Hydrogen optimisation at minimal investment

Refiners making long-term investments to meet clean fuel specifications could at the same time, with already-available technology, improve their existing hydrogen resources to boost profitabilty in the short term. The authors review the options

Nick Hallale and Ian Moore *AspenTech Ltd*
Dennis Vauk *Air Liquide*

Oil refineries in Europe and North America are currently developing and implementing projects to comply with future gasoline and diesel fuel specifications. The increased demand for hydrogen needed to meet these new specifications is well known. In order to meet various levels of increased demand, some refiners are applying "hydrogen pinch" techniques to optimise their future hydrogen balances and minimise capital investment.

Although these techniques offer some valuable insights, the hydrogen targets generated can be both wildly over-optimistic and fundamentally inaccurate. Improved methodologies to overcome these deficiencies have generated practical and accurate targets, and they also make it easier to identify and model projects for meeting them.

Yet, should refiners only focus on long-term profitability? The experience of Pro-En services, an alliance between AspenTech and Air Liquide, is that by first focusing on existing operations, refiners can achieve very significant no-cost or low capital expenditure (low-Capex) savings that boost short-term profitability and reduce long-term investment. This is demonstrated based on recent case studies, together with an overall strategy permitting refiners to make the best use of hydrogen resources while complying with clean fuels legislation.

Refineries generally fit into one of three situations with respect to hydrogen:

Type 1: The refinery has an excess of hydrogen, which is routed to the fuel gas system. Refinery operations are not constrained by the hydrogen balance. Hydrogen is priced based on its fuel gas value. Direct pressure control letdowns to fuel gas have no economic penalty. Process unit high-pressure purge rates can be increased to increase hydrogen partial pressure in process reactors without penalty.

In these cases, catalytic reformer hydrogen is normally the only source of hydrogen supply.

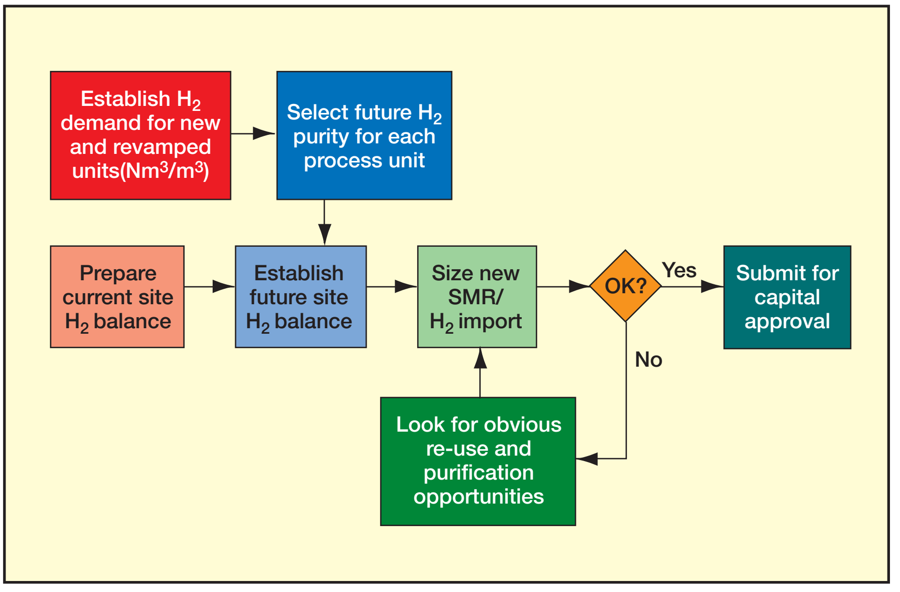

Figure 1 *Typical approach to clean fuels by meeting hydrogen demand through "on purpose" hydrogen production or external import*

Typical hydrogen price (depending on marginal fuel price) is 350/tonne.

Type 2: The refinery is often short of hydrogen, with the catalytic reformer(s) acting as the swing hydrogen producer. Refinery operations (and profitability) are constrained by the hydrogen balance. Process units compete for hydrogen. Hydrogen is priced (via the site LP model) based on the reduced refinery profitability (gasoline over-production).

Direct pressure control letdowns have a high economic penalty. Process unit high-pressure purges are minimised, reducing reactor hydrogen partial pressures. In these cases, catalytic reformer hydrogen is normally still the only source of hydrogen supply, although it can also apply when on-purpose generation or import capacity is limited and operating at maximum. Under these conditions, hydrogen value can be 1000/tonne.

Type 3: The refinery can meet hydrogen demand through "on-purpose" hydrogen production such as with steam methane reforming (SMR) or through external import. These are the refinery swing hydrogen producers. Refinery operations are not constrained by the hydrogen balance. Hydrogen is priced based on its marginal production or import value. Direct pressure control letdowns have an economic penalty based on marginal hydrogen value relative to its value as fuel.

Process unit high-pressure purge rates are optimised to trade-off value of hydrogen partial pressures (yield, capacity, catalyst life) against purge loss. The value of hydrogen is dependent on whether a capital allowance is included in the hydrogen price or not. The total cost of hydrogen from production or import, used for investment decisions, can approach 900/tonne. The incremental production cost, used for operational optimisation, is typically 500/tonne.

Most refiners are on a painful journey from the fondly remembered days of Type 1 to a current situation of Type 2. Larger and more profitable refineries are developing and implementing plans that take them to Type 3, while a small number may choose to stay within Type 2 as major investment simply cannot be justified.

Clean fuels approach

Many refiners faced with becoming a Type 3 refinery tend to follow an approach such as that illustrated in Figure 1 (previous page). First, a current hydrogen balance is prepared showing the hydrogen that is produced, consumed, purified and purged. The refinery then obtains preliminary estimates of hydrogen consumption (Nm^3/m^3) from the licensors for revamped units and new process units. Then the current balance and future demands are merged in order to establish a future site balance.

This will give an indication of how much on-purpose production or import is needed. If the estimate is acceptable, the refinery can submit it for capital approval. If it is not acceptable, improved ways of recovering hydrogen in-plant via rerouting or purification can be sought. These should have the effect of reducing on-purpose production or import.

While this approach gives a refiner the big picture of future hydrogen demand, at each step in the procedure there are hidden opportunities for reducing operating costs and capital investment.

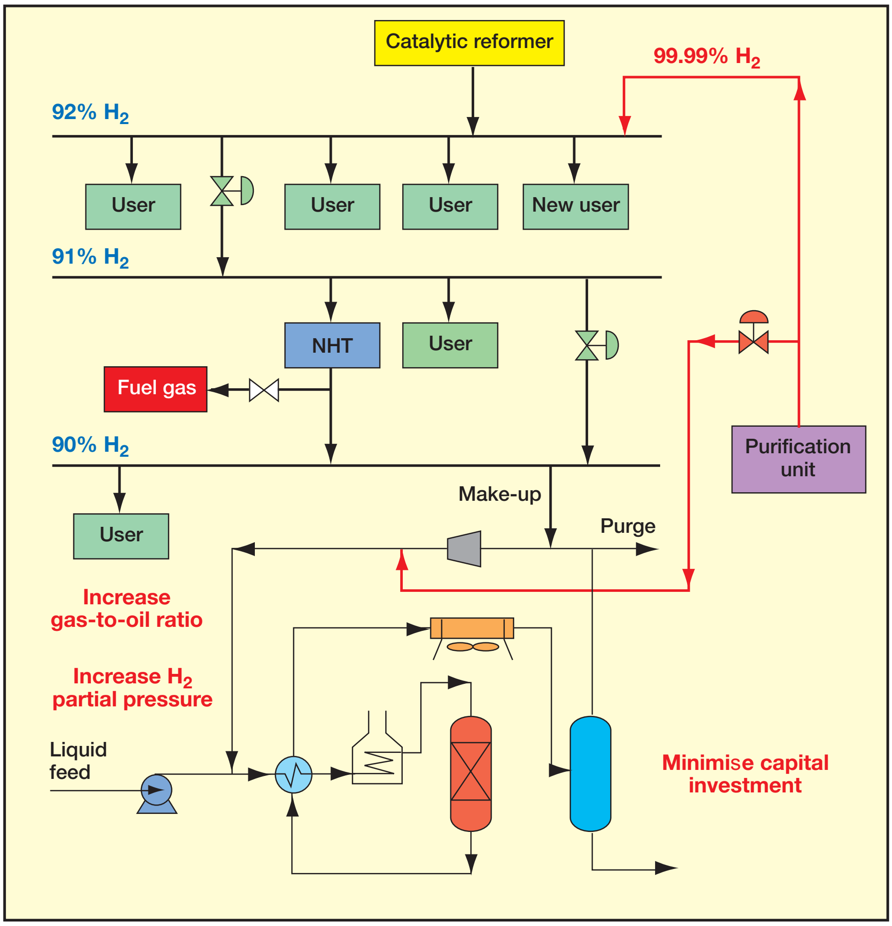

***Figure 2** Optimising use of high purity hydrogen while boosting gas-to-oil ratio*

Accurate H_2 balances

Refinery hydrogen balances never balance, as is often said in the industry. And it is certainly true that closing a refinery hydrogen balance is not a trivial task. Without accurate flowmeter corrections, very large errors in site-wide hydrogen balances can be expected. However, balances that close to within 2–3% are achievable through a systematic and thorough approach.

Flow errors are particularly sensitive to the light ends content of hydrogen-rich gas, due to the disproportionate impact on overall gas molecular weight (MW). Errors can be a true measurement error, on just the difference between the measured value and the value stored in the data historian for flow correction (if different). Refiners typically correct flowmeter readings for temperature and pressure, but not for composition. If they do correct for composition, the compositions are not usually measured and updated regularly.

Does it really matter if the refinery hydrogen balance cannot be closed? There are three reasons why it should.

First, surprisingly large benefits can be gained by identifying inefficiencies and losses. For example, recent optimisation studies identified an open hydrogen valve on hydrogen line to flare; open valve on hydrogen line to empty reactor; bypassing on feed line to LPG recovery unit (twice); compression of hydrogen gas followed by direct letdown. While these may seem obvious, in fact all of these were hidden by a combination of inaccurate flow measurements and an absence of flow meters at key locations. Yet, each of these led to inefficiencies costing the refiners more than 1 million/year.

Second, uncertainty in the current hydrogen balance tends to escalate in future plans. One refiner had a current unaccounted use of 15%. The same percentage unaccounted use was assumed in the future design case, which in effect doubled the fixed value of the loss. This was justified on the basis that nobody can predict the future, so over-sizing of the new hydrogen plant would not be a bad thing. Yet when the design basis was reviewed for the new hydrogen plant, it had correctly considered alternative future scenarios.

The large unaccounted use was just adding unconscious over-design on to an already conservative sizing. The incremental capital investment for the "unconscious" over-design was of the order of 10 million.

Finally, inaccurate flow measurements can constrain current operations. In a recent study, the profitability of the refinery was at times constrained by the throughput of a diesel hydrotreater. The charge rate to the unit was limited by a minimum required gas-to-oil ratio (GOR). Due to an incorrect molecular weight correction, the true GOR value was 50% higher than that calculated in the data historian. By updating the flow meter correction procedure within the data historian, the refinery debottlenecked the process unit.

Licensor/vendor interaction

Licensors revamping reactors and supplying new reactor units base their designs on information supplied by the refiner about the available makeup hydrogen. The refiner will specify to the licensor the makeup composition and pressure. This information is then used to size the reactor and set the recycle and purge flow rates and compositions.

The licensor normally optimises the design of the revamped or new process unit in isolation of overall hydrogen network considerations, as this is outside the scope of the revamp project. However, there is scope to optimise the feed purity and conditions as the future hydrogen network evolves.

For example, in a recent hydrogen recovery study for a European refiner, a parallel hydrotreater revamp study was under way. The licensor was given current makeup purity (90 vol%) and pressure on which to base the revamp design. Replacement of the recycle gas compressor was to be avoided due to the unacceptably high investment cost.

As the study progressed, it was proving difficult to meet required product specifications due to hydrogen partial pressure and GOR constraints. Around this time, the hydrogen recovery study concluded that the best option was to install a new purification unit to produce hydrogen at 99% purity. The refiner proposed routing the recovered hydrogen to the main hydrogen header to allow maximum flexibility of hydrogen supply.

However, knowing the constraints imposed on the hydrotreater revamp design, Pro-En engineers suggested that some of the PSA hydrogen be fed directly to the hydrotreater downstream of its recycle compressor. This boosted the GOR and hydrogen purity fed to the revamped reactor and allowed its size (and hence capital cost) to be reduced significantly. This project is shown schematically in Figure 2.

As refineries invest in alternative sources of hydrogen supply, they move from having a single purity supplier (catalytic reformer gas) to multiple supplies at differing purities and pressures. This introduces much more scope for optimising the use of high-purity hydrogen, both during the design process and in the longer term for operations improvement.

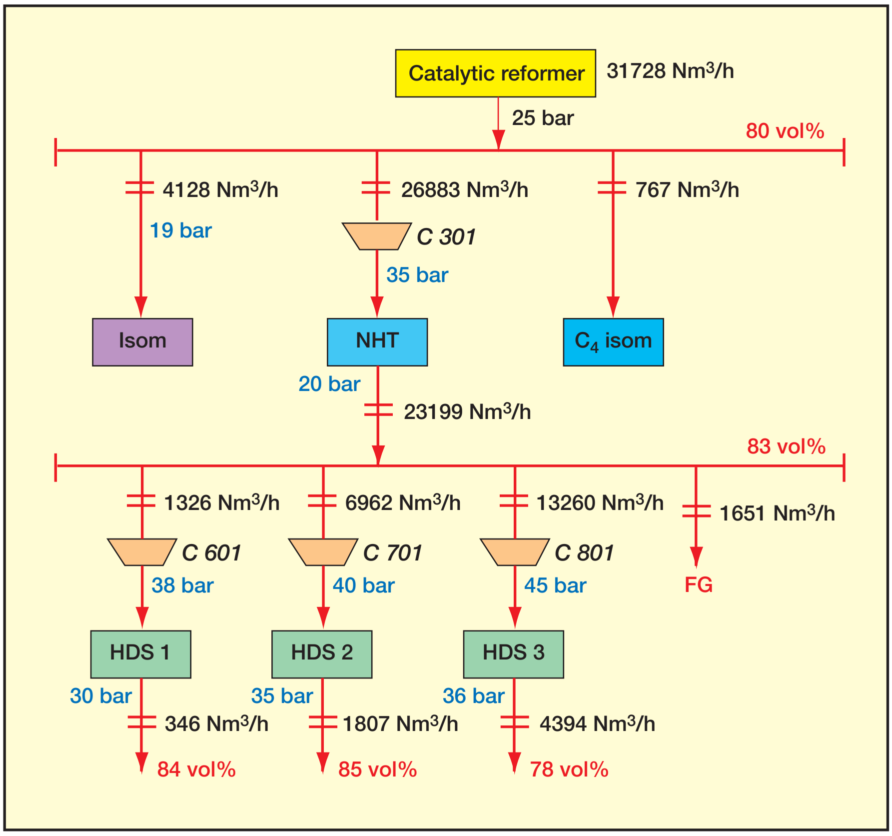

***Figure 3** Network schematic for hydrogen pinch case study: catalytic reformer as single source of hydrogen*

Future balances

When developing future hydrogen scenarios, most refiners concentrate only on the global hydrogen balance to assess whether there is an overall shortfall in hydrogen. Rarely are changes in high pressure and low pressure purge flows, and the subsequent impact on amine treating, LPG recovery and the fuel gas system considered. Therefore, major bottlenecks can lie in these systems. If no changes are made to the hydrogen network, then the shortfall in hydrogen defines the requirement for either a new hydrogen plant, such as an SMR, or third party supply of hydrogen. However, before seeking capital approval, refiners will generally look for re-use or purification opportunities to minimise the required investment. Two techniques are generally applied to evaluate re-use and purification options, good engineering practice and the so-called hydrogen pinch technology. Improvements can be made simply by identifying the largest losses of hydrogen to fuel gas, and looking to recover this through the use of a membrane or PSA unit.

This often leads to a costly solution where all higher purity purge streams are combined, compressed and routed to a large purification unit for recovery.

Sources	NHT	Isom	C_4 Isom	HDS 1	HDS 2	HDS 3	Purifier	Fuel	Total
Cat ref. HP	26833	4128	767					0	31728
NHT prod. sep.				1326	6962	13260		1651	23199
Isom HP sep.		16478						0	16478
HDS1 HP sep.				4690				346	5036
HDS2 HP sep.					15091			1807	16898
HDS3 HP sep.						28056		4394	32450
Cat ref. LP								1288	1288
Isom LP								1250	1250
C_4 isom LP								338	338
NTH LP								2787	2787
HDS1 LP								596	596
HDS2 LP flash								747	747
HDS2 stripper								1129	1129
HDS3 LP flash								862	862
HDS3 stripper								1837	1837
Pur prod.									0
Pur resid.									0.0

***Figure 3a** Matrix representation of current hydrogen network*

Sources	NHT	Isom	C_4 Isom	HDS 1	HDS 2	HDS 3	Purifier	Fuel	Total
Cat ref. HP	18370	4128							22498
NHT prod. sep.	3206		479	1534	4444	13536			23199
Isom HP sep.		16478							16478
HDS1 HP sep.					5036				5036
HDS2 HP sep.	128			4197	12573				16898
HDS3 HP sep.	5129					27321			32450
Cat ref. LP								1288	1288
Isom LP								1250	1250
C_4 isom LP								338	338
NTH LP								2787	2787
HDS1 LP								596	596
HDS2 LP flash			288			459		0	747
HDS2 stripper								1129	1129
HDS3 LP flash				285				577	862
HDS3 stripper								1837	1837
Pur prod.									0
Pur resid.									0.0

***Figure 3b** Unconstrained hydrogen target from pinch case study*

It is also interesting to note that the most common location for a purification unit in a refinery, processing catalytic reformer net gas, rarely improves overall hydrogen availability. Reduction in process purge losses through higher purity makeup is offset by hydrogen losses in the residue gas.

The purpose of such units is to improve reactor hydrogen partial pressures, and the presence of such purifiers in a hydrogen network is not an indication of overall hydrogen efficiency.

Hydrogen pinch

To address the need for a more systematic approach to hydrogen recovery, AspenTech and six other companies funded the development of hydrogen pinch technology at the University of Manchester Institute of Science and Technology (UMIST), in he UK. The method aims at maximising the in-plant re-use and recycling of hydrogen in order to minimise the on-purpose or utility hydrogen production.

The method is simple to use, requires relatively few data and has an intuitive graphical representation. However, it does have severe limitations especially when applied to network design, due to its lack of constraint handling and assumption of binary mixtures (hydrogen and "other").

The hydrogen pinch approach is best illustrated using a real case study, as shown in Figure 3. There is a single source of hydrogen production, the catalytic reformer. Three process units use this hydrogen-rich gas directly, including the naphtha hydrotreater (NHT) unit. As is often the case, once-through hydrogen flow through the NHT leads to an increase in hydrogen purity due to a re-contacting effect between gas and naphtha. NHT offgas is then supplied to HDS1, HDS2 and HDS3, with a direct purge to fuel gas for pressure control. The schematic shows just high pressure purges and makeup compressors, with low pressure purges and recycle gas compressors omitted for clarity.

In the hydrogen pinch technique, hydrogen sources and sinks are extracted to produce a graphical representation of hydrogen surplus as a function of purity. The hydrogen generation flow rate can be reduced until a zero surplus is experienced. The purity at which this occurs is termed the "hydrogen pinch" and the corresponding on-purpose hydrogen flow rate is the minimum target and is determined before any network design.

It is important to realise that this target considers no constraints on the hydrogen system except for hydrogen purity, so can be described as the "unconstrained target".

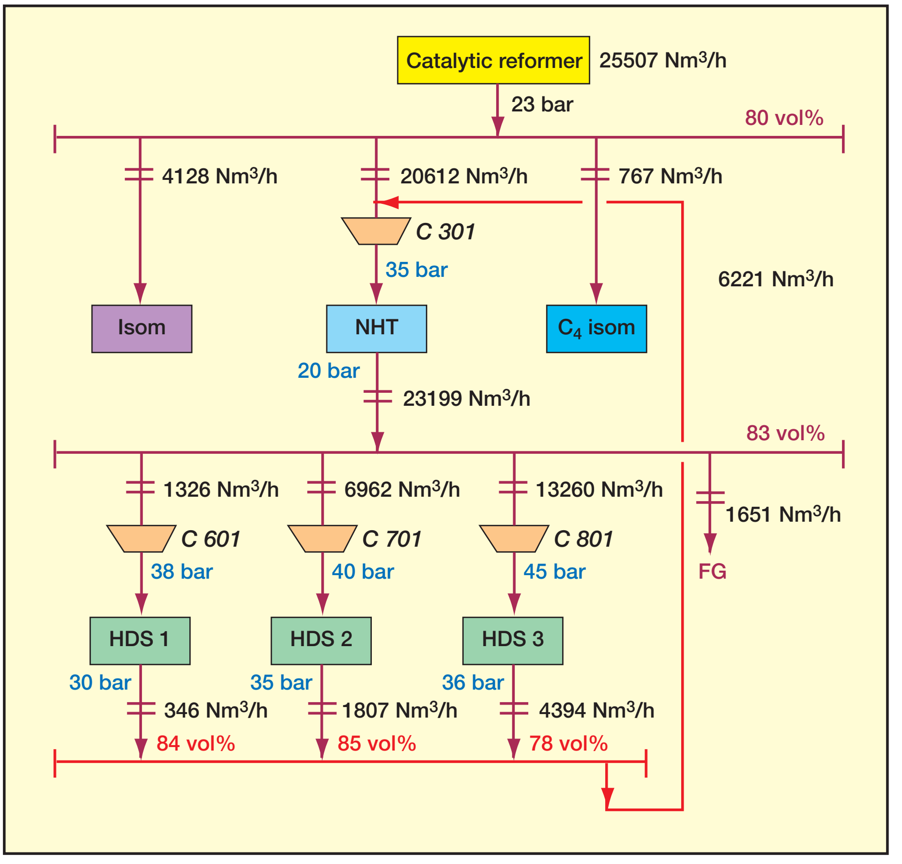

***Figure 4** Network for binary assumption placing constraints on gas impurities and maximising use of existing compressors*

For the case study shown, the target demand for reformer gas represents a saving of 29% over the base case. This looks very attractive, but the user can be expected to raise three questions: how realistic is this unconstrained target? what projects are required to achieve this target? and what if the operator does not wish to minimise hydrogen?

In fact, many users of hydrogen pinch have struggled to progress beyond the target phase to generate a revised network that achieves the indicated saving. The hydrogen network shown in Figure 3 can be represented in a grid format as illustrated in Figure 3a.

Each block on the grid shows the flow rate between a particular source and demand. The blank (brown-coloured) blocks are connections that are not feasible without flow-through at existing compressors due to pressure constraints. If the operator is willing to allow any connection between sources and sinks, provided that purity constraints are respected, then the unconstrained hydrogen target from the hydrogen pinch is achieved with the new re-routing projects shown in Figure 3b.

These projects are automatically generated by the optimiser. An option to automatically place a purifier within the network has not been activated. At this stage the same underlying mathematics used to generate the hydrogen pinch target are used.

To achieve these 29% hydrogen savings, the following projects are required:
—Total re-use of HDS1, HDS2 and HDS3 purges, primarily for ISOM and C_4 ISOM makeup gas
—Re-use of HDS2 and HDS3 LP flash gases
—Elimination of NHT purge to fuel gas for pressure control.

In reality, the only acceptable source of makeup hydrogen for the ISOM and C_4 ISOM process unit is catalytic reformer gas. Hydrotreater purge gas is not acceptable due to ISOM catalyst contamination concerns. Re-use of LP flash gases will require new compressors as the pressure is lower than any point in the hydrogen distribution network. In other words, most of these project ideas are unrealistic. So where do we go from here?

Constrained design

As we can see, the graphical unconstrained pinch targeting method only considers flow rate and purity, but does not incorporate other important practical constraints such as pressure, layout, safety, piping, operability and of course capital cost. Unfortunately, new compressors are very expensive and so a retrofit design should aim to make the best re-use of the existing compression equipment. Direct re-use of hydrogen between consumers is only possible if the pressure is sufficient. However, it is possible to re-use a hydrogen stream indirectly (such as by routing through an existing compressor, provided that certain conditions are met). First, there has to be sufficient capacity in a compressor to accommodate the stream. The initial pressure of the re-used stream needs to be high enough to be fed to the compressor. In addition, the compressor should be able to compress the stream to a high enough pressure that it can be used in the required consumer.

A whole host of additional constraints can also be incorporated, such as space limitations, forbidden matches or no new compressors allowed. Hydrogen sulphide issues are addressed by preventing re-use of sour gas streams without prior processing in amine scrubbers. In order to account for pressure and these other constraints, a mathematical programming or optimisation approach is required using a combination of linear and non-linear programming.

Referring back to the case study, by placing constraints on gas impurities and maximising use of existing compressors, an optimised solution is developed as shown in Figure 4. This solution reduces reformer gas demand by 20%, compared to the unconstrained target saving of 29%. The design has two main features: re-use of HDS1, HDS2 and HDS3 purges as makeup to NHT, and elimination of the NHT purge to fuel gas.

At this point it should be feasible to begin process engineering of the proposed re-use project. However, upon proceeding, it would be evident that the simulated benefits are very much lower than those predicted by the optimiser. Another major limitation of the hydrogen pinch approach has been encountered, its assumption of a binary mixture.

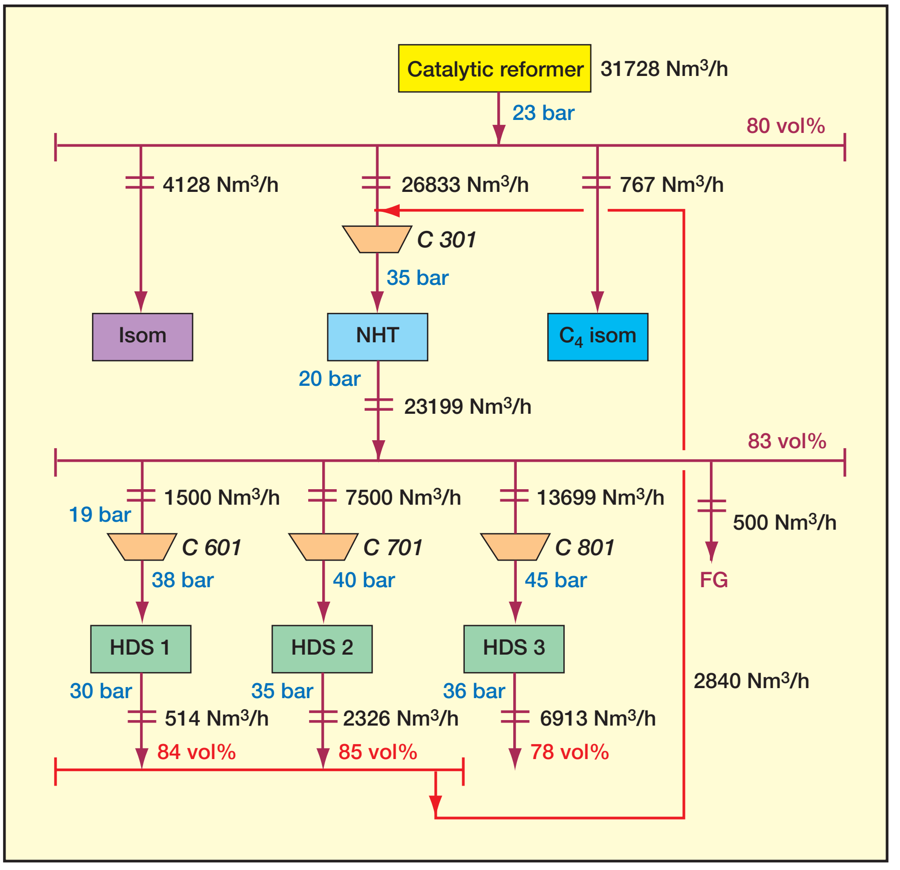

***Figure 5** Optimised network case study maximising HFDS3 throughput within hydrogen availability*

Multi-component methodology

Consider two hydrogen streams, each of 85 mol% purity. The first is ethylene plant export, containing almost 15% methane. The second is catalytic reformer export, containing roughly equal amounts of methane, ethane and propane, plus small amounts of heavier material. Hydrogen pinch techniques cannot differentiate between these streams, and would identify no penalty or benefit from switching between them as a source of makeup gas.

Yet in reality the ethylene plant gas would require operation with a much higher purge rate, due to the tendency of methane to build-up in recycle loops. In fact, in certain circumstances it is more efficient to substitute a makeup supply with a lower purity hydrogen source (but lower methane content), while the hydrogen pinch methodology would lead to doing the complete opposite.

To meet this challenge, Pro-En engineers have developed a multiple-component optimisation methodology that fully accounts for the behaviour of individual components within the process reactors, separators and the recycle gas loop. While in the binary pinch approach, the composition and flows of reactor feed and separator gas are fixed, the new multiple-component approach allows these compositions to float, so long as constraints such as minimum hydrogen partial pressure and minimum GOR are met.

Simulation models for process reactors, high pressure and low pressure separators are used to correctly model overall process behaviour. A new network simulation tool has been developed based on AspenTech's Aspen Custom Modeler (ACM) software.

By extending the analysis to include components other than hydrogen, downstream amine scrubbers, LPG recovery systems and the entire fuel gas system can be optimised simultaneously. The benefits from increased LPG recovery can far outweigh the value of hydrogen savings.

Results of the case study's multi-component based optimisation (with all other constraints kept constant) show that the apparent 20% hydrogen saving is substantially reduced to a true saving of 13%, as the binary approach failed to correctly model the buildup of light ends components in the hydrogen networks. This is very different from our initial unconstrained target of a potential 29% hydrogen saving.

Hydrogen network

As previously stated, the third question asked after generating the unconstrained target from the hydrogen surplus cascade was ”what if I don't wish to minimise hydrogen?”

In the case study presented, there is no incentive to reduce reformer gas production. Reformer operating conditions and throughput are in line with the desired refinery production plan. However when processing certain crudes the refinery is short of hydrogen, requiring HDS3 throughput to be reduced. Therefore the true objective function is to maximise HDS3 throughput within hydrogen availability.

The marginal hydrogen value is based on its ability to upgrade HDS3 feed material to product, minus the value of hydrogen as fuel gas and other operating costs. In this case, the net upgrade value is 13/tonne and hydrogen is constrained for 150 days/ year.

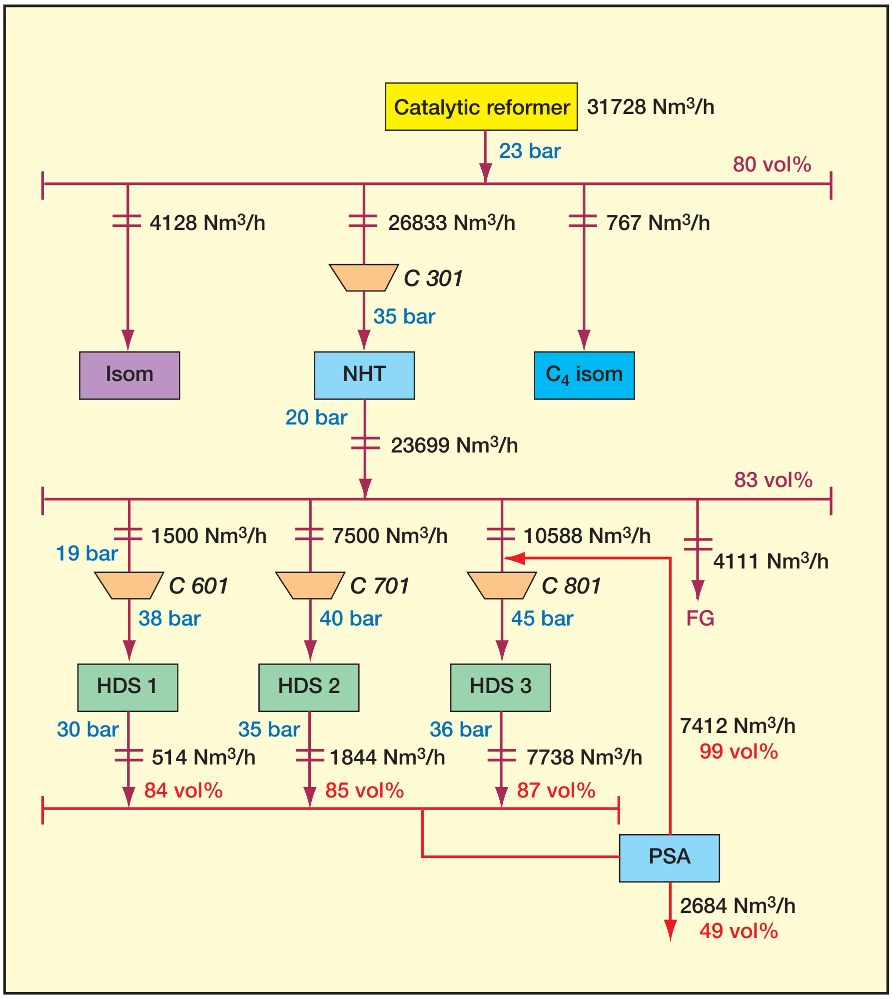

***Figure 6** Optimised solution with PSA*

With this new optimisation approach, it is just as easy to maximise functions such as process unit throughput and reactor inlet purity (to increase yields or extend catalyst life) as it is to minimise hydrogen. The revised results of the case study are shown in Figure 5.

There are two major projects involved: re-routing of HDS1 and HDS2 purge gases to HDS2 makeup, and reduction of NHT purge loss to a maximum value of 500 Nm^3/hr using advanced control. Together these allow HDS3 throughput to be increased by 460t/d during constrained operation, worth 0.9 million/year.

The new methodology also allows automatic placement of new purification equipment, something else that cannot be accomplished with conventional hydrogen pinch techniques. Further increases in HDS3 throughput can be achieved by installing a PSA unit to recover hydrogen from the remaining high pressure purge streams, as shown in Figure 6.

Throughput is increased by a further 670t/d, worth an incremental 1.3 million/year. These savings alone may not justify installation of this new equipment, but a closer inspection of optimisation results shows NHT purge has increased to 4111 Nm^3/h. This is excess hydrogen that cannot be used to boost HDS3 throughput because HDS3 makeup and recycle compressors have reached maximum capacity. Either the PSA unit can be made smaller to eliminate this excess, or this hydrogen can be used to meet increased hydrogen demands in other process units.

HDS3 is now severely constrained on the minimum required GOR, and the large recycle of material from HDS3 purge through the PSA and back to the makeup compressor is primarily to maintain the GOR. Any reduction in minimum GOR requirement will allow a capacity increase for HDS3.

The reactor inlet purity for HDS3 has risen from 80 vol% to 90%, with a corresponding increase in HP separator purity. This may well give additional benefits in terms of product quality improvement and/or extension of catalyst life.

The next step in a Pro-En study would be to use AspenTech's rigorous reactor models to establish the benefits for HDS3 from improved reactor gas inlet purity, and evaluate the optimum GOR for this unit. This will allow the true economics of installing the PSA unit to be evaluated.

Hidden opportunities

In conclusion, there are several hidden opportunities that are typically not addressed by refiners when developing plans for clean fuels. Time spent in investigating the current balance pays back. Investigation of the current balance can identify substantial operating savings, and eliminate unconscious over-design in future investments.

There is scope to reduce both capital investment and future operating costs by maximising the benefits from high purity hydrogen sources. Reactor modelling is an important part of evaluating these benefits and optimising hydrogen use.

Hydrogen is not the only consideration. Any thorough optimisation methodology needs to extend beyond the hydrogen system to include low-pressure purges, amine treating, LPG recovery and the fuel gas system. Purification upstream of LPG recovery systems can debottleneck these systems and increase their overall recovery efficiency, adding significantly to the value of recovered hydrogen. Reduction in hydrogen loss to fuel can have both positive implications (improved calorific value) and negative implications (increased fuel oil firing to maintain fuel pool and hence increased SO_X and emissions).

The moral is, don't wait for the future. New model-based network optimisation methodologies allow non-Capex and low Capex projects to be identified to improve current operations, particularly for refineries of Types 2 and 3. These savings are often in excess of 1 million/year, with payback times measured in months.

***Ian Moore** is a senior adviser for AspenTech Ltd, UK, managing refinery-wide hydrogen management and energy reduction projects executed by Engineering Products Services. He has BEng and MEng degrees in chemical engineering, and has managed several Pro-En projects in North America and Europe.*

***Nick Hallale** is a senior engineer for AspenTech Ltd, UK, working in Engineering Products Services. He specialises in the development and application of new methods for hydrogen management. He graduated with a BSc and PhD in chemical engineering from the University of Cape Town, South Africa, and has worked on some 10 Pro-En hydrogen projects.*

***Dennis Vauk** is a senior process consultant for Air Liquide's Pro-En Services group and holds a BS in chemical engineering from the University of Idaho, USA.*