturate aromatics in the refinery liquid fractions.

When hydrogen availability is pinched by new hydroprocessing demands, the refinery needs alternative sources of hydrogen, higher H₂ purities for improved hydrotreater operation, and optimized solutions that integrate into the entire hydrogen supply and demand scenario. Each refinery's configuration, crude slate and new production requirements are different, so various hydrogen network optimization considerations must be considered. These include recovering hydrogen from fuel streams, expanding or adding a new on-purpose hydrogen plant or outsourcing to an industrial gas company.

ROG recovery technologies

Hydrogen from off-gas sources, typically ranging from 50 ~90% with a few of them as low as 10%, is an increasingly important alternative to refiners. The wide range of off-gas hydrogen content makes choosing a recovery technology critical to obtain economically attractive hydrogen product. In addition, a recovery solution should consider effective utilization of existing compression, and minimizing new compression requirements.

Commercially proven hydrogen recovery technologies include Membrane, Adsorption, and Cryogenic systems. Each of these technologies has its unique capabilities and constraints. Table 3 summarizes important considerations when determining a technology fit to provide economically attractive hydrogen for a specific refinery application.

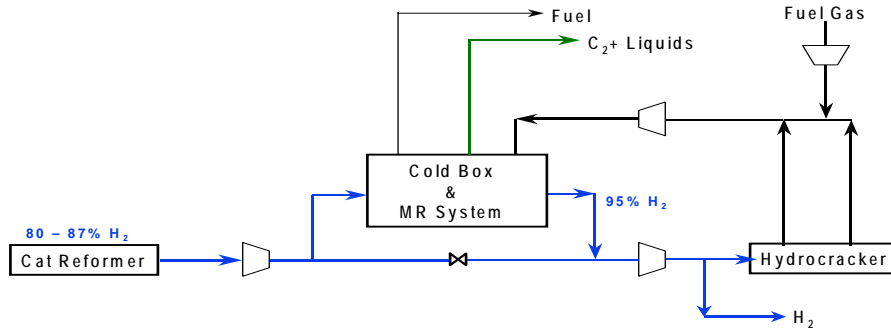
Adsorption (PSA system) is the best choice when ultra-high purity, 99%+, hydrogen product is required. Adsorption is applicable throughout a full range of capacity, up to 200+ KNm³/hr, and produces hydrogen at essentially ROG feed pressure. Impurities and unrecovered H₂ are delivered at low pressure and available for fuel. Hydrogen recoveries for an Adsorption PSA system are typically lower than those available from the other technologies. However, the ability of PSA system to produce hydrogen at high purity can provide benefits to the refiner through longer catalyst life, and reduction of inerts introduced into the hydroprocessing unit. PSA system designs for ROG feeds must account for variability in feed gas conditions. For example, catalytic reformer off-gas H₂ can change by 10-15% from start to end of run catalyst conditions. Hydrotreater off-gas composition changes as a function of makeup hydrogen purity and specific purge rate set points. When multiple ROG streams are mixed, different operating scenarios can significantly change PSA feed composition. ROG feed contaminants can include a long "tail" of heavy C₅₊ hydrocarbons, including aromatics. Some heavy hydrocarbons

and aromatics can create problems if they are irreversibly adsorbed. Therefore, it is advantageous to design ROG H₂ PSA systems using various available adsorbents and tailoring the adsorbent quantities and mix to each application to provide feed flexibility while striving for best achievable recoveries and high operating bed utilization. Hydrogen recoveries (typically greater than ~ 80%) are dependent on feed conditions, hydrogen product specifications, and system configuration.

Prism[®] membranes can provide the lowest cost solution for high pressure ROG feeds, especially when integration with existing hydrogen compression is possible. Membrane systems are bulk separators that produce refinery-quality hydrogen purities of 90 to 98% at high recoveries (85% or better). Since pressure drives the separation, they are best suited for high-pressure feeds (>20 barg or 300 psig) such as hydroprocessing purge gases. A common disadvantage of membranes is that the hydrogen product stream is produced at pressures much lower than the feed pressure, and may need recompression. The hydrogen product may be sent to existing make-up or recycle compression in hydroprocessing loops. An important consideration for ROG applications is that H₂S is also a “fast gas” through the membrane polymer and will end up in the hydrogen product. Prism[®] membrane systems have been utilized in almost 50 refinery installations with feed capacities up to 39 thousand Nm³/hr (or 35 MM scfd) and design pressures up to 172 barg (or 2500 psig). In refinery operation, they are flexible to changing ROG feed conditions and provide a robust separation system when upstream units are designed to handle various feed contaminants such as water, particulates, amines and hydrocarbon liquids. A detail review of potential impurities in the feed stream particularly during upsets, must be completed prior to selecting the technology.

Cryogenic Systems provide an excellent vehicle to purify or recover refinery-quality hydrogen when by-product liquid hydrocarbons, especially ethylene and propylene, can subsidize the higher capital expenditure. Even low pressure (>5 barg or 75 psig) and dilute hydrogen ROG feeds, such as FCC offgas, are good candidates for a cryogenic separation system. Without liquids recovery to offset the higher capital costs, cryogenic separation systems cannot generally be justified over the other separation technologies. Figure 3 illustrates a cryogenic system for liquids recovery and hydrogen purification integrated into a refinery.

Figure 3: Cryogenic System for Liquids Recovery & H₂ Purification Integrated into Refinery



The refiner, working with suppliers of these separation technologies, must determine which technology to use and which off-gas streams can provide the most economical hydrogen product. Many off-gas streams can be eliminated from consideration because the pressure or hydrogen concentration is too low, rendering the recovered hydrogen uneconomical relative to other sourcing options. In addition, these off-gas recovery options may not provide sufficient quantities of hydrogen to meet the refiner’s clean-fuel project requirements. Therefore, the refiner must evaluate other methods of obtaining the necessary hydrogen.

Table 3: Hydrogen Recovery/Purification Technology Comparison

| Features | Adsorption | Membranes | Cryogenics |
|---------------------------------|-------------------------------|-------------------------------|--|
| H ₂ Purity | 99.9%+ | 90 – 98% | 90 – 96% |
| H ₂ Recovery | 75 – 92% | 85 – 95% | 90 – 98% |
| Feed Pressure | 10 – 40 barg | 20 – 160 barg | > 5 – 75 barg |
| Feed H ₂ Content | > 40% | >25 – 50% | > 10% |
| H ₂ Product Pressure | Feed Pressure | << Feed Pressure | Feed / Low Pressure |
| H ₂ Capacity | 1 – 225 K Nm ³ /hr | 1 – 50+ K Nm ³ /hr | 10 – 75+ K Nm ³ /hr |
| Pretreatment Requirements | None | Minimum | CO ₂ , H ₂ O Removal |
| Multiple Products | No | No | Liquid HC’s |
| Capital Cost | Medium | Low | Higher |
| Scale Economics | Moderate | Modular | Good |

Expansion of Existing On-Purpose Hydrogen Plant

Generally complex refineries source 30 ~ 60% of their total hydrogen requirements from on purpose hydrogen capacity. Overall, approximately 95% of the on-purpose hydrogen is supplied by steam reforming of light hydrocarbons. The endothermic steam reforming reaction is accomplished by flowing feed gas through catalyst filled tubes that are located in a furnace. The resulting hydrogen and carbon oxides are further processed in shift reactors to convert carbon monoxide to additional hydrogen. Many existing refinery hydrogen plants produce a medium purity (94 ~ 97%) hydrogen product stream by removing the carbon dioxide in a solvent absorption system accompanied by a methanation step. Newer plants use PSA technology to recover and purify the hydrogen to purities in excess of 99.9%. These PSA based hydrogen plants have a higher efficiency than the conventional low purity plants due to additional export steam credits.

Existing hydrogen plants can be debottlenecked and expanded through various methods. Current limitations can include:

- Reformer furnace firing capacity - - reformer tubes/convection section coils overheating, fuel system control limits, or burner firing limitations.
- System pressure drop limitations - - maximum pressure through catalyst bed or full use of available feed pressure from supplier or feed compressor.
- Induced-draft fan capacity limiting available draft for the reformer furnace firing.
- Purification equipment limitations - - flooding in CO₂ absorber, CO₂ stripper capacity, overheating in methanator, bed fluidization in PSA, or insufficient adsorption capacity in PSA.

The refiner must be aware of not only the major bottleneck, but also other areas of the plant that are near their respective limits. If the first bottleneck is resolved, another is often right behind. Secondary limitations are usually difficult to identify. In many plants, multiple bottlenecks may need to be addressed to accomplish a meaningful expansion in capacity. This could be very costly and may require significant downtime.

Revamping and debottlenecking an existing hydrogen plant can be a cost effective way of fulfilling incremental hydrogen needs. Increasing hydrogen production from 5% to 30% may be possible depending on the plant's age, extent of previous debottlenecking work, utility availability, constraints

of emission permits and flexibility of the refinery with respect to product hydrogen pressure, steam production, and design margins. Debottlenecking options available for the SMR are discussed below.

Increase Reforming Firing

Increasing plant throughput by increasing reformer firing is usually the starting point for most users. Increasing flow through the reformer beyond design conditions will require an increase in reformer firing rate. As flow rate through the tubes and the firing increase, the metal temperature of the reformer tube also increases. Since the tube life is a function of tube metal temperature at a given wall thickness, tube life will be reduced. This problem is solved by reducing the reformer outlet temperature (and conversion), or by accepting a lower tube life. Other equipment limits need to be examined such as the Induced Draft (ID) fan, valve sizes, etc.

Lower Steam-to-Carbon Ratio – PSA-Based Plants

Lowering the steam to carbon ratio can be incorporated as a standalone option or in conjunction with other debottlenecking options. Non-naphtha feed plants should have steam to carbon ratios between 2.5 and 3.5. Plants have a potential of easily increasing hydrogen production if they are operating at steam to carbon ratios higher than 3.5. Lowering the steam to carbon ratio in a conventional (non-PSA based) plant will lower the hydrogen purity and reduce the energy available for the CO₂ unit.

Pre-Reformer

In a pre-reformer, adiabatic steam-hydrocarbon reforming is performed upstream of the fired reformer. The heat required for the endothermic reaction is provided by hot flue gas from the reformer convection section. Since the feed to the fired reformer is now partially reformed, the reformer is unloaded and can then operate at an increased feed rate. An additional advantage of the pre-reformer is that it allows flexibility in feedstock composition (refinery off-gas streams, LPG, butane, or light naphtha), while maintaining relatively constant operating conditions within the fired reformer.

Post Reformer (EHTR and O₂ Secondary)

An Enhanced Heat Transfer ReformerTM (EHTR) uses heat from the effluent of the fired reformer to reform additional feed and has been operated (mid-1980's) by Air Products in California. Recently, Technip installed an EHTR unit for a Repsol refinery in Spain. These units utilize a heat exchanger containing catalyst in the tubes, into which steam and hydrocarbons, which bypassed the primary

reformer, are fed. The primary reformer effluent provides the heat for the EHTR by passing reformed gas counter-flow outside the catalyst tubes. EHTR can increase existing plant capacity by up to 25% and eliminate or reduce excess steam generation from the SMR.

Another post reformer design in commercial operation is called oxygen secondary reforming, utilized in revamping ammonia plant reformers to hydrogen service, which Air Products has operated (mid-1990's) in Louisiana. An oxygen secondary reformer is installed immediately downstream from the primary reformer, allowing the shifting of a portion of the reforming load from the primary to the secondary. It provides a low methane slip and the ability to lower the outlet temperature of the primary, providing a means of processing more feed gas in the primary reformer without increasing the reformer-firing rate. The secondary reformer vessel is a refractory lined carbon steel vessel housing an oxygen burner in its top neck and a fixed catalyst bed. Installation of a secondary reformer usually requires significant changes to the CO₂ removal system. Purities of hydrogen can be increased up to 98%. The economics are generally dependent on a reliable source of low cost oxygen.

PSA Modifications

A number of options are available to increase hydrogen production as a result of modifications to or around the PSA. PSA related options include intermediate hydrogen off-gas feed, adsorbent replacement, cycle time adjustment, operating at atmospheric purge gas pressure, and purge gas recycle.

Adding CO₂ Wash To PSA Plants

Adding a carbon dioxide (CO₂) wash system to a PSA hydrogen plant can improve the hydrogen recovery of the PSA by reducing the total volume and CO₂ content of the feed gas. Improvements in hydrogen recovery from the PSA of 3 to 5% are possible. The incremental hydrogen benefit is not sufficient to make this option economically attractive unless the recovered CO₂ has value. A liquid or gaseous CO₂ market must therefore be present.

Table 4: Expansion Options Comparison

| Debottleneck Option | Incremental Hydrogen | Steam Rate | Feed Rate | Fuel Rate | Cost | Issues |
|--------------------------------------|----------------------|--|---|--------------------------------------|------------|---|
| Increase Reformer firing | 7 – 10% | Proportional, assuming adequate convection surface | Proportional to increased production | Proportional to increased production | Low | Tube Life |
| Reduce steam to carbon ratio | 0 – 4% | Increase | Increase | Decrease | Low | Lower H ₂ purity and steam |
| Pre-reformer | 8 – 10% | 10 – 15% decrease | Proportional | Same | Medium | Pre-reformer catalyst cost |
| Post Reformer | 20 – 30% | 15 – 30% decrease | Increase slightly higher proportion than increased H ₂ | Same | High | Metal dusting (EHTR); O ₂ cost (Secondary) |
| Improved PSA recovery | 1 – 2% | Same | Same | Increase | Low | Low purge gas pressure |
| Addition of CO ₂ recovery | 3 – 5% | 6 – 10% decrease | Same | Decrease | Low / High | Specific market |

New On-Purpose Hydrogen Capacity

When considering a new on-purpose hydrogen plant, the refiner must identify which hydrocarbon feedstocks are available to produce hydrogen so that the right generation technology can be determined. The lighter fractions, such as methane (natural gas) through naphtha and various refinery offgases, can be converted into hydrogen by either steam reforming technology or partial oxidation (POX) technology. The heavier fractions, such as vacuum residue, deasphalted bottoms, refinery sludges, and petroleum coke can only be processed into hydrogen using POX technology (also known as gasification technology).

The refiner may have preferences for using specific hydrocarbons as feeds depending on the overall refinery configuration and operation. Typical considerations may include:

- Refinery offgases that contain unrecoverable hydrogen can be used as feedstocks. The hydrocarbons can be converted into hydrogen, along with recovering the contained hydrogen.
- Butane or pentane may be in excess during the summer months as RVP limits force its removal from the gasoline pool.
- The “bottom of the barrel” (heavy residues) normally sold as high sulfur fuel oil, and/or petroleum coke, may present a growing disposal problem.

The final selection of the appropriate feedstock and technology requires a detailed analysis to determine which combination provides the lowest cost hydrogen. The primary factors to be considered include: the costs of feedstock and utilities; byproduct credits (e.g., for steam, carbon monoxide, syngas, carbon dioxide, sulfur and power as appropriate); the cost of capital; and fixed operating expenses. The required investment and operating costs are typically obtained from the various suppliers of the technology. It is critical, however, to ensure that the scope basis and the hydrogen supply reliability are consistent when evaluating vendor proposals.

ROG Integration with Hydrogen Supply

Streams that are hydrocarbon rich can be used as part of the reformer feedstock network after being pretreated for unacceptable levels of sulfur, olefins, and/or chlorides. After pioneering multiple reformer feeds at Air Products’ onsite hydrogen plant serving Equilon in California in 1995, ROG feeds have been the design basis for many of our recent refinery hydrogen projects. Refinery offgases such as coker gas, isomerization vent gas, flexicoker gas, butane, propane, and hydroprocessing purge gas are some of the feeds that have been recently used to supplement natural gas. The range of feedstock stream compositions in Air Products hydrogen plants includes 5-60% H₂, up to 10% olefins and heavy hydrocarbons tailing to 5% C₅₊. LPG alternative feedstock can provide protection from anticipated natural gas curtailments. Typically, 800 to 1000 barrel per day of LPG can produce about 11 thousand Nm³/hr (or 10 MM scfd) of hydrogen.

In July 2000, Air Products commissioned a 6 thousand Nm³/hr (or 6 MM scfd) H₂ PSA that recovers hydrogen from four different hydrotreater purge gases at about 29 barg. This 4 bed ROG PSA system supplements a 110 thousand Nm³/hr (or 100 MMSCFD) on-site hydrogen plant for a major U.S. refinery. The PSA design feed contains about 72% H₂ with C₅₊, H₂S and NH₃ impurities and produces a hydrogen product > 99.9% H₂. The system contains multiple adsorbents that were tailored to balance

H₂ recovery with long adsorbent life. Actual feed conditions are dynamic with H₂ contents ranging from <72 to 85%. Automatic cycle adjustments can be made to optimize PSA performance while preventing impurity breakthroughs with feed composition swings. Feed composition variability also translates into BTU swings in the tail gas fuel. Tail gas and H₂ are compressed in a multi-service machine for return to the refinery. Figure 4 illustrates the final design basis for integrating the ROG PSA into the SMR/ Cogen facility providing a proper balance of flexibility, operability, reliability and economic H₂ supply.

Figure 4: On-Site Hydrogen Plant with Integrated Offgas Recovery H₂ PSA

For the light refinery hydrocarbon feedstocks, steam reforming technology is expected to continue to be the technology of choice for hydrogen production, much as it has been during the last 40 years. Steam reforming is a simple, efficient, well-proven technology with significant flexibility in operating with different light hydrocarbon feedstocks. These plants can also be configured to produce steam, power, and/or carbon dioxide as byproducts. Valuing byproducts at the appropriate pricing for the particular locale can reduce the hydrogen cost by as much as ten percent.

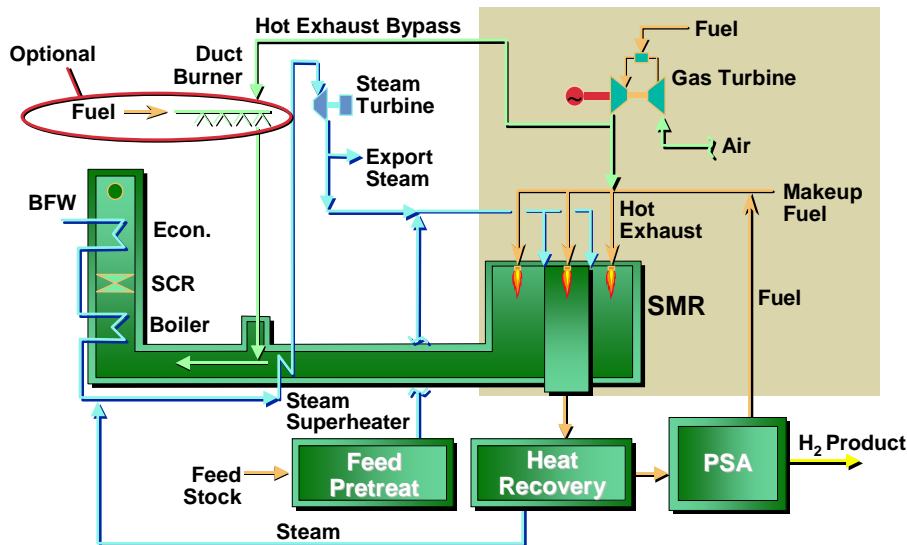
POX of heavy residues and petroleum coke can produce hydrogen at a lower cost than steam reforming under certain conditions. The key factors in this evaluation are the relative costs of the feedstock, oxygen, and natural gas. Heavy feedstocks can provide a significant fuel value discount compared to natural gas. The higher capital cost of a POX plant is attributable to extra equipment associated with feedstock storage and handling, soot and metal recovery, increased water gas shift duty, redundant

equipment to allow for reliable supply, and sulfur removal/recovery. Depending on the value assigned to the feedstocks, these higher capital costs and the cost of oxygen can outweigh the lower feedstock cost benefits, resulting in an overall higher hydrogen product cost.

Hydrogen, Steam, and Power Integration

The steam reforming plant, which is principally designed for the production of hydrogen, can also produce steam and electric power economically as illustrated in the simplified flowsheet in Figure 5. One of the key benefits of is the ability to use the hot exhaust from a gas turbine in the radiant section of the steam reformer. This hot exhaust gas at ~540°C still contains ~ 13% oxygen and serves as combustion air to the reformer. Since this stream is hot, fuel consumption in the reformer furnace is reduced. The reformer convection section is utilized as heat recovery steam generator (HRSG) in a cogeneration design. Steam raised in the convection section can be put through either a topping or condensing turbine for additional power generation. Steam raised in the convection section can be put through either a topping or condensing turbine for additional power generation.

Figure 5: Totally Integrated Gas/Steam Turbines with a Steam Reforming H₂ Plant



The steam system in the hydrogen plant is upgraded above 45 barg to 105 barg. All the high-pressure steam generated is sent to the topping turbine for power recovery before process use for the reforming reaction and export to the refiner. Appropriate bypasses can be incorporated into the plant design to de-couple hydrogen and steam production from power production.

The system can also be designed such that production of hydrogen and steam can continue in the event of loss of the power generation units through the incorporation of fresh air intakes into the reformer furnace. This permits outages of the gas turbine for maintenance and repair. Separately, a gas turbine exhaust bypass system allows the gas turbine to be decoupled from the reformer. In the event of a reformer trip, the gas turbine can operate and continue to produce power and some export steam. Depending on the natural gas cost, economics for this integration scheme can result in a very favorable power cost. Air Products and Technip have constructed six hydrogen/cogen facilities for refiners.

Integration with Industrial Gas Company Hydrogen Supply

Air Products' global hydrogen supply business grew significantly in the 1990's from a base operation of 150 thousand Nm³/hr to 1.6 million Nm³/hr (140 MM scfd to 1435 MM scfd) in 2003. To a refiner, the availability of hydrogen is often as important as its price, since it is critical to the operation of their hydrocrackers and hydrotreaters. As refiners enter the ULS gasoline and diesel era, reliability and availability of high purity hydrogen supply will become increasingly critical to refinery operations due to the potential to diminish costs associated with the inefficiencies of rerouting and reprocessing off specification hydrocarbon products.

Air Products understands the importance of reliability of hydrogen supply to refiners and demonstrates that commitment with work processes designed to reduce or eliminate outages. Air Products is the primary or secondary supplier of hydrogen to over a dozen hydrocrackers and high- pressure gas oil hydrotreaters in US and European refineries. Multiple-sourced pipeline systems provide lower costs of hydrogen due to economies of scale as well as additional degrees of availability and reliability to customers by having reserve capacity. In addition, multiple sources on a pipeline system can be operated at higher rates to meet peaking demand needs of refiners and improve their potential profit margins. In effect, the industrial gas company's hydrogen pipeline system with its multiple sources, combine with reserve hydrogen capacity to become a large "flywheel" to provide backup hydrogen product during unplanned and planned outages. Case histories illustrating the multiple benefits a hydrogen pipeline supply can create for refiners are documented in previous papers noted in the references⁽¹²⁾.

Conclusion

Hydrogen network optimization is increasingly more important to maximizing higher value transportation fuels production, minimizing clean fuels investments and to overall refinery profitability. Refiners must now unlock the value of hydrogen contained in refinery offgases, improve hydroprocessing network purities and consider new hydrogen production options. The optimum solution for an overall refinery hydrogen network can be complex and involve the screening of numerous options. These options can involve: (1) new or improved hydrogen recovery/purification equipment properly located within the refinery flowsheet; (2) ROG and/or LPG integration with on-purpose hydrogen production; (3) integration with petrochemical operations; (4) improving hydrogen plant efficiency; (5) expanding or replacing the existing hydrogen plant capacity; and (6) providing new hydrogen via pipeline supply.

Air Products provides complete Hydrogen Management Services along with a full hydrocarbon separation equipment portfolio for refineries. As the global alliance leaders in “over the fence” supply of hydrogen supply for refineries, Air Products and Technip can integrate new hydrogen supply options into your current refinery hydrogen network or use our design and operating expertise to help improve, expand or replace your existing refinery hydrogen generation facilities.

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