Optimising hydrogen production and use

Knowledge of hydrogen producing and consuming process technologies, systems analyses and process controls can be leveraged to optimise hydrogen use

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Hydrogen plays a critical role in the production of clean fuels, and its use has increased with the introduction of low-sulphur gasoline and diesel fuels. The reduction of benzene in gasoline via benzene saturation will also increase hydrogen consumption, as will the trend toward diesel cetane improvement and aromatics reduction.

Changes in marine fuel oil specifications are also expected to increase hydrogen demand. In 2008, MARPOL Annex VI regulations were passed, setting a framework for regional and global specifications on marine fuel oil quality. These regulations are expected to further increase the demand for hydrogen for desulphurising residual fuel oils and, through the increase in distillate fuel demand, to replace residual fuel oil in marine fuels (see Figure 1).

The overall reduction in demand for heavy fuel oils has encouraged many refiners to install bottoms upgrading capacity such as delayed coking units. The streams produced by coking typically contain higher contaminant levels (sulphur and nitrogen) than the equivalent straight-run streams. Hydrotreating these coker products has also increased hydrogen consumption.

Hydrocracking has become increasingly important for converting heavier crude fractions into high-quality clean fuels. Increased reliance on hydrocracking for clean fuels production has also led to a rise in hydrogen consumption. A hydrocracking unit is typically the largest hydrogen consumer in the refinery, and
hydrogen can account for more than 80% of the unit’s operating cost (see Figure 2).

The quality of crude oil is gradually declining. Globally, crude API gravity is declining and the sulphur content is gradually increasing (see Figure 3). Both of these trends in crude quality will contribute to increased hydrogen consumption during refining. The use of synthetic crudes derived from oil sands and other unconventional sources is expected to increase to 2 million b/d by 2020. These synthetic crudes will require additional hydrogen to be refined into usable products.

One of the major sources of hydrogen and gasoline pool octane is the catalytic reformer. The blending of ethanol has reduced the octane requirements from other refinery product streams to maintain the gasoline pool octane; often, refiners respond to this situation by reducing the catalytic reformer’s severity to produce a lower-octane reformate product. However, a lower catalytic reformer severity typically produces less hydrogen. Lower hydrogen production from a lower severity operation is in opposition to the increased demand for hydrogen in the rest of the refinery and compels the refiner to obtain hydrogen from other sources. Some refiners have decided to operate their catalytic reformer for hydrogen production and tolerate some octane giveaway in the gasoline pool.

Many refiners produce or purchase hydrogen to have a sufficient supply available for their refinery. The steam reforming (SR) process is used to produce most of the additional hydrogen required by refiners. The cost of the hydrogen produced is directly proportional to the feed costs. In the US, most of the hydrogen is produced in steam methane reforming (SMR) units and the cost is typically tied to the price of natural gas.

The production of hydrogen by a steam reformer requires significant energy; one tonne of hydrogen produced requires 3.5 to 4 tonnes of hydrocarbons as feed and fuel. Hydrogen production can account for up to 20% of refinery energy consumption. Additionally, the production of hydrogen generates significant amounts of carbon dioxide (CO₂); the production of 1 tonne of hydrogen generates 8–12 tonnes of CO₂. Future environmental legislation may regulate the amount of CO₂ that can be generated and may increase the costs of hydrogen production.

Availability of hydrogen is a requirement for the production of clean fuels, and demand for hydrogen is at an all time high. Anticipated future trends and regulations are expected to further increase hydrogen consumption. At the same time, the production of additional hydrogen is expected to become more expensive.

While it is well understood that the ability of a refiner to produce clean fuels depends on having sufficient hydrogen, what many refiners recognise is that optimum use of hydrogen will maximise refinery profits.

Hydrogen network analysis and improvements
Refinery hydrogen networks typically interconnect many producers, consumers and purification units with different pressures, purities and operating objectives. The network grows with each subsequent refinery project, modified in ways that minimise complexity and the interruption of existing units rather than for refinery-wide optimisation. Hydrogen production costs and constraints on availability are typically much greater than when the network was first envisioned. All of these factors lead to the conclusion that most operating hydrogen networks are not optimised for today’s environment — not for the
minimal cost of hydrogen production, nor for maximised refinery margins.

**Optimising the hydrogen network**

In many hydrogen optimisation schemes, it often occurs that the greater the number of degrees of freedom, the larger the improvement that is possible. The most successful programmes for improving the hydrogen network draw the largest possible envelope and take advantage of all the “knobs” that are available to turn, including network connectivity, increased hydrogen production capacity, target hydrogen partial pressures, process changes in producers and consumers, catalysts, operating procedures, revamped and new purification capacity, pressure swing absorption (PSA) unit feed to product bypass, feed to hydrogen plant, compressor modifications, ability of LP models to accurately represent hydrogen availability constraints, and header pressure control system improvements.

For the optimisation of hydrogen use, the benefits are driven by identifying and alleviating critical constraints in the refinery-wide hydrogen network. Every refinery is different and, from time to time, the active constraints in a refinery can change with different crude feed operating objectives. A refinery network may be constrained by total moles of hydrogen available, hydrogen purity, hydraulics, purifier capacity, compression, H₂S scrubbing, fuel system constraints or other refinery-specific issues.

What is ultimately constrained is a refinery’s profitability. When there is insufficient quantity or purity of hydrogen, charge rates, the processing of more difficult feeds or product quality are limited and refinery margins are reduced. When sufficient hydrogen is available, the effect of inefficiencies is higher operating (hydrogen production) costs.

**Hydrogen and process performance**

Hydrogen has a significant effect on process performance and profitability. Hydrogen partial pressure, a variable completely under the operator’s control, can be utilised to increase catalyst life in hydrotreating units, increase throughput, increase conversion, improve product quality, or process more profitable feeds. The potential benefits of affecting refinery profitability through hydrogen management are much greater than those from simply reducing hydrogen production or purchase costs. Of course, the benefits must be considered in concert with the capital and operating costs of increasing the hydrogen partial pressure in order to determine the most profitable targets.

Establishing and faithfully maintaining the target hydrogen recycle purity of key hydrotreating units is an important component of effective hydrogen management. For refiners who want to maximise the effectiveness of their hydrogen network, further optimisation is possible when targets for recycle hydrogen purity are modified through major operating changes, such as variation in charge rate, feed properties and severity. The measured variable that represents hydrogen partial pressure is recycle purity. Make-up purity and purge rate can both affect the hydrogen partial pressure, but they do not determine it.

**Essence of hydrogen network optimisation**

The first step in improving the hydrogen network is to clarify the objective. The objective should always be overall refinery profitability rather than hydrogen production costs. Operating costs, capital costs and refinery margins are all part of the picture.

At a high level, the process of hydrogen network optimisation is:

- Identify the constraint that is most limiting profitability
- Identify ways to alleviate the constraint and select the most cost-effective approach.
- Consider all the options listed above. Many improvements can be implemented quickly without capital projects.
- Utilising a broad range of tools makes comprehensive optimisation possible.

**Tools**

Network analysis

Hydrogen network pinch analysis is a valuable analytical method to identify the theoretical minimum hydrogen requirements for a given network through unconstrained modification and connectivity (including turning hydrogen recycle units into once-through and cascading the purge to
another unit). It provides a target and a pinch purity that can guide the analyst in proposing changes to the existing network. However, pinch analysis is limited in a number of ways. Its key limitations are that it is not concerned with the pressures of sources and sinks, it treats all light hydrocarbon components the same (in reality, methane has a much greater tendency to build up in the recycle loop than propane), it does not consider the significant effects on compressors and hydraulics of changing a hydrogen recycle hydroprocessing unit into a once-through unit, nor does it consider sulphur levels.

To evaluate potential network improvements, a detailed refinery-wide model of the hydrogen network should be employed. One of the critical features of this model (as opposed to a spreadsheet model) is that it simulates the non-linear relationships between charge rate, make-up rate, make-up purity, and recycle purity (hydrogen partial pressure) and purge rate. With this model, potential modifications can be tested, such as changing make-up source, trading off purity against recovery in an existing purifier, adding new purification, or changing the target hydrogen partial pressure in a hydrogen-consuming process unit. The same model can be used by the refiner for operations and project planning.

Process and purification models
Process models of catalytic reformers enable the analyst to understand the effects of operating, mechanical or catalyst changes on hydrogen yield and purity.

The hydrogen network model predicts the effect of changing a hydrogen consuming unit’s target recycle purity on the required make-up and purge rates. A hydroprocessing model will predict the effect of changing the hydrogen partial pressure on process performance (catalyst life, product quality, conversion) and hydrogen consumption.

Purifier (PSA and membrane) models are used to predict the impact of changing a purifier’s feed composition and operating conditions on hydrogen product purity and recovery. These models are also used to identify the potential for debottlenecking existing purifiers.

Refinery economics
The right question to ask is not “How much money am I spending on hydrogen?”, but “Am I utilising the right amount of hydrogen to maximise my refinery margin?” With the addition of a refinery economic model to the toolkit, the analyst can consider how the addition of lower-value, more difficult feeds affect hydrogen consumption, desired hydrogen partial pressures, the hydrogen network and refinery margins.

Design-phase full optimisation
We have had the opportunity to optimise grassroots refineries before individual process unit design bases are set. When we optimise at this stage of a project, all parameters are available for optimisation and we can be that much more effective in minimising capital and optimising refinery margins.

For example, in the design work for a major new refinery for Petrobras, we had full freedom to route and recover streams, since design pressures and make-up purities were not yet fixed. We set the separator pressure of one hydrotreater such that the flash gas could be sent to the suction of the make-up compressor of another hydrotreater and the revised make-up hydrogen purity could be taken into account in the design of the consuming unit. The flash drum in another unit was set at a pressure such that its flash gas could easily be purified and recovered in an existing PSA unit.

Given that no external fuel could be purchased for this refinery, the fuel balance was not only critical from an economic standpoint but it determined the feed selection for the hydrogen plant. In our early estimates, we expected that an internally generated LPG stream would have to be burned to meet the fuel balance. After energy optimisation of the preliminary design, the fuel gas balance shifted to positive, and we were able to utilise lower-value fuel gas as hydrogen plant feed. As an additional benefit, we could isolate hydrogen-rich fuel gas streams and utilise them as hydrogen plant feed. Not only is fuel gas less valuable than LPG, but the hydrogen content enables a significant reduction in firing and energy consumption in the hydrogen plant furnace compared to other hydrocarbon feeds.

Optimising beyond the hydrogen network
Broadening the optimisation
envelope even further, it is possible to consider optimising more than just the hydrogen system at one time. There are often additional benefits when several systems are optimised together. For example, when designing a refining complex with new catalytic reforming and hydrocracking units, it is possible to consider the hydrogen and LPG recovery systems at the same time. As standalone designs, each unit would have its own LPG recovery system and produce moderate-purity hydrogen to be purified/recovered (reformer net gas and hydrocracker flash gas). The reformer net gas contains the recoverable LPG and hydrogen, while the recoverable hydrogen and LPG are found in the purge and flash gas streams of the hydrocracker.

LPG recovery is much more efficient in the hydrocracker than in the reformer because the gas stream has a lower hydrogen concentration. Also, it is more cost effective to process both hydrogen streams in one PSA unit. It is possible to integrate the two systems together by designing a single PSA unit that takes both hydrogen streams as its feed and sending the PSA unit tail gas to the LPG recovery system in the hydrocracker. Since the PSA unit concentrates LPG in the tail gas, recovering the LPG from the tail gas in the hydrocracker recovery system requires less energy and capital than if it was recovered separately in the reformer. An additional benefit of the integration is that a PSA unit product bypass can now be integrated with the hydrocracker to enable optimisation of the hydrocracker make-up purity — a degree of freedom that would not otherwise exist.

**Hydrogen network improvements**

The potential for improving hydrogen efficiency is estimated by evaluating the hydrogen-containing streams currently going to fuel, flare and hydrogen plant feed. The potential financial benefits will also be a function of the value of hydrogen in a refinery. The potential benefit of improvements in process performance through hydrogen optimisation can be estimated roughly by evaluating current constraints to process performance, refinery drivers and refinery economics. Our hydrogen management studies generally identify $2 million to $20 million in annual benefits. In seven studies, UOP identified a total of $137 million in annual benefits. A third of the opportunities identified were no/low-cost changes and the remainder required capital projects (all with a simple payback of less than two years).

While 38% of the opportunities for improvement came from adding or improving hydrogen purification capacity, a much broader scope of evaluation is required to achieve these benefits. Operating changes and better management of hydrogen partial pressure targets were important, as well as

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**Figure 4 Typical results: summary of benefits was $137 million/y in seven studies**

- **Capital project**: 66%
- **No/low cost**: 34%
- **Purification**: 38%
- **Other operations**: 15%
- **Other**: 25%
- **Catalyst**: 2%
- **H₂ partial pressure**: 12%
- **Change flow piping**: 5%
- **Control improvements**: 3%

Potential financial benefits will also be a function of the value of hydrogen in a refinery.
many other issues. Some of the improvements found in these seven studies include:

- Operators adjusting the PSA capacity factor to improve hydrogen recovery
- Addition of a new purification unit
- Cascading the purge from an isomerisation unit to the make-up of another unit
- Reducing the make-up purity of a hydrocracking unit to reduce hydrogen purification losses, while still meeting the minimum hydrogen partial pressure target
- Increasing the make-up purity to a diesel hydrotreating unit to improve process performance
- Changing feed streams to an existing membrane purifier to obtain more efficient purification
- Sending a hydrogen stream of moderate purity to hydrogen plant feed rather than fuel, reducing the operating costs of the hydrogen plant
- Modifying a compressor to eliminate hydrogen leaking through the seals to flare. (Wasting hydrogen to flare is much more costly than wasting hydrogen to fuel.)
- Replacing pressure safety valves with pilot-operated valves so that the reactor operating pressure can be increased by 5%, enabling an increase in hydrogen partial pressure.

### Options for hydrogen recovery and purification

In the refining industry, high-purity hydrogen can improve the performance of hydro-processing units (hydrotreaters and hydrocrackers) by increasing the recycle gas purity and the hydrogen partial pressure in these units.

In existing hydrotreating units, the use of high-purity hydrogen to increase the reactor section’s hydrogen partial pressure can deliver the following benefits:

- Reduce the quantity of make-up gas required
- Enable the processing of more feed
- Provide the ability to process more difficult feeds
- Improve product quality, especially distillates
- Increase catalyst life
- Reduce the quantity of purge gas required to maintain recycle gas purity
- Debottleneck existing make-up gas compressors.

The design of a new hydrotreating unit can benefit in the following ways from a higher hydrogen partial pressure through the use of high-purity hydrogen as the make-up gas:

- Reduced capital cost (from lower total plant pressure, smaller make-up gas compressors, smaller recycle gas compressor, smaller reactors and less catalyst.)
- Reduced power and fuel requirements.

### Improved distillate product quality

There are various technology options for the production of high-purity hydrogen by recovering hydrogen from lower-purity streams. The major technologies used for hydrogen recovery and purification are PSA and membranes. A few hydrogen cold boxes have been constructed, but they are only warranted when recovery of a valuable liquid product is required. Selection of technology will be guided by the specific application. Table 1 is a guide to selecting between PSA and membrane technologies for hydrogen recovery and purification.

The UOP Polybed PSA System is a cyclical process in which the impurities in a hydrogen-containing stream are adsorbed at high pressure and subsequently rejected at low pressure. The hydrogen produced is at just slightly below the feed pressure and is typically upgraded to 99.9+% purity, with hydrogen recoveries of 60–90+. The Polybed PSA System operates as a batch process. Multiple adsorbers operating in a staggered sequence are used to produce constant feed, product and tail gas flows. The vast majority of

<table>
<thead>
<tr>
<th>Variable</th>
<th>Polybed PSA</th>
<th>Polysep Membrane</th>
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<tbody>
<tr>
<td>Product purity</td>
<td>• 99–99.999 mol%</td>
<td>Up to 98 mol%</td>
</tr>
<tr>
<td>Remove CO₂, H₂S, H₂O</td>
<td>• –</td>
<td>–</td>
</tr>
<tr>
<td>High product pressure</td>
<td>• –</td>
<td>–</td>
</tr>
<tr>
<td>Economy of scale</td>
<td>• –</td>
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</tr>
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<tr>
<td>H₂ recovery</td>
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<td>Very easy</td>
</tr>
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Table 1

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Polybed PSA Systems have been in hydrogen service. The economic justification for a PSA unit will depend on the hydrogen content of the feed stream and the how the refiner values chemical hydrogen versus hydrogen as a fuel. Generally the following rules apply:

- Hydrogen feed concentrations >55% are easily economically justified
- Between 40 and 50% hydrogen can be economically upgraded dependent on site-specific requirements
- Below 40% hydrogen, economics become more difficult to justify.

The UOP Polysep Membrane System separates a gas mixture by the differences in permeation rates of various gases through the polymeric membrane. The more permeable gas (hydrogen) is enriched on the permeate side of the membrane, while the less permeable gas enriches on the feed side of the membrane. The membrane separation of these gases is a pressure-driven process and requires a high feed pressure. The hydrogen product stream (permeate) is produced at a lower pressure by taking a pressure drop across the membrane. The non-permeate stream is available at essentially feed pressure. The membrane process is continuous and produces permeate and non-permeate streams at constant flow, pressure and purity.

The membrane process is the most economical process for high-pressure purge gas upgrading. The membrane system is normally designed to produce hydrogen at 300–600 psig, 92–98 vol% purity and 85–95% hydrogen recovery. The product delivery pressure is chosen to allow the product to enter one of the stages of the make-up hydrogen compressors.

In addition to adding a new PSA or membrane unit, there are often opportunities to improve the performance of existing units. PSA and membrane units are often revamped to increase hydrogen production, recovery and/or purity. These revamps can be as simple as replacing adsorbents or as complex as adding additional equipment. Frequently, refiners elect to perform the revamps in phases, where each phase adds additional capacity. The following are examples of revamps conducted by refiners in North America.

**Case study 1: adsorbent reload**

A major North American refiner started up a plant with two identical steam reformer Polybed PSA-based hydrogen units, each with a product capacity of 27.5 million scfd and a third Polybed PSA unit to upgrade net gas from a UOP CCR Platforming Process unit with a product capacity of 28.3 million scfd. The product hydrogen from the three PSA units was combined and used as the make-up hydrogen to a hydrocracker.

The refiner wanted to process more crude and, therefore, the demand for hydrogen increased. The CCR Platforming unit’s net gas purity was greater than 90% hydrogen and was deemed acceptable for direct feed to the hydrocracker when blended with high-purity hydrogen from the PSA unit. Re-routing the net gas from the PSA unit to the hydrocracker reduced hydrogen loss to the PSA unit’s tail gas but, more importantly, it freed up this PSA unit for other uses.

First, the PSA units were modified in a number of stages. The refiner debottlenecked the two steam reformers, which were then producing over 20% more raw hydrogen than was originally intended. The CCR PSA unit (that is, the PSA unit processing net gas from the CCR Platforming unit) was revamped by changing the software and design conditions to allow it to operate on SMR gas in parallel with the original two SMR PSA units. The adsorbent in the CCR PSA unit was, however, far from optimum for service on SMR gas. The three PSA units could easily handle the amount of flow. Since capacity was not a problem, a study was made with the objective of increasing the amount of hydrogen recovered.

The adsorbent in the PSA unit originally treating the CCR Platforming net gas was replaced with adsorbent optimised for SMR gas. This was done in conjunction with the first set of vessel inspections, and the PSA units were balanced and optimised for the revised flow scheme. The hydrogen recovery in this PSA unit increased by over 6% and simultaneously resulted in an improved CO specification on the product hydrogen.

The next vessel inspection was of one of the SMR PSA units. For the inspection, the adsorbent was again vacuumed from the vessel through the top flange (manway) and then screened and replaced in its original position. About 15% of the adsorbent was lost during this procedure due to screening losses and interface losses.
between adsorbent layers. This presented an opportunity to replace the existing adsorbent with higher-performance adsorbent to provide higher recovery and capacity.

After reloading with higher-performance adsorbents, the previously identical PSA1 and PSA2 units for their respective SMR units were in operation side-by-side with advanced and original adsorbents in service. PSA1 demonstrated a capacity increase of 10% over the original adsorbent (still installed in PSA2) as well as a 2% increase in hydrogen recovery.

Figure 5 shows these improvements as trends recorded by the distributed control system. The new adsorbents in PSA1 enabled it to produce more hydrogen from the same or less feed.

Case study 2: phased revamps
A large residuum desulphurisation (RDS) facility in the Americas was designed using hydrogen make-up from a steam reformer hydrogen plant with a product flow of 55 million scfd. The steam reformer was scrubbed of H₂S and throttled down to the steam reformer’s feed pressure, and the low-pressure vent was compressed to match the steam reformer’s feed pressure. Figure 6 shows the overall flow scheme.

Various revamps have taken place to meet the refinery’s increasing needs for hydrogen over the years (see Table 2).

Phase 1
As designed, the feed gas to the steam reformer was predominantly natural gas, and supplemental feed was derived from the high-pressure vent and the low-pressure flash gases of the RDS unit. The high-pressure vent gas was scrubbed of H₂S and throttled down to the steam reformer’s feed pressure, and the low-pressure vent was compressed to match the steam reformer’s feed pressure. Figure 6 shows the overall flow scheme.

Phase 2: first revamp of steam reformer PSA
The first plant expansion saw total hydrogen production increased from 55 million scfd to 70 million scfd. The initial capacity increase was achieved through debottlenecking of the steam reformer and SMR PSA unit to increase hydrogen output by 18% from 55 million scfd to 65 million scfd. The SMR PSA unit’s debottlenecking was achieved through a process redesign and changes to the control system software, with essentially no hardware modifications. Reducing the
number of pressure equalisations enabled the unit to process a much higher feed rate with a small decrease in hydrogen recovery, while still maintaining design product purity. This increase in feed capacity more than compensated for the small decrease in hydrogen recovery; the net result was an increase in hydrogen production by 18%.

The high-pressure vent stream (over 2000 psig) was routed to a membrane system. The hydrogen product was delivered to the suction of the hydrogen make-up compressor. This change added 5 million scfd of hydrogen to the refinery’s hydrogen header.

Phase 3: a new PSA unit
Next, a UOP CCR Platforming unit was installed and the net gas was fed to a new 10-bed PSA unit. By compressing the tail gas, it was possible to maximise the hydrogen recovery in the PSA unit while still sending the tail gas to the refinery fuel system. This new PSA unit, processing net gas from the CCR Platforming unit, added 50 million scfd to the hydrogen balance. Five years later, this unit was revamped (see Phase 5).

Phase 4: second revamp of steam reformer PSA unit
A second revamp took place to further increase the capacity of the steam reformer and its associated PSA unit from 65 million scfd to 85 million scfd. This additional debottlenecking required modifications to many of the control valves and piping on the piping skid, but maintained the existing adsorber vessels and tail gas mixing tanks. As flow rates had increased by over 50% since the original design, pressure drop problems encountered in the feed, product and tail gas piping had to be overcome. This was achieved by installing valves with larger discharge coefficients to replace some of the existing valves, and pressure drops through the unit were reduced to acceptable levels.

The new cycle was designed

<table>
<thead>
<tr>
<th>Phase</th>
<th>Steam reformer</th>
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<th>Total</th>
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<td>5</td>
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<td>165</td>
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</table>

Table 2

Figure 7 Case study 2: revamped flow scheme after phase 5
such that any component could fail and the unit would continue to operate at design rates and maintain design hydrogen purity. This further improved on-stream factors and unit reliability, as no single component would cause a unit trip or reduction in feed capacity.

Minor modifications were made to the skid instrumentation and the entire control system software was reprogrammed to implement the new cycle. The revamp, design and hardware was completed, ready for installation, in less than six months after the project was authorised. All field modifications were completed during a two-week turnaround.

Phase 5: revamp of CCR PSA unit
Next, the PSA unit processing net gas from the CCR Platforming unit was debottlenecked, as additional hydrogen net gas feed was available from the CCR Platforming unit. By installing more tail gas compression and updating the cycle, the PSA unit’s hydrogen production was increased to 60 million scfd with the design hydrogen purity maintained. Fabrication and installation of the new compressors determined the project’s overall schedule, and changes to the PSA unit were implemented well within the time frame.

Phase 6: planned future expansion
Due to changing demands, the refinery is still short of hydrogen, and UOP was asked to evaluate options to further increase the CCR PSA unit’s capacity. The most recent PSA unit revamp resulted in the ability to process all of the available CCR Platforming net gas and, at the time, there was still some spare tail gas compression capacity available. The CCR PSA unit can be further revamped to meet current demand by fully utilising the existing compression.

One approach being considered is to make cycle changes similar to those implemented in the steam reformer PSA unit at this plant. Future hydrogen production is predicted to increase to 75 million scfd. This revamp would reuse the existing adsorber vessels and adsorbents, but would require changes to the existing valves and piping skid. These changes would allow the CCR PSA unit to produce 50% more hydrogen than the original design and maintain the hydrogen recovery already obtained from the previous revamp. This revamp would fully utilise all the tail gas compressors to their design capacities.

Additionally, partial adsorbent replacement with the current high performance adsorbents would allow hydrogen recoveries of both units to improve, thereby further increasing hydrogen production. Implementing Phase 6 would bring the total hydrogen availability for this refinery to 165 million scfd, three times the original capacity.

**Case study 3: adsorbent and cycle changes add 30% capacity**
A Polybed PSA system was originally designed as a six-bed unit processing 12 million scfd of SMR feed and producing hydrogen with 10 ppmv CO. The plant needed additional hydrogen and had available a refinery off-gas stream containing ~76% hydrogen and C3-C6 hydrocarbons. Two choices were considered. The first was to process the new feed in the SMR and send the total effluent to the PSA unit. The second was to send the gas blended with the current SMR gas directly to the PSA unit. In the first case, the hydrogen would pass through the steam reformer on a free ride and there would be a need for additional modifications to the SMR to process the gas. In the second case, the SMR flow rate would stay constant and the PSA unit would need an adsorbent replacement for the heavier hydrocarbons in the feed, plus a new process design.

The refiner chose the second option, to replace the PSA adsorbents and modify the PSA cycle. This PSA unit revamp increased hydrogen production by ~30% from the combination of a new cycle and new adsorbents (see Table 3).

**Hydrogen optimisation: sustaining the benefits**
It is one thing to optimise your hydrogen network on paper. It is quite another to actually realise the benefits. Daily operating targets must be optimised to reflect the day-to-day changes of the refinery. Operations must know the critical operating parameters of the hydrogen network to monitor and manage, and have that data readily available. Ideally, one person is responsible for the network as a whole and can manage the network to
maximise the overall refinery margin, to avoid each individual operator making decisions based on just their own unit.

It is common practice to produce additional expensive hydrogen and burn it, just as a safety margin in case it is required in a hurry. Operating procedures, control improvements, automation including multivariable control and better operator communications all can mitigate this inefficiency and waste.

To optimise the network continually, the refiner must understand the key constraints within the network (purity, compression and so on) and aim to meet those constraints every day. Operations must understand and monitor these constraints and know what adjustments they can make to increase the hydrogen network’s efficiency by pushing closer to a real network constraint. For example, in a cascaded system, one might regularly reduce the DHT make-up purity (bypass around a PSA) while increasing the make-up and purge rates and maintaining target recycle purity, up until the make-up compressor is at its maximum capacity. Monitoring the compressor spillback and adjusting regularly will minimise hydrogen losses in the PSA under all refinery operating conditions.

Every operator should be aware of the value of hydrogen, the costs of sending hydrogen to fuel and the penalties for operating too conservatively. Running a PSA unit so that there is no detectable impurity in the hydrogen product is safe, but it can represent a 1–10% decrease in PSA recovery, thus wasting hydrogen. Operating a hydrogen processing unit with higher than target purity for recycle hydrogen is safe, but it represents unnecessary losses of hydrogen to fuel, either as purge or as an excessive feed rate to a purifier with associated hydrogen losses to the tail gas.

When analysis of recycle gas purity is infrequent or unreliable, the operator is almost forced to run conservatively. In this case, refiners should consider installing one of the new inexpensive, very low maintenance, direct hydrogen-reading analysers that are now on the market.

Representation of the hydrogen network in the refinery’s linear programming (LP) model is an often overlooked opportunity to significantly enhance profitability while evaluating the hydrogen network. This is not significant if hydrogen does not constrain the refinery, but if charge rate and severity targets are set in the LP model or in the field in response to hydrogen constraints, it is critical that the LP model accurately reflects the actual constraints. While, typically, LP models do reflect the hydrogen yields in catalytic reformers with feed properties and severity, they can be modified and maintained to reflect accurately hydrogen compressor constraints and the impact of hydrogen processing feed properties and severity on hydrogen consumption, partial pressure, purge rates and make-up rates. Where even greater detail is warranted, the LP model can reflect the relationship between hydrogen consumption and product properties in these units.

Conclusions
Hydrogen is an increasingly important component of refining, particularly in view of the increased demand for clean fuels. There are opportunities to optimise the use of hydrogen in a refinery to maximise profits:

- Hydrogen network studies and flow scheme optimisations
- PSA and membrane technologies to recover and purify hydrogen
- Reforming process and catalyst technologies to produce more hydrogen
- Hydroprocessing and catalyst technologies to consume less hydrogen.

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