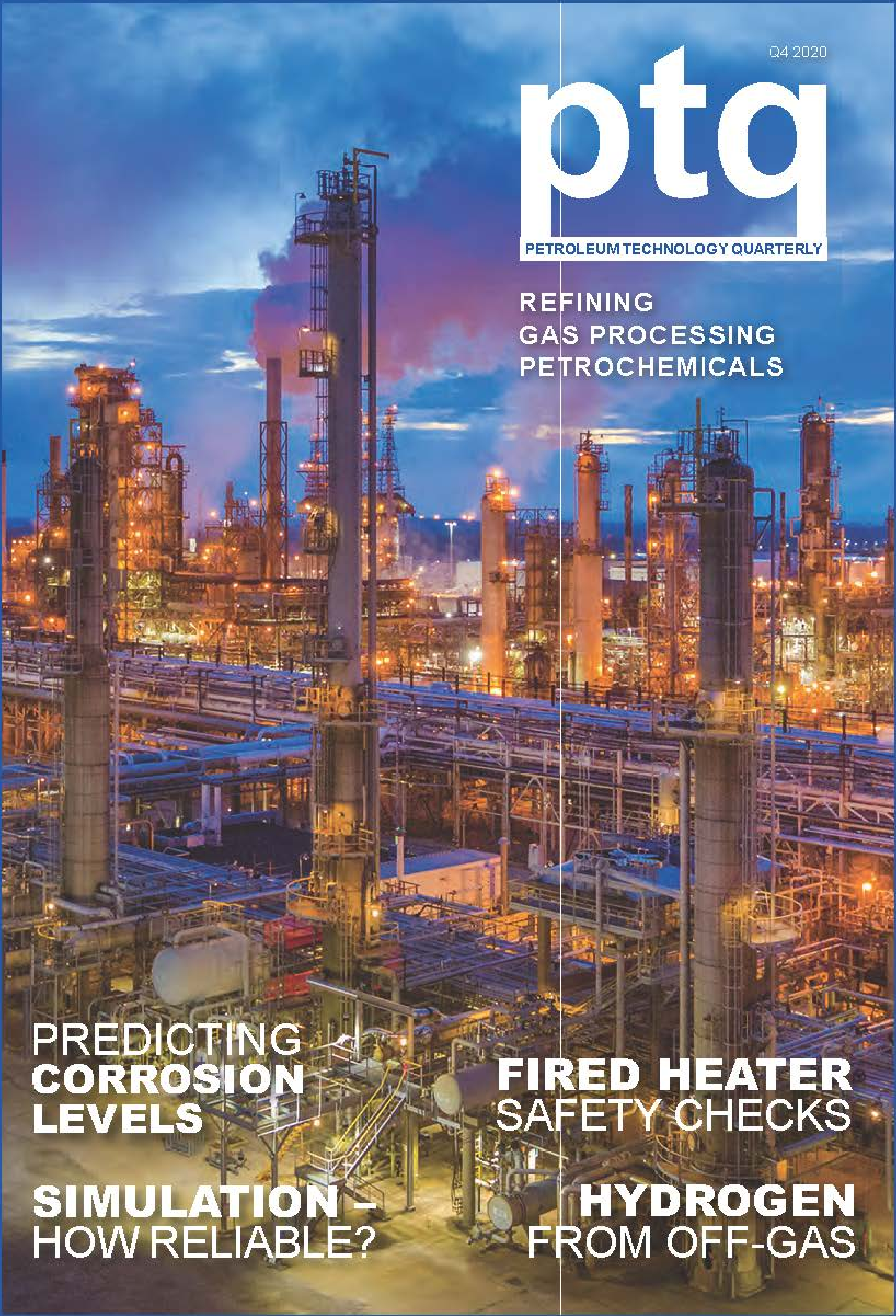

Q4 2020

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REFINING
GAS PROCESSING
PETROCHEMICALS

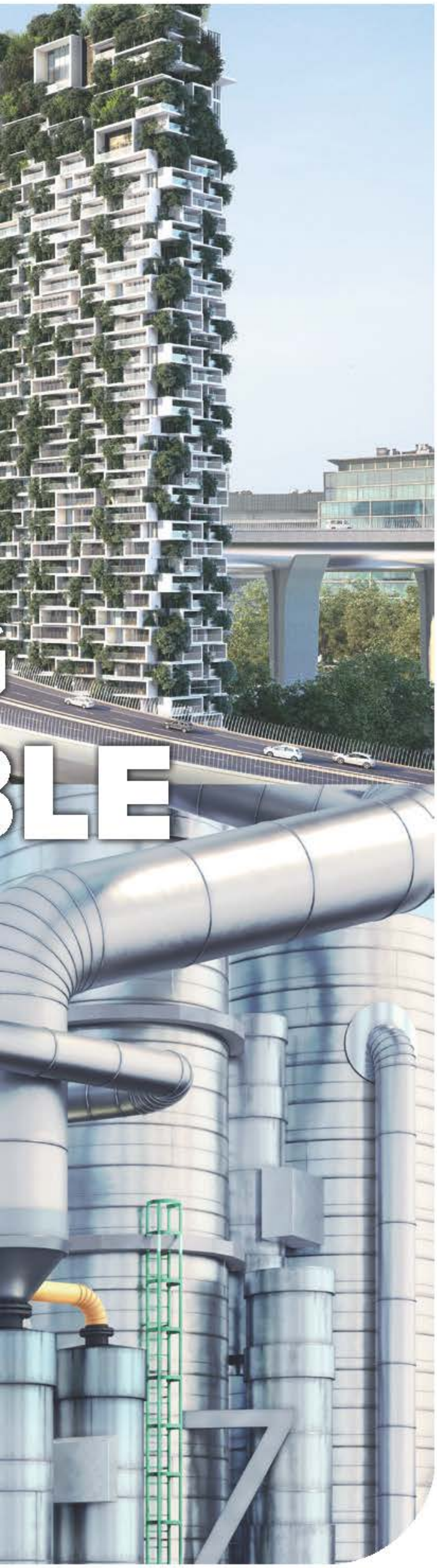
PREDICTING **CORROSION LEVELS**

FIRED HEATER SAFETY CHECKS

SIMULATION – HOW RELIABLE?

HYDROGEN FROM OFF-GAS

POWERING A SUSTAINAB FUTURE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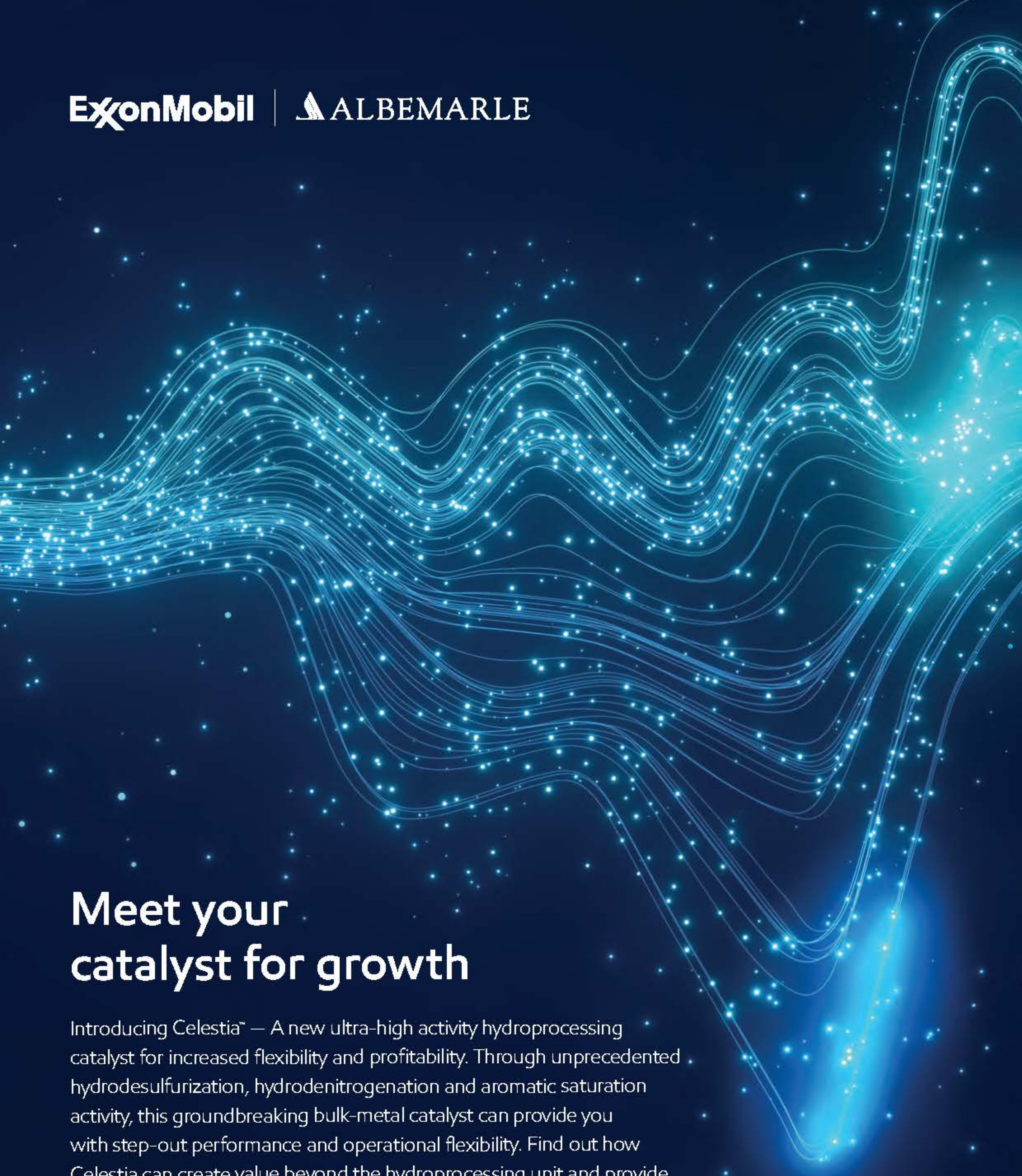

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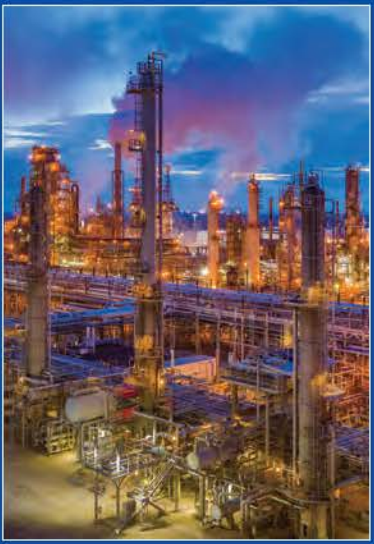

Cover
Marathon Petroleum may convert its Martinez refinery for renewable diesel production

Photo: Marathon Petroleum

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Open and shut cases

At its low point in 2020, North America's refining industry shut down 800 000 b/d of production. Despite recovery in demand for road transport fuels – but not yet jet fuel – how much of that will remain closed remains unclear as refiners decide whether to counter historical debt with very tight margins. They must also consider the cost of maintenance which, the longer shutdown continues, the more expensive it will be. The same applies to much of Europe's refining industry.

Some of the US's ageing fleet was due for closure anyway, pandemic or no. Some also was up for sale, which is probably more of a pointer to the future of the industry than widespread full-scale closures. Refineries are complex sites to dismantle hence a new owner with an eye to a market opportunity is perhaps more likely than a scrap metal dealer to acquire a site.

A further alternative to 'closure' has been in the news of late with the decision by Phillips 66 to convert its 140 000 b/d San Francisco refinery to renewable diesel production. While both start life as bio-waste, renewable diesel and biodiesel are not the same species. The renewable fuel is a product of high temperature hydrotreating and can therefore be produced using existing refinery equipment, while biodiesel is an ester that needs simpler processing. As a 'drop-in' fuel, renewable diesel can be blended more effectively than biodiesel with conventional, petroleum-derived fuel.

Marathon was considering the same route at press time for its 160 000 b/d Martinez refinery. Both refineries are in California where they can derive credits for non-fossil fuels production.

In contrast to western thoughts of closure, plans for new major processing operations are going ahead in the Middle East and Asia-Pacific. These, though, are less about adding fuels manufacturing capacity than expanding output of petrochemicals. For instance, Indian Oil wants to build a 1.2 million b/d oil to chemicals complex on the Maharashtra coast, at a projected cost of $44 billion and with funding partially provided by Saudi Aramco. In Saudi Arabia itself, the Aramco-Total joint venture (SATORP) export refinery in Jubail will be joined by a $5 billion petrochemicals complex which is currently at the front-end engineering stage. And in China, Rongsheng Petrochemical recently built an 800 000 b/d plant on Zhoushan Island. The site is scheduled to ramp up to full output by the end of 2020.

A developing view in Asia is that construction of fuels-only refining operations is past its sell-by date and that integrated refining-petrochemicals operations are the only economically secure way forward. At the core of this, Asia in particular has the fastest growing market for plastics products yet is a net importer of ethylene and propylene. It is expected that more than half of the world's additional oil refining capacity over the next decade will be built in Asia, with the major part of that serving plastics production, according to reports.

However, among these plans for integrated plant openings across Asia, there will be attrition for fuels-only producers. In particular, China's independent refiners are bracing themselves for shutdown as more surplus refining arrives on-stream.

CHRIS CUNNINGHAM

Flexibility is profitable

Flexibility Matters

In uncertain times, refineries can maximize profit (or at least minimize loss) through flexible operations. Crude units are the first link in the refinery processing chain, and making large changes in crude diet or throughput stresses even the most state-of-the-art unit.

SHORT-TERM STRATEGIES

Certain operating strategies can maximize reliability, yields, and product qualities. Some practical short-term options include:

- KEEP THE BOTTOMS STRIPPING STEAM

  At turndown, consider maintaining normal crude tower and vacuum tower bottoms stripping steam rates and lowering heater outlet temperature to control cutpoint. This allows the stripping steam to do the work while heater firing is minimized to protect the heater tubes at low mass velocities.

- LOWER THE PRESSURE

  Lowering tower pressures at turndown lowers the density of the vapor, which keeps trays loaded and can avoid weeping and loss of efficiency. Lower pressure also lowers draw temperatures, increasing pumparound rates and hopefully avoiding minimum flow limits for pumps and tower internals.

- MOVE HEAT UP

  In multi-pumparound towers, shifting heat to the upper pumparounds at turndown increases tray vapor loads and internal liquid reflux rates. Keeping the upper pumparounds loaded can also help avoid low pumparound return or tower overhead temperatures that condense water and cause salting or corrosion problems. It may even make sense to turn off a lower pumparound.

LONG-TERM SOLUTIONS

Thinking longer-term, cost-effective revamps can add critical flexibility to allow for wide swings in unit throughput and crude blends while still operating in control. The right process design enables operators to consistently:

- Control desalter inlet temperature,
- Control preflash column inlet temperature and naphtha production,
- Control pumparound return temperatures and rates independent of pumparound heat removal requirements, and
- Precisely control vacuum column top pressure.

This advice is, of course, generic. To discuss challenges unique to your own crude/vacuum unit, give us a call. Process Consulting Services believes crude units should have flexibility. We believe that revamp solutions should be flexible too – one size doesn't fit all. We look forward to working together to find the most cost-effective and reliable solution to your crude processing problems.

Q What is blue hydrogen and what equipment do we need to produce it?

A Joris Mertens, Principal Consultant, KBC (A Yokogawa Company), Joris.Mertens@kbc.global

Blue hydrogen is hydrogen produced by conventional steam reforming technology using fossil feed and fuel, mostly natural gas, but with capture and storage or utilisation of the CO_2 generated.

CO_2 capture is done by absorption/desorption with amine solutions and requires an absorption column, a CO_2 stripper, piping, pumping, and compression. The desorption/stripper step requires substantial amounts of relatively low level heat (steam), which in itself will increase the gross production of CO_2 unless waste heat is available.

The global CCS institute claims a current levelised capture cost of $50-60/t CO_2, going down further to $40/t by 2030. The cost is dropping mainly due to economies of scale.

Transportation and storage will require compression, piping, and the availability of storage facilities such as caverns or depleted oil/gas fields. Therefore, the overall cost will be very site specific.

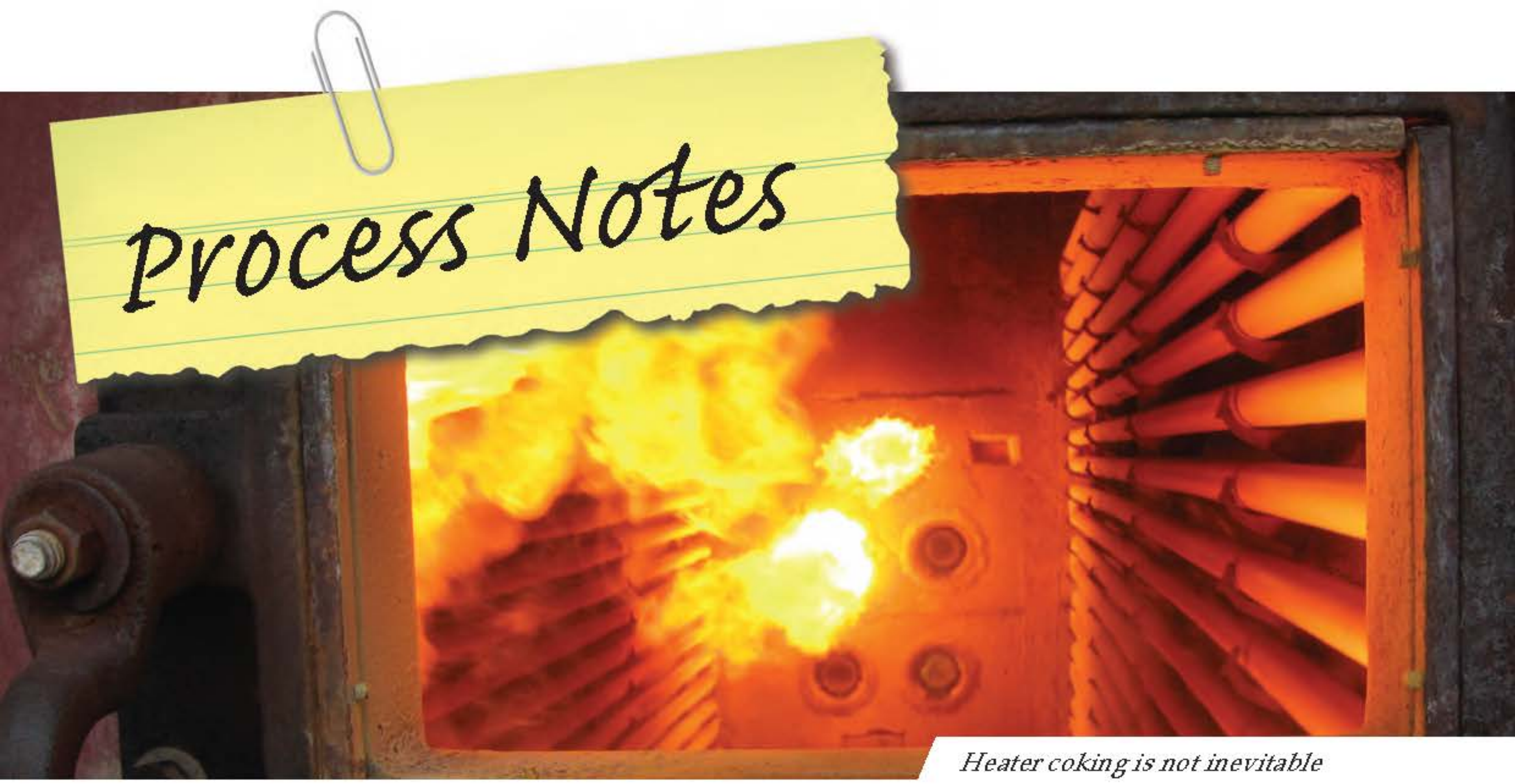
A Sandra Winter-Madsen, Product Line Director, Haldor Topsoe, sw@topsoe.com

Blue hydrogen is decarbonised hydrogen. It is typically produced by steam reforming (SMR) of hydrocarbon feed like natural gas or autothermal reforming (ATR) including oxygen as feed. High amounts (90+% depending on local conditions) of CO_2 are removed/captured, typically in an amine wash; the CO_2 is purified, compressed, and stored. The most efficient process is to capture the CO_2 at high pressure from the synthesis gas at the outlet of the autothermal reformer. When using a SMR then CO_2 needs also to be removed from the flue gas which is a much more capital and energy intensive process. Different hydrogen product purities may be required depending on application, and if pure hydrogen (99+%) is required a pressure swing adsorption (PSA) process is required.

A Tom Ventham, Sales & Technical, Europe and Africa Unicat BV/G. W. Aru, LLC tom.ventham@gwaru.com **and Gary Bennington, Business Development Manager, Magma Ceramics & Catalysts,** g.bennington@magmacatalysts.com

Blue hydrogen is a transitional technology that some consider a stepping-stone until fully green, net zero carbon hydrogen production can be realised on an industrial scale. As such, blue hydrogen is still produced from natural gas and relies on carbon capture and storage (CCS) technology to remove resulting CO_2. With regard to the main equipment, a location for storage of large volumes of CO_2 is required. This tends to be an underground or undersea reservoir with, ideally, enhanced oil/natural gas recovery for added economic benefit (although questionable overall green credentials). The rationale of blue hydrogen technology is the ability to eliminate steam methane reformer (SMR) furnace flue gases, typically emitted directly to the atmosphere, through the use of a direct fired autothermal reformer and downstream convective post-reformer. CO_2 is produced from the direct firing of a portion of the natural gas to give the energy necessary to drive the endothermic reforming reaction, which can then be removed from the product stream for CCS. A full life-cycle analysis is required to fully determine the environmental benefits of such a proposal, for example the carbon footprint to fabricate and construct significant new process and ancillary equipment, which may only be used for a short time until green hydrogen is available. As well as a detailed analysis of the life-cycle energy requirements of utilities, including the air separation unit such schemes are usually equipped with or fed by to provide the oxygen injection needed to avoid over-sizing equipment if air is used as the alternative.

A more sustainable approach would be to utilise existing equipment in a more efficient manner by taking advantage of advanced catalyst technologies that are now available. This strategy offers the option to immediately reduce CO_2 emissions at source by reducing fossil fuel input to the process (rather than burning even larger quantities of fossil fuels and relying on downstream CCS to handle additional CO_2 in a long term and sustainable manner). As the majority of CO_2 generated during the production of hydrogen is from the steam methane reformer combustion chamber, an improved design of catalyst that can reduce the quantity of fuel that needs to be fired will achieve CO_2 reductions quickly, safely, and in a cost-effective manner. Newly introduced MagCat technology, from Magma Catalysts, has been shown to have a significantly higher heat transfer coefficient compared to competitive catalysts. This allows SMR operators to reduce the firing requirement within the reformer furnace whilst also maintaining full hydrogen production. Added to this benefit is an enhanced reformer tube life due to lower operating temperatures and reduced pressure drop leading to lower operating costs and energy input on energy intensive equipment such as gas compressors. In summary, a full-life cycle analysis is essential to fully understand the environmental credentials of a particular option, such as those mentioned for blue hydrogen today. In almost every case, the re-use of existing assets and re-optimisation of those assets using modern, advanced catalyst technologies will be the most environmentally friendly approach, both in terms of total carbon footprint and the time required to implement the improvement, as a provisional or interim measure before the full availability of 100% green hydrogen.



Heater coking is not inevitable

Avoid Fired Heater Coking

For many refiners, heater coking in Crude and Vacuum Distillation Units (CDU/VDUs) is a common occurrence. Many units around the world are shut down every two years, every year, or even every six months to deal with chronic heater coking. However, with the right design features driven by a solid understanding of heater coking mechanisms, fired heater run length can be extended beyond five years, even with relatively challenging crudes.

The two primary drivers of heater tube coking in CDU/VDU services are oil film temperature and residence time. Secondary factors such as crude coking tendency, solids content, and blend instability can further accelerate heater tube coking. So, which heater design parameters will maximize heater run length and avoid shutdowns for high heater tube metal temperature or high heater pass pressure drop?

MASS FLUX IS KING

Mass flux (lb/s/ft^2 or kg/s/m^2) is found by dividing the mass flow through a heater tube by the tube's cross-sectional area. High mass flux begets high velocity and suppresses coking in several important ways. First, high mass flux means that the fluid moves through the tube faster, minimizing residence time. Second, high velocity results in high heat transfer coefficient, which minimizes internal oil film temperature. Finally, high mass flux creates high wall shear inside the tube, minimizing build-up of solids or asphaltenes.

HEAT FLUX CAN SURPRISE

Heat flux (BTU/hr/ft^2 or kcal/hr/m^2) measures the amount of heat absorbed through a given outside surface area of a heater tube. High heat flux raises tube metal temperature and causes high oil film temperature inside the tube. Popular fired heater design programs use a well-stirred firebox model and calculate peak heat flux by applying a simple multiplier to the average heat flux. In reality, heater design parameters such as firebox height/width ratio, burner type, burner sizing, burner placement, and air/flue gas flow patterns can result in actual peak heat fluxes that are much higher than the "calculated" peak heat flux on the heater datasheet. Localized areas with very high heat flux will coke and suffer from high tube metal temperature.

Of course there are many other variables that must be considered, such as pass arrangement, vertical or horizontal tubes, cylindrical or box or cabin, coil steam, etc. Problems stemming from blend instability are becoming more common as refiners are increasingly mixing light shale crudes with heavy crudes. As the crude begins to vaporize, asphaltenes can precipitate out of unstable mixtures and coat the heater tubes, forming coke and creating hot spots.

Even with challenging crudes, refiners have achieved Crude Heater and Vacuum Heater run length goals through careful design and respect for the basics of coking. Contact Process Consulting Services, Inc. to learn more.

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Q What are the essential elements of a corrosion control programme?

A Collin Cross, Senior Product Analytics/Support Manager, SUEZ – Water Technologies & Solutions, collin.cross@suez.com

In practice, the specific elements used in overhead corrosion control programmes vary widely across refineries. Because of a variety of philosophies surrounding this topic, opinions may vary as to what methodologies are considered most essential. In general, the particular elements adopted in a specific refinery often arise from the historical processing strategy and depend on the crudes being processed, unit operations, mode envelopes, metallurgy, overall design, constraints, and control schema of the unit itself.

From a design and engineering perspective, good desalting, appropriate operational envelope, water washing, caustic injection, and judiciously applied advanced metallurgy are all widely accepted means for reducing crude oils corrosion potential and hardening a unit to the impact of ongoing corrosion. Most refineries have some combinations of these methods, with a fewer number having all of them due to a variety of practical and economic reasons.

After these means, chemical injection directly into the overhead is also commonly used. Here, however, philosophies begin to differ over a wider scale. Overhead neutralisers are probably the most widely accepted chemical used for corrosion mitigation, with the additional usage of a filming inhibitor being a close second. Beyond that, niche products such as salt dispersants, salt displacement aids, amine scavengers, and amine partitioning aids are sometimes used to help resolve spurious or ongoing problems that are more difficult to solve.

One of the most important areas of a corrosion control programme is the monitoring and analytics programs. However, these elements also vary over a wide range for both processing units and operational philosophies. Traditionally, pH, chlorides, and iron are all commonly measured in the overhead receiver to help assess the changes to ongoing corrosion potential, while coupons and electrical resistance probes (ER probes) are used to assess direct measurements of ongoing corrosion. These methods provide a means to rapidly respond to ongoing changes and adapt programs over time.

More recently, due to the growth in the number of refineries processing non-conventional and opportunity crudes, salt induced corrosion and fouling have become much more prevalent, relative to ICP corrosion. To help combat these types of mechanisms, the more frequent chemical analysis of low molecular weight organic acids and tramp amines has become more widespread. These data are used to increase the accuracy, granularity, scope, and utility of salt point calculations as well as pH buffering and excursions.

New developments have also arisen in the ability to conduct key chemical and physical measurements rapidly and economically; many of these methods are also available in online configurations, which are becoming more prominent. A few important examples of these technologies are wireless and online ultrasonic thickness (UT) devices, as well as improved instruments for both total chloride measurement and broad based amine speciation in the incoming crude, the overhead water, desalter brine, and elsewhere.

Finally, new technologies now exist that take a wide variety of the chemical, physical, and computational measurement data, automate the measurements, pass it through sophisticated analytics packages, and then use the output to achieve layered feed-backward and feed-forward control of both chemical pumps and overhead operations.

While all the above technologies are not strictly required to effectively control corrosion in many refineries, on the other hand, users who do choose to invest in these newer, more comprehensive and more sophisticated technologies are seeing significant return on investment in terms of improved production, reliability, flexibility, maintenance, and safety.

A Louise Maratos, Senior Staff Consultant, KBC (A Yokogawa Company), Louise.Maratos@kbc.global **and Andrew Layton, Principal Consultant, KBC (A Yokogawa Company),** ALayton@kbcat.com

The essential elements of a corrosion control programme are set into two areas. The first element is to ensure there is a very clear management system. This would include a strong set of policies, processes, and procedures supported by a very clear organisation structure with enablers, controls, and measures. Examples of enablers, control, and measures include key personnel training and competency, assurance, management review, communication, risk management, contractors, resources incident review, documentation, organisation, and management of change. These elements allow for planning, executing, and continuously improving the ability of the organisation to manage the threat of corrosion for existing and future assets.

The second element is to have a comprehensive technical corrosion control programme focusing on:

- Equipment online corrosion rate monitoring
- An equipment replacement strategy
- Highlight the different areas of corrosion risk for equipment and piping
- Development of online process and mechanical KPIs (critical indicators).
- Apply the KPI information into live feedback to operators and engineers using both instantaneous information and historical trends
- Link longer term the data feedback to external digital twin-like models to better predict or check measured corrosion parameters (especially where direct measurement is more difficult)
- Upgrade operating procedures to consider corrosion

A Berthold Otzisk, Senior Product Manager - Process Chemicals, Kurita Europe, berthold.otzisk@kurita-water.com

A successful treatment concept for corrosion protection includes several elements as part of a comprehensive corrosion control programme. The selection of suitable crude oil qualities with low salt contents or other corrosive components is a good option to keep the corrosion potential at the lowest possible level when processing crude oil in the refinery. However, such crude oils are often significantly more expensive than conventional crude oils, which makes their use less economical.

The installation of corrosion resistant alloys (CRAs) is significantly more expensive, but provides excellent protection against uniform attack, localised corrosion, or stress corrosion cracking. These alloys are mixtures of various metals such as iron, chromium, nickel, tungsten, titanium, copper, molybdenum, and cobalt. Carbon steel is very unstable in acids and corrosion rates increase sharply. Chemical treatment programmes can help to reduce the corrosion potential. Corrosion inhibitors such as oxygen scavengers, neutralising amines, or film-forming amines are an important tool in many applications to prevent or at least significantly slow down corrosion.

A very important part of a successful corrosion control is the use of suitable measuring instruments which quickly indicate a corrosion attack and thus enable an immediate counter-measure. A number of powerful corrosion measurement devices are field proven and well established technologies. Coupons, electrical resistance probes (ER) and ultrasonic wall thickness measurement devices are examples to control and minimise the corrosion.

A **Chris Claesen, Director, Technical Consulting, Nalco Water,** cclaesen@ecolab.com

A comprehensive corrosion control programme needs to follow an integrated approach. Poorly managed corrosion control programmes can have a serious impact on plant safety, reliability and availability. Years ago, starting with our Scorpion naphthenic acid corrosion control programme and more recently with 3D CrudeFlex, we moved from a focus on the corrosion inhibitors to an integrated approach covering all elements of what we called the jigsaw puzzle. The essential elements of this puzzle are:

- Risk assessment: the possible risks are identified and assessed based on the process unit design and construction materials, feed properties, operating conditions, and corrosion history
- Economics: evaluation of the total cost of operation. Opportunistic feedstocks and operating conditions can improve profit but will increase risks. Metallurgy upgrades and state of the art corrosion control and monitoring will reduce the risk but will have a cost
- Mitigation programme selection: when the economic evaluation has been done the proper mitigation programme can be selected. It can be a combination of metallurgy upgrades, plant revamps, corrosion inhibitors, and upstream (crude tank farm, desalters) improvement programmes
- Monitoring and inspection: the selection of corrosion monitoring and inspection equipment, locations, and intervals. Determination of critical analytical data and analysers such as the 3DTCOS to get on-line chloride, NH_3, pH, and Fe
- Reporting: evaluation and reporting of the monitoring data; regular team meetings of key people; incorporation of recommendations in actions and improvement plans

When working with a chemical vendor to provide corrosion inhibitors and corrosion management services, there need to be clear goals and defined key performance indicators. The vendor needs to have extensive experience in the industry and be a consultant rather than a vendor only. Proper selection of corrosion inhibitors and the specialised monitoring and automation capabilities are critical parts of the corrosion control programme. Another important piece is communication, roles and responsibilities need to be clear, processes and procedures for handling upsets and changes (MOC) and best practices should be in place and aligned.

Q **We want to increase the proportion of heavy components in our FCC feed. Should we hydrotreat the feed first?**

A **Gary Cheng, Regional Marketing Manager, Asia Pacific, W. R. Grace & Co,** Gary.Cheng@grace.com **and Chuck Olsen, Global Technology Manager, DHT, Advanced Refining Technologies LLC,** Chuck.Olsen@grace.com

Increasing the proportion of heavy components in the FCC feed typically results in a feed cost advantage, enhancing the overall unit profitability. However, this feed shift will present challenges to the FCC operation which hydrotreating can help mitigate. There are numerous benefits to hydrotreating FCC feed, including:

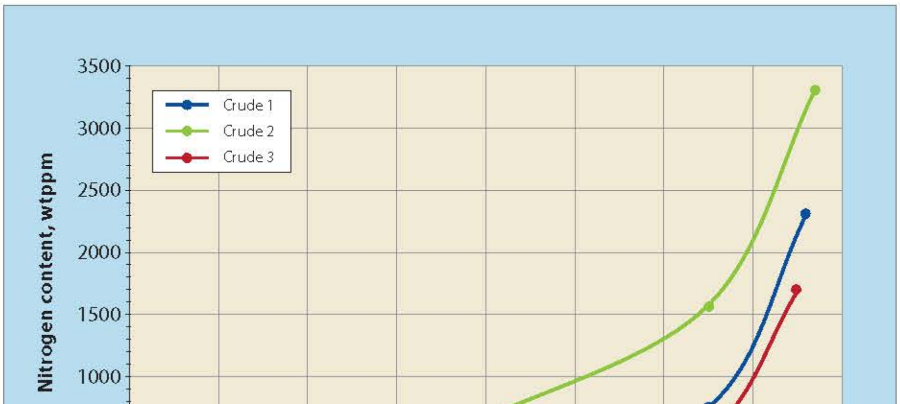


Figure 1 Feed nitrogen content with increasing feed endpoint

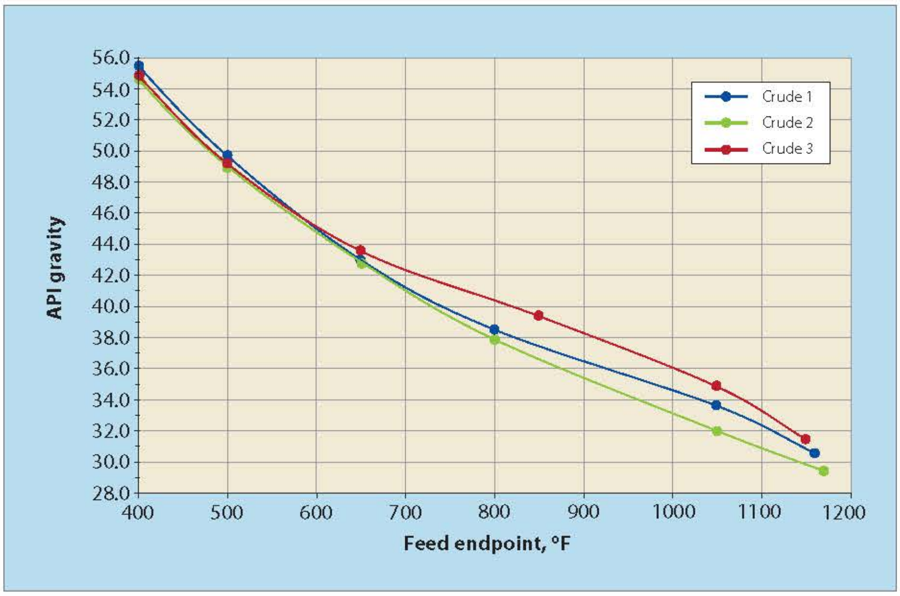


Figure 2 Feed API gravity with increasing feed endpoint

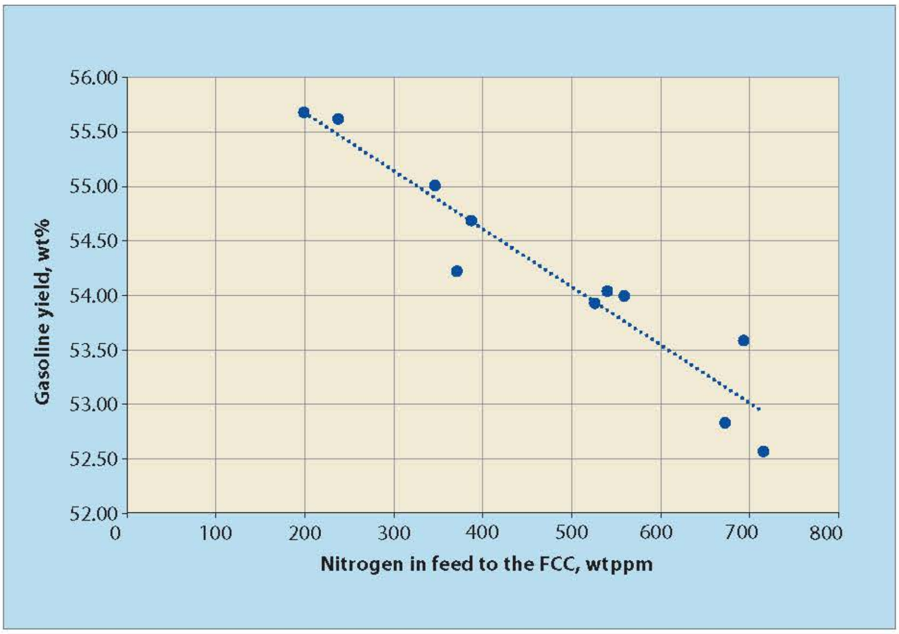


Figure 3 Impact of FCC feed nitrogen on FCC gasoline yield

- Lower sulphur in the FCC gasoline
- Reduced SOx emissions
- Increased FCC conversion and gasoline potential
- Increased H_2 content of the FCC products
- Reduced coke make due to saturation of poly-ringed aromatics in the FCC feed
- Lower nitrogen content, resulting in less catalyst activity poisoning and lower coke make
- Reduced Ni and V in the FCC feed, yielding lower gas and coke and preserving active catalyst sites

When contemplating an increase in heavy feed components it is important to consider the impact on feed quality. **Figures 1** and **2** show how the nitrogen and API gravity change as the feed endpoint is increased for three different crudes. It is apparent that the feed nitrogen content increases dramatically as feed endpoint is increased, especially when the endpoint is above 1000°F. The distribution of sulphur in the feed shows a similar trend.

The API gravity shows a steady decrease as the feed endpoint increases, and there is a 3-4 number decrease as the endpoint increases from 1000 to 1100°F. This is an indication that the feed is becoming more aromatic as the endpoint increases.

These data demonstrate that increasing the amounts of heavy components will result in a feed that has higher concentrations of sulphur, nitrogen, and aromatics/PNAs.

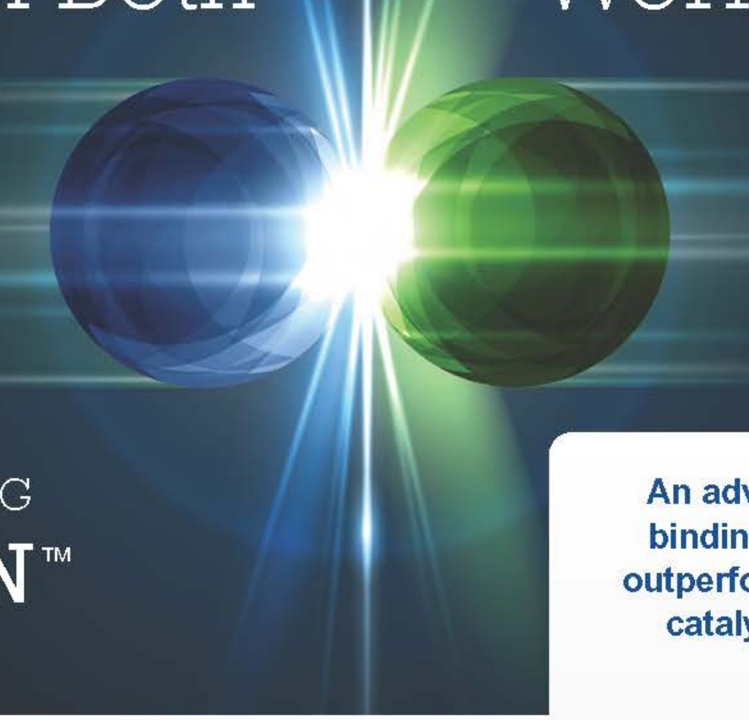
Processing heavier feeds in the FCC unit without hydrotreating will have an impact on FCC performance. **Figure 3** summarises results from pilot plant testing showing the impact the nitrogen content in the FCC feed has on FCC gasoline yields. There can be a significant decrease in gasoline yield as the FCC feed nitrogen content increases.

FCC performance is also affected by PNAs in the FCC feed. FCC gasoline yield increases as the feed PNA content decreases.

The FCC feed sulphur relates to the sulphur content of the FCC products. Allowing the FCC feed sulphur to increase results in an increase in FCC gasoline and LCO sulphur. This can have an impact on the gasoline pool at the refinery and, if there is an FCC post-treater, may result in higher octane loss if the post-treater operation becomes more severe (higher sulphur conversion).

However, if hydrotreating capacity is not available and the preference is to process unhydrotreated heavy feeds directly in the FCC unit, there are several unit handles that can improve the operation and handle the shift in feed quality. These include:

- Higher fresh catalyst additions to purge contaminant metals (such as Ni and V) and mitigate the negative effects of temporary catalyst poisons (such as N)
- Employ metals traps in fresh catalyst, such as nickel passivating alumina and vanadium traps, to minimise the impact of contaminant metals, improve coke selectivity, and preserve conversion and Ecat activity
- Inject antimony to passivate Ni on Ecat and reduce dehydrogenation reactions
- Use of gasoline sulphur reduction additives to control gasoline sulphur levels while increasing feed sulphur
- Applying SOx and NOx reducing additives to maintain environmental compliance while increasing feed sulphur and nitrogen



- Lower feedstock temperature, deeper partial burn (if possible), and/or higher catalyst cooler duty can help maintain cat/oil ratio and minimise any drop in conversion. Higher coke yield will be required
- Optimise dispersion and stripping steam to help ensure feedstock atomisation and to avoid excessive regenerator temperature

Overall, the decision to hydrotreat the heavy portion of the FCC feed will ultimately depend on a particular refinery's layout, constraints, and available capacity. There are certainly significant benefits that can be realised by hydrotreating the feed, and there are handles available within the confines of the FCC operation to help mitigate any detrimental impacts due to heavier feed components. In many cases, the optimum approach may well be a combination of hydrotreating and adjustments to FCC operations to best handle more difficult, heavy feed components. Holistically, this feed shift should offer the refinery a feed cost advantage and improve overall profitability.

A **Mark Pilling, Head Engineered Solutions Refinery Group, Sulzer,** mark.pilling@sulzer.com **and Celso Pajaro, Head Refinery System Business AME, Sulzer,** celso.pujaro@sulzer.com

One method to increase the proportion of heavy components is revamping the vacuum unit to a deep cut mode. As a fundamental starting point, it is important to have complete distillation data for the atmospheric residue (long residue). When properly done, the HVGO yield will increase without a significant change in metals or Conradson carbon residue (CCR) content. The revamp typically requires modifications to the fired heater, transfer line, vacuum column, and associated equipment.

The revamp design should be performed by an experienced company. Improper designs will lead to poor HVGO quality with high metals and CCR content. This will reduce the FCC unit conversion by raising the regenerator temperature and increase catalyst consumption due to a higher catalyst deactivation rate.

VGO hydrotreatment improves the oil quality by reducing CCR, metals, sulphur, and nitrogen compounds which improves the FCC conversion, reduces catalyst consumption and sulphur content in the FCC products. A VGO hydrotreating unit represents a big investment for the refinery. Unless there is a significant increase in FCC feed rate, the investment is typically not justified.

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Hydrotreating FCC feed has a number of advantages but the ultimate decision on the overall value is very site specific. Stripping out sulphur and nitrogen upstream of the FCC can alleviate SOx emissions concerns, achieve product specification targets, allow the FCC unit to reach higher conversion levels, and reduce FCC catalyst consumption, as some examples. Some of the options that can be considered in the broad spectrum of technologies of FCC feed pretreatment include saturating polyaromatic molecules, thus reducing feed Concarbon and feed contaminant metals introduced to the FCC unit. The deepness of the hydroprocessing of the heavier feed portion will determine overall FCC yield structures and fresh catalyst requirements. Adding in heavier portions of feed that are not already being hydrotreated today can impact cycle lengths on the hydrotreatment reactors in the refinery. The refiner should verify that run cycles of the hydrotreaters are consistent with the required maintenance plans in place. Plan carefully to avoid the scenario where a reactor ends a cycle early or shuts down on an unplanned basis. It may be justified to plan shorter hydrotreater run lengths to ensure good feed properties for the FCC towards the end of the cycle, but make sure to investigate the various pros and cons and have total refinery buy-in before a final decision is taken.

Although it is easy to look at the positives of hydrotreating a portion of the FCC feed, potential negative impacts should be given serious consideration. This can include difficulty maintaining FCC heat balance due to a minimal amount of coke or feed metals introduced with the feed and a limitation in the amount of conversion coke that can be generated to compensate this loss. As delta coke decreases, cat:oil will increase to maintain the required unit coke yield. If there is a limit on circulation, such as slide valve dP or cyclone loading, meaning the balance cannot be satisfied by catalyst circulation increases, remedial and destructive measures can be necessary including an intentional detuning of the stripper or continuous use of torch oil or the direct fired air preheater. This scenario is an extreme case of what could be considered over-pretreatment. If the purpose of hydrotreating part of the feed is to accept more heavy components into the mix, the end result may be a bimodal or dumbbell distribution of feed properties. Although this balancing of the feed may achieve the desired goals of the unit, it also introduces extreme sensitivity to any slight changes in the properties or proportions of either type of feed, leading to an unstable or cyclical operation.

Another issue when processing hydrotreated feed is observed when analysing the hydrogen balance of the unit. Cracked products from hydrotreated feeds tend to be highly paraffinic in nature. This can introduce a number of problems, including a reduction in cat gasoline octane number and ZSM-5 effectiveness, as well as a possibility of fouling in the bottoms circuit as asphaltenes can precipitate out and flowing viscosity of the bottoms product increases. It should also be ensured that the new product yields will satisfy pumparound and heat integration requirements. On the FCC regenerator side, although hydrotreating a portion of the feed can reduce total feed sulphur, it is normally observed that the quantity of sulphur in aromatic feed molecules dictates FCC SOx emissions. Simple hydrotreating will generally remove easy sulphur from feed molecules, leaving difficult sulphur in aromatic molecules in the heavy tail of the feed – destined to form coke in the


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FCC unit. Therefore, attention should be paid to SOx emissions when changing feed source in a radical way and any uncontrolled SOx models should be updated or rectified based on the new feed mix.

Reviewing the most optimum and cost-effective SOx control solution will be key to realising the full benefits of such a feed shift. A change in the coking tendency of the feed, a likely outcome when hydrotreating feed or moving to a bimodal mix, can impact afterburn and CO control in full burn and shallow partial burn FCC units. A cooler regenerator is a common impact from a more hydrotreated feed. A reduction in the temperature driving force in the kinetic reaction of CO to CO_2 can necessitate an increase in available promotion activity in the form of a platinum or palladium based CO promoter addition. Not only does this increase in CO promoter use have a cost, offsetting some of the savings gained from hydrotreating, but increased doses of either a platinum or palladium CO promoter will increase NOx emissions, perhaps to a level that exceeds current limits. New CO promoter technology from G. W. Aru, LLC reduces precious metal loading in the FCC, minimising unexpected cost and NOx increases.

Q What are the advantages of deasphalted oil hydrocracking for a resid upgrading project?

A Sid Mohanty, Technical Service Manager, Advanced Refining Technologies and Arun Arora, Director, Technology, Chevron Lummus Global, arun.arora@Lummus.Tech.com

The heteroatoms and asphaltenes tolerance of an ebullated bed resid hydrocracker (RHC) is significantly higher than a fixed bed resid hydrotreater, making deasphalted oil (DAO) an easier feed than vacuum resid (VR) in an RHC. Chevron Lummus Global (CLG) and ART have an extensive research database and commercial experience of high lift DAO processing in both fixed bed resid hydrotreating and LC-Fining resid hydrocracking units. Based on our experience processing DAO, especially high lift DAO using C_5 type solvents in RHC units, DAO primarily offers high conversion at lower H_2 consumption and improves unit reliability.

DAO processing requires some special considerations. Careful attention to DAO quality is required in designing a unit-high lift or low lift, straight-run DAO (generated using straight-run VR) or cracked DAO (generated using unconverted oil from intermediate LC-FINING VR reactors). Additional consideration must also be given to the catalyst selection for DAO processing. Catalyst with an optimum balance between activity and pore size can help maximise catalytic conversion while minimising instability in the unconverted oil.

Adding straight-run DAO to straight-run VR feed can debottleneck an existing RHC unit processing difficult crudes, such as Urals, which are prone to sedimentation. It can also provide lower sulphur content in the unconverted oil, thereby reducing cutter stock required to meet IMO 2020 low sulphur fuel oil specifications. However, the impact on overall conversion needs to be evaluated when adding straight run DAO to existing operations.

In an alternative configuration, as offered in CLG's LC-Max technology, the unconverted oil from a resid hydrocracking reactor is deasphalted in an intermediate SDA unit. This cracked DAO can be further hydrocracked in a dedicated reactor to extinction with almost no sedimentation to achieve >90% conversion. The lower sediment in the reactor effluent results in lower fouling rates in downstream piping and equipment, resulting in improved operating factors. Lower asphaltenes and feed metals result in lower H_2 consumption and catalyst usage in the RHC unit, thereby resulting in cost savings for the refiner.

ART ebullated bed catalyst has been successfully employed in the resid hydrocracking of a blend of VR and DAO from straight-run VR in a CLG licensed LC-Fining RHC unit, resulting in significant margin improvement for the refiner. With ART's LS and HSLS Plus catalyst platform, the refiner was able to significantly increase resid conversion and reduce unconverted oil sulphur content while decreasing catalyst addition rates.

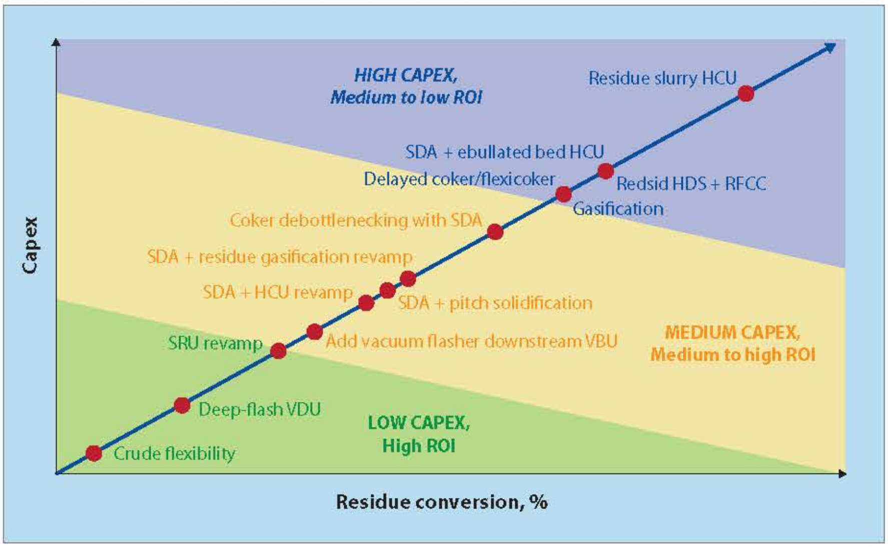
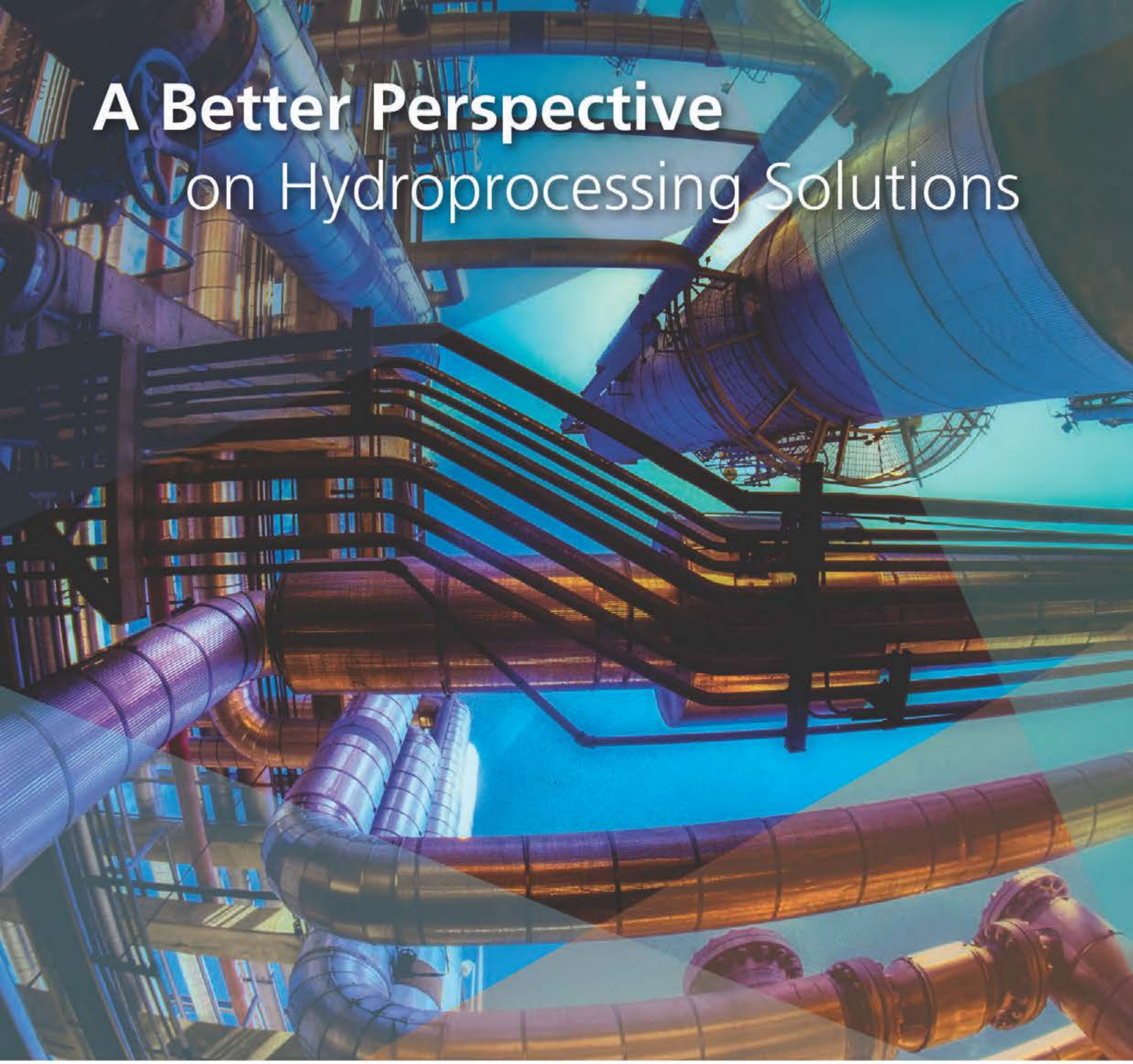


Figure 1 Relative economic advantage of combining solvent deasphalting and DAO hydrocracking

A Ward C Koester, Hydroprocessing Licensing Technology Manager, Shell Global Solutions (US) Inc., W.Koester@shell.com **and Brian A Heasley, Refining Technology Manager, KBR Technology Solutions,** Brian.Heasley@kbr.com

The biggest advantage of deasphalted oil (DAO) hydrocracking for a residue upgrading project is the affordability that the combination of solvent deasphalting (SDA) and DAO hydrocracking offers to most refiners relative to other conversion technology options. This is illustrated in **Figure 1**. The second advantage is the flexibility of such a configuration, offering realistic projects combining new SDA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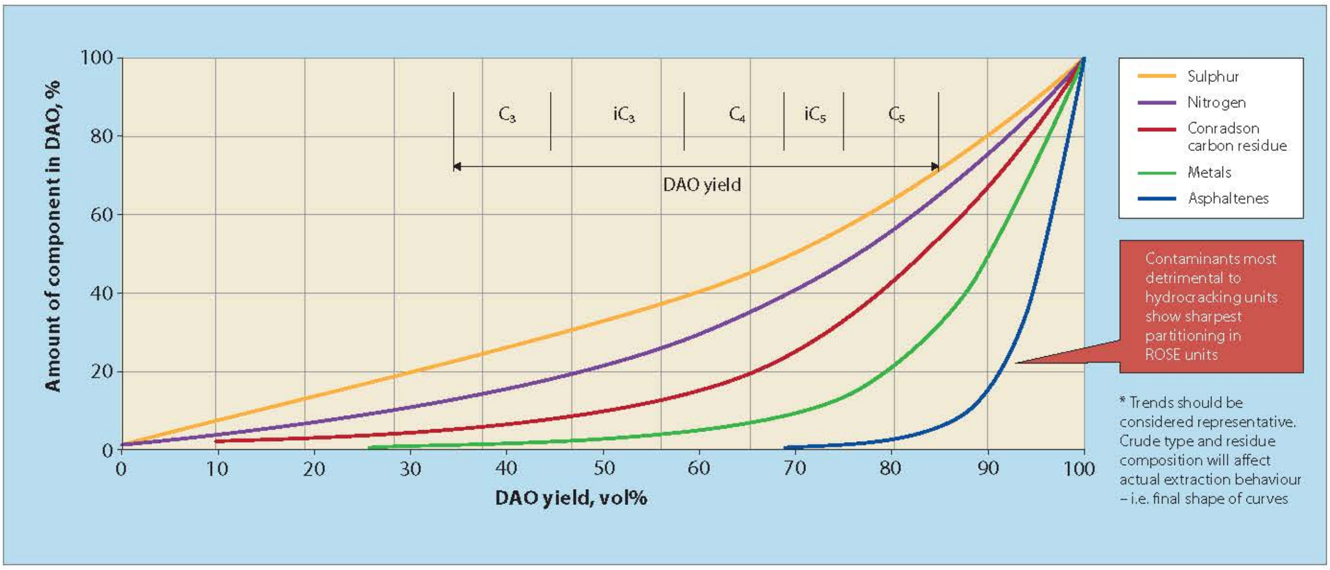

Contaminants most detrimental to hydrocracking units show sharpest partitioning in ROSE units

* Trends should be considered representative. Crude type and residue composition will affect actual extraction behaviour – i.e. final shape of curves

Figure 2 DAO product has significantly reduced contaminant levels

with revamp of an existing VGO hydrocracker or even revamp of an RHDS unit to DAO hydrocracking. The configuration is fully proven and offers a high degree of reliable operation, with upgrading of DAO to max naphtha (for petrochemicals) or max middle distillates for the traditional fuels market or partial conversion to produce heavy base oils from the unconverted DAO.

The main driver for a residue upgrading project is to increase margins by making products that are more valuable than residue. There are several things that are driving the value of residue down, including the IMO 2020 marine fuel specifications, the desire to produce cleaner fuel for power plants around the globe, and a reduction in fuel oil demand due in part to the wider availability of natural gas and the expansion of the LNG market. Responding to the reduction in residue demand can be complex and involves several key factors that will influence individual refiners' investment decisions, including the current refinery configuration, how much they believe HSFO will be discounted, and the amount of Capex they can afford.

A range of conversion techniques can be applied for residue conversion, but there is no one-size-fits-all solution. Coking and visbreaking are widely applied thermal processes, but these offer no hydrogen addition to improve liquid yield or product quality. Residue hydrotreating offers improved product quality with the addition of hydrogen, but conversion of 1000+°F material remains relatively low. Residue hydroconversion includes ebullated bed and slurry hydrocracking (SHC) which offer moderate to high 1000+°F conversion, but they both require significant Capex, and SHC is an emerging technology. Integrated solutions that utilise SDA in combination with revamps of existing refinery conversion assets such as cokers, gasifiers, resid hydrotreaters, hydrocrackers, and resid FCCs are often the preferred solutions that provide the best return on investment.

KBR's ROSE supercritical SDA technology is a preferred component of an integrated residue upgrading solution because the units are relatively simple, deliver high energy efficiency with low capital and operating costs, and have demonstrated reliable operation. ROSE technology is a versatile and flexible means to process vacuum residue, atmospheric residue, thermally or catalytically cracked feeds, and feedstocks from a wide range of crude slates. A ROSE supercritical SDA efficiently sends the right molecules with an acceptable level of contaminants to downstream destinations and can add value to a resid upgrading project.

ROSE utilises light paraffinic hydrocarbon solvents to extract DAO from feedstocks containing asphaltenes. The recovered DAO is primarily paraffinic in nature and, although the boiling point is high, the K-value is also high, indicating the feed is ideal feed for a catalytic conversion unit. The other product stream is asphaltene rich, containing those molecules least desired in a catalytic conversion unit, but very suitable for thermal cracking (coking), solidification, or gasification.

ROSE separates the solvent from the DAO under supercritical conditions, providing significant energy savings (40-50% compared to conventional solvent extraction). Depending on the crude slate and solvent availability, units can be designed for a DAO yield (or DAO lift) up to 60-80 wt% or higher subject to feed quality. The unit can be designed for capacities ranging from 2000 b/d up to the largest ROSE unit in operation at 80 000 b/d.

ROSE greatly improves the quality of residue feedstocks for processing in a downstream conversion unit. By extracting asphaltene-rich molecules, the resulting DAO product has significantly reduced asphaltene content, metals (nickel and vanadium), Conradson carbon residue (CCR), nitrogen, and sulphur (see **Figure 2**). All these components can impact the downstream unit catalyst and operation. The desired DAO quality is set by the DAO hydrocracker design. The DAO quality is primarily a function of feedstock, solvent type, and DAO lift. Characterisation of DAO is important to accurately predict the impact on a DAO hydrocracker or other downstream units

The combination of SDA and DAO hydrocracking is

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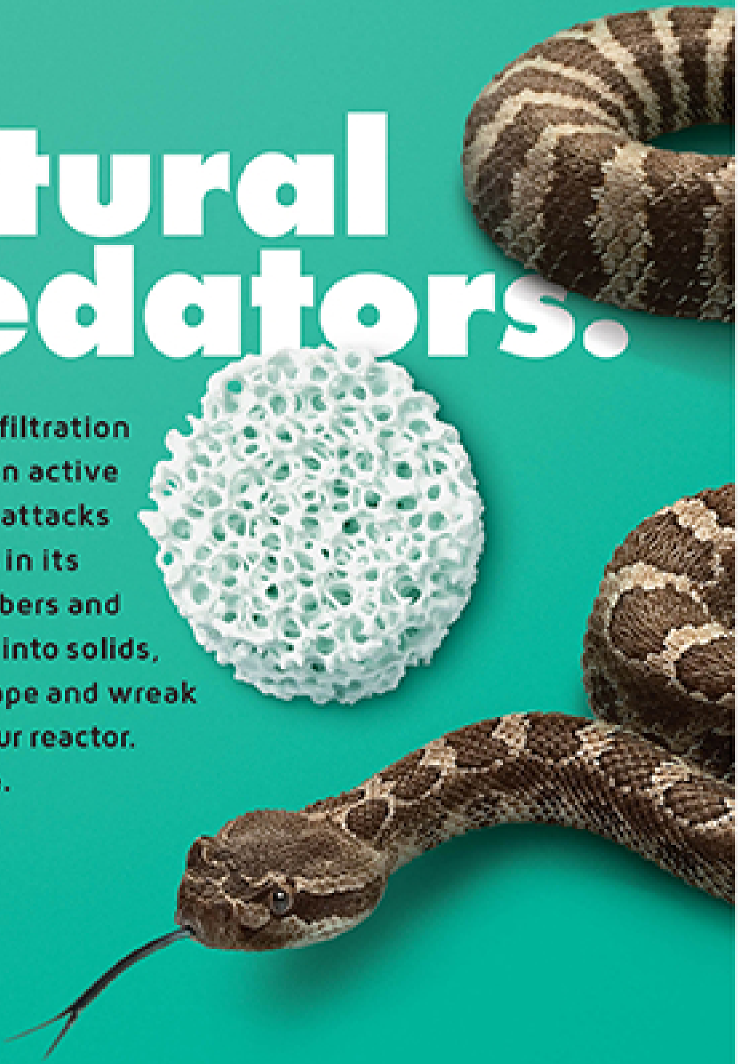

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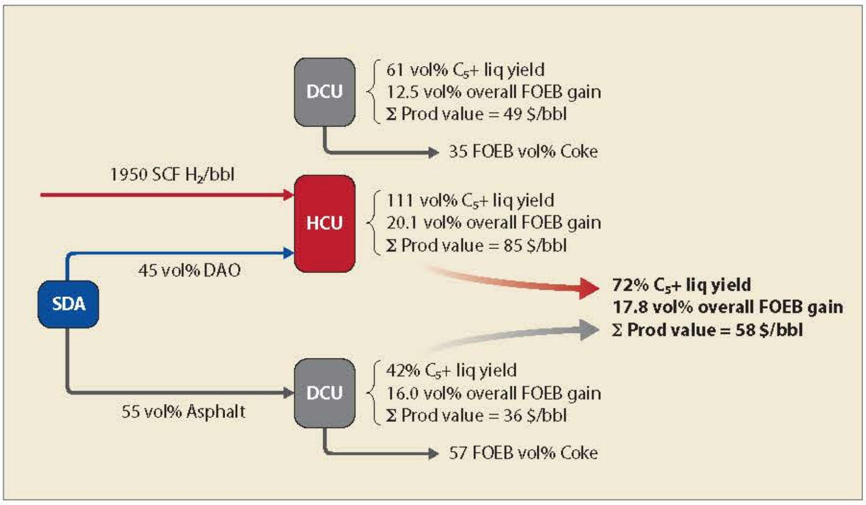

Figure 3 Processing short resid via two options

an attractive option for residue upgrading because it enables the production of a range of high quality transport fuels and the hydrocracker unconverted oil (hydrowax) can be used as feed for the FCC, ethylene cracker, or lubes base oil plant. When integrated into a refinery that already contains a delayed coker unit (DCU), compared with a coker operation alone, it can generate an overall product value that is up to $10/bbl higher than a DCU/GOHT operation. **Figure 3** demonstrates the processing of short resid with the two options. In this example, the petroleum coke and the off-gases have been converted to a fuel oil equivalent barrels (FOEB) basis for the comparison. Much better liquid yields are obtained from catalytically cracking the paraffinic DAO with hydrogen in the HCU vs thermal cracking of the short resid in a DCU. The SDA/HCU combination also allows for heavier crudes to be processed without requiring a coker expansion. The product value in this example assumes that a combination of finished products and intermediate feeds are generated. For example, the light coker gasoil is considered ULSD value assuming it will be processed in a downstream hydrotreater, while the heavy coker gasoil is given VGO feed pricing assuming it will be processed in an FCC.

In the example shown in **Figure 3**, the asphalt was processed in a DCU. While this option eliminates 100% of the pitch, it still generates a large amount of petroleum coke. An alternative option would be to install a gasifier in place of the DCU to convert 100% of the asphalt into hydrogen and then utilise this hydrogen as feed to the hydrocracker. The CO_2 from the process is captured at high purity, allowing the refiner to further reduce their CO_2 footprint via CO_2 sequestration and storage. Alternative products from the gasifier option are petrochemical products such as methanol, oxo-alcohol, and acetic acid. Shell's Gasification Process (SGP) is popular in regions with high hydrogen prices and with customers aiming to maximise petrochemical production from crude oil. Another option is producing a solid product for fuel. KBR's Asphaltene integrated Management System (AiMS) enables users to transform solid asphalt product into pitch flakes or pellets that can be used as fuel in circulating fluidised bed (CFB) boilers. This option can be used in high DAO lift applications where there is limited cutter stock availability and it is more conducive to produce a solid product.

With fixed-bed DAO hydrocracking, feed metals (Ni+V) are limited to less than about 35 ppm which limits the potential DAO lift that can be achieved at the SDA unit. However, with application of Shell's Hycon moving bed technology for hydrodemetallisation, the SDA unit lift can be increased up to the asphalt viscosity limit while producing DAO with up to 100 ppm metals. The benefits of installing the Hycon moving bed reactor technology in front of a fixed-bed DAO hydrocracker include:

- Increasing hydrocracker cycle length
- Enabling increase in hydrocracker conversion
- Maximising HDM utilisation through increased SDA lift and DAO heaviness or increased DAO rate
- Improving crude flexibility through selection of heavier, higher margin crudes
- Improving pressure drop management for better flow distribution and improved catalyst utilisation in existing fixed-bed demetallisation reactors

Q How much slop oil can we add to our crude charge before fouling becomes an issue downstream?

A **Simon Calverley, Consulting Product Integration Director, KBC (A Yokogawa Company),** Simon.Calverley@kbc.global

Many refineries keep the slop below 2% on crude, indeed KBC typically recommends 2% slop as a maximum. Some refineries run slop in a batchwise manner at higher percentages on crude. We would not recommend this operation.

KBC has seen high slop rates resulting in high basic sediment and water (BS&W) in the desalted crude. One client was intermittently feeding slop at approximately 7% on crude – the operation being performed when the slop tank was full, with no slops being fed at other times. High BS&W from the desalter was observed when slop was being run. When the client switched to running slop continuously at up to 2% of crude, the BS&W in the desalted crude reduced.

Slop containing cracked materials can cause fouling, particularly if it is fed from tanks that are not nitrogen blanketed. Light slops can cause asphaltene precipitation which also leads to fouling.

There are various other reasons why fouling may occur that are not related to slop rates. Crude tank operation and incompatible crudes are two of the most common reasons.

Crude fouling can be monitored using KBC's HX-Monitor. The benefits of cleaning exchangers in the crude preheat can be estimated using the tool.

A Mark Pilling, Head Engineered Solutions Refinery Group, Sulzer, mark.pilling@sulzer.com **and Celso Pajaro, Head Refinery System Business AME, Sulzer,** celso.pujaro@sulzer.com

The amount of slop oil that can be processed into the crude unit depends on the slop quality and the contaminants present (solids, olefins, dissolved oxygen, and so on).

Some refineries can segregate slop into cracked streams that have olefins and non-cracked slop streams. Non-cracked slop can be processed in the crude unit. The major concern is that the strong water-oil emulsion and solids present in the slop can produce desalter upsets which generate more slop. One method to avoid this problem is by pretreating the slop, particularly the slop generated in the wastewater plant.

Slop generated in wastewater plant can be pretreated by:

- Heat plus chemicals to break the emulsion and separate the solids with water
- Centrifuge

Proper pretreatment allows maximum slop addition in the crude unit without major problems. For crude units with no spare capacity, non-cracked dry slop can be injected directly into the crude column pumparound.

Cracked slop can be processed directly in the coker (first choice) or FCC unit. Dry slop with no solids can be injected directly into the main fractionator. Wet slop with solids is preferentially injected into the coker drum.

If the refinery cannot segregate and pretreat some of the slop, the maximum processing capacity will depend on the nature of the slop:

- Presence of significant cracked (olefin) material combined with oxygen will tend to polymerise in the heat exchangers, reducing heat transfer efficiency
- Presence of solids can impact the desalter operation, leading to oil carry-under with desalter water

A Chris Claesen, Director, Technical Consulting, Nalco Water, cclaesen@ecolab.com

This will depend on the quality of the slop oil. Some slop oils cause problems at 0.1% of the charge, others may not cause a problem at 10% of the charge. Slop oil is a term used for a whole range of materials coming from different sources. The source of the slop oil should be known as well as the contaminants or products such as dispersants that have been added to it. Some slop oils such as off-spec distillates can be very easy to process but others such as gasoil with an added dispersant that was used during a cleaning operation may cause a lot of emulsion and fouling problems. Also, slop oils from conversion units that contain olefins can cause polymer formation and fouling in the CDU preheat. Some materials such as API or wastewater skimmings should not be added to the slop and preferably not be processed via the CDU feed, especially if they have already been treated with polymers. Good source determination and composition analyses are key parameters to help decide how the slop oil should be processed. Basic sediment and water, filterable solids, % emulsion, density, and olefins content are some of the parameters that can be checked. Nalco and some other companies can offer special on-site evaluation tools to predict the effect of the slop oil on the crude oil stability, the desalters, wastewater, preheat, and furnace. Nalco has a range of demulsifiers, solids wetters, antifoulants, and stabilisers that if needed can be added to the slop to mitigate the effect of the slop oil addition. Slop oil should be added to the crude charge from a separate slop oil feed tank; this makes it possible to adjust the rate based on the quality and the downstream effects on the desalter, preheat, and furnace. Ideally, before slop oil is sent to the slop oil feed tank it is treated in a separate tank to resolve any emulsion and remove solids and water.

If a refinery is continuously having to process difficult slop oil streams or if slop oil generation continuously runs above 1% of the refinery throughput, the root sources need to be identified. Some of the slop oil streams can have a significant impact on operations and impact the refinery total cost of operation. If these are eliminated upstream of the slop oil system, significant improvement in operational costs can be made. A typical example is poor desalter performance due to emulsion formation and effluent water with emulsified oil that is sent to the effluent treatment plant. In such a case, the desalter demulsifier treatment and operation should be reviewed and adjusted so that the emulsion is resolved inside the desalter and the desalter effluent has no free or emulsified oil.

Q Can we recover economic quantities of hydrogen from refinery off-gases?

A Torkil Ottesen Hansen, Product Line Director, Haldor Topsoe, tih@topsoe.com

There are actually two relevant questions in this connection. One is the direct recovery of the hydrogen present as H_2 in the off-gases. The other is what amount of H_2 you can make from the off-gases.

We will address the latter issue. Normally a refinery off-gas is used exclusively as fuel while the feed to the steam reformers making H_2 uses more expensive imported natural gas. In a future refinery where heat recovery has high priority then the need for fuel gas will be lower. It is a natural thought to make use of the fuel gas as feed to the steam reformer units.

The typical fuel gas contains fair amounts of olefins and even diolefins. Furthermore, the sulphur compounds are not all readily removed in an amine system to acceptable levels for steam reforming. These restrictions have prevented fuel gas being a feed to H_2 plants.

It is however possible to clean the off-gases combined in a catalytic unit. It requires a maximum of three steps. The first step will handle the di-olefins and can therefore be omitted if there are no di-olefins.

The next step is an olefin and sulphur hydrotreating reactor. Olefins become saturated and sulphur compounds react with H_2 to form H_2S. The sulphur reactions have potential equilibrium complications if oxygen compounds such as CO and CO_2 are present. Thus, a third step may be needed. It can be necessary to add a hydrolysis reactor where the final traces of organic sulphur react to form H_2S.

After this catalytic unit, the gas can be passed through an amine unit before it is ready as feed for steam reforming. It will then be a very useful steam reforming feed, and in case it contains some H_2, which it typically does, the normal gas recycle within a steam reforming unit can be stopped. References for this type of unit do exist.

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The economics of hydrogen recovery depend on the supply and demand side, on both the cost and the value of recovery.

The value of recovery

If hydrogen is produced from \$2/MMBTU natural gas, then the hydrogen will be worth only around \$400/t. There are even refineries that flare excess hydrogen, in which case hydrogen recovery has no value at all. The other extreme is a site with a high margin hydrocracker being constrained by lack of hydrogen, which can make the value of hydrogen reach \$3000/t.

The cost of hydrogen recovery

The cost of hydrogen also varies widely. In general, it will be much cheaper to avoid hydrogen slippage to fuel gas than to recover it after it is lost to fuel gas. Valve leaks and unintended control losses of hydrogen to fuel gas can be avoided without significant cost. Reducing high pressure hydrogen bleeds or cascading hydrogen comes at a cost in terms of catalyst cycle length but should be considered.

Direct hydrogen recovery from fuel gas streams is more costly due to the low pressure and lower hydrogen contents, which in most cases are too low to allow purification in a membrane or PSA unit. Hydrogen in lower purity streams can potentially be recovered by processing them as feed on a steam reformer where the feed hydrogen will unload the furnace.

A more expensive option is cryogenic hydrogen recovery. In most cases, the investment in a cryogenic unit only is economic if the fuel gas stream contains other components with a higher value (for instance LPG, naphtha). This may change in the future as excess refinery fuel gas will become more common due to increased energy efficiency and residue conversion levels. Sustained and real time optimisation of the fuel and hydrogen networks can be achieved by incorporating the hydrogen network into the (digitalised) refinery energy management system.

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Operating with appreciable amounts of hydrogen in refinery fuel gas has a number of particularly important drawbacks. Hydrogen has a low molecular weight giving it a low calorific value per unit volume, is costly to compress, and introduces more pressure drop in the fuel gas headers. On top of this there is a concern for hydrogen embrittlement in piping sections, valving, and fittings that are not suitable for handling hydrogen rich streams (using basic carbon steels). However, the most obvious downside is the financial cost of burning valuable hydrogen. Hydrogen sources in fuel gas can be from reformer or isom units where the make gas or off-gases are not separated off as a hydrogen rich stream for hydrotreating, selective hydrogenation, or other hydrogen intensive processes. More commonly the main source of hydrogen in refinery fuel gas is from FCC dry gas which contains a mixture or hydrogen, H_2S, C1, C_2, and other non-condensables.

Many refiners are choosing to capture and purify the hydrogen from fuel gas streams by using a pressure swing adsorption (PSA) unit. PSA units are a straightforward and flexible option to recover hydrogen at a high purity. The unit can be sized to the feed flow rate it is processing, and the range of contaminants typically found in refinery fuel gas streams, such as methane and CO_2, can be easily purified. After recovery of hydrogen for use in downstream processes, purge gas from the PSA is injected back into the fuel gas system, minimising any losses and maximising total value. As the process to purify the stream using a PSA is straightforward, the unit can run with minimal outside utilities or requirement for operator involvement. The plot space needed is compact and it is an easy and straightforward option as a refinery upgrade. This has led many refiners to consider their PSA system as a 'black box' which they only need to think about once every 10-15 years to change out the adsorbent layers and inspect the integrity of the pressure vessels. A poorly specified or optimised PSA will not be maximising profitability for the refinery. Unicat can independently assist refineries maximise the potential of their PSA unit, whether it is a new installation or an operating unit.

FCC catalyst boosts bottoms upgrade

A combination of novel matrix technologies in a new FCC catalyst increased bottoms upgrading of residual feeds and improved profitability

OLAF PETER HARTMETZ and BERNHARD ZAHNBRECHER *Bayernoil*
SABEETH SRIKANTHARAJAH and MARIA LUISA SARGENTI *BASF*

Since the beginning of 2020, most of the recognised analyst companies have been making predictions about the refining products market, first related to the impact of IMO 2020 and later to Covid-19. We have seen how refineries are more and more under pressure. It is not unexpected that they will continue to struggle with challenges that include more physical constraints, increasing costs of environmental regulations, changing and declining demand of products, and additional supply issues.

In particular, the combination of a narrowing crude market and weak demand is set to keep refining margins at historic lows over the coming months and FCC units will face more challenges to maximise their profits.[1,2]

What will be the threats for FCC operation? Probably there is not a unique answer to this question. The observed trends require the FCC unit to be able to deliver a favourable contribution to profitability and – in most units – to maximise its capacity to process residual feeds.

Implementation of the IMO regulations already resulted in drastically changing markets and created short-term opportunities requiring refiners to show maximum adaptability to capture value. Thus it has become imperative that refiners take advantage of the most effective options available to them. Resid feeds are known to be an example of opportunity crudes that can drive higher profitability for a refinery, given their low purchase cost. However, the processing of this type of crude requires flexible operation and catalyst to convert such crudes to lighter molecules and higher value products.[3]

More residue processing and optimised slurry oil production requires the catalyst to further upgrade bottoms and provide additional unit flexibility by overcoming and releasing operational constraints.

BASF has been targeting catalytic solutions to fulfill the need for resid FCC units to anticipate IMO challenges among others. The primary focus was, in one direction, maximisation of processing capacity for residual streams or, alternatively, optimisation of slurry oil production. Both routes would support FCC operation to achieve the target product slate in preparation for IMO implementation.

> **The observed trends require the FCC unit to be able to deliver a favourable contribution to profitability and – in most units – to maximise its capacity to process residual feeds**

As a result, BASF has introduced the next generation of catalyst for moderate resid operations, Altrium, with a focus on three key functionalities:

- Higher meso-macro porosity for a better pore connectivity network to increase diffusion and conversion of large molecules
- Enhanced nickel passivation capabilities to minimise dry gas and coke yields
- Maximum light cycle oil (LCO) to bottoms conversion to generate more valuable products.

In addition, the benefits delivered by Altrium helped to release the unexpected additional pressures and operational disruptions caused by Covid-19.

Linking the benefits

Altrium is based on the combination of two technologies: AIM (Advanced Innovative Matrix) and IZY (Improved Zeolite-Y). These technologies have been linked to deliver high performance and value for moderate resid processing applications.

AIM consolidates several novel matrix technologies that are selectively incorporated into the catalyst design for a broad selection of performance targets and applications. It offers the flexibility to fine-tune the zeolite to matrix ratio in order to maximise conversion to transportation fuels.

With the introduction of AIM, BASF initiates a new generation of matrix families capable of delivering high performance through improved porosity which further enables the diffusion of large molecules to more and better distributed active sites.

Furthermore, the matrix and zeolite in Altrium are produced in a single manufacturing process step to make sure they are intimately dispersed and adjacent to each other. This *in situ* process enables maximum flexibility and control of matrix morphology, resulting in a catalyst with higher attrition resistance, no chloride, and the lowest sodium content available.

The manufacturing process allows for additional flexibility. Firstly, a

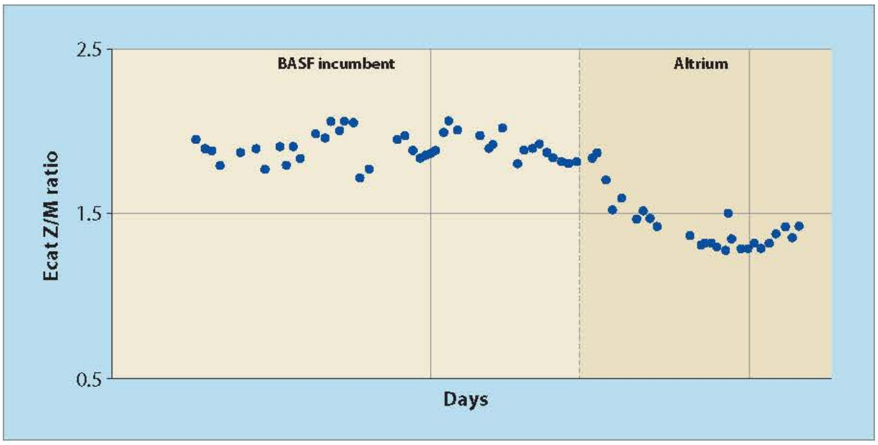

Figure 1 Trend of Ecat Z/M ratio during the change to Altrium FCC catalyst

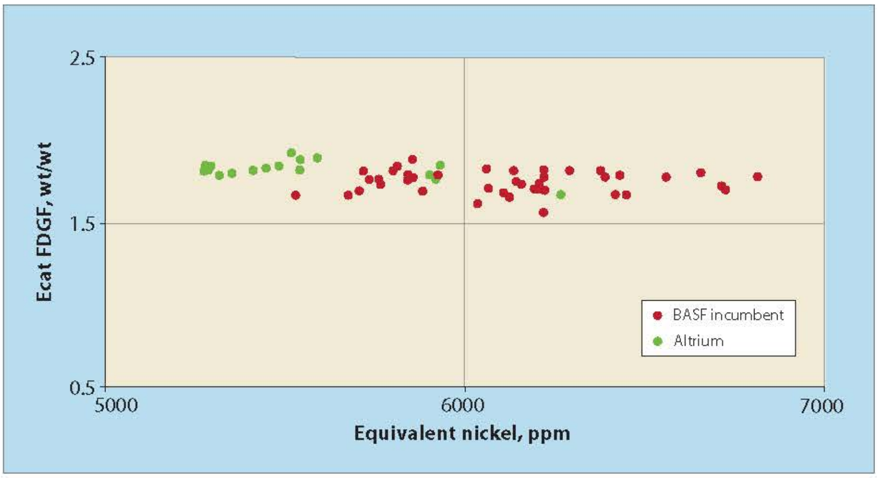

Figure 2 Trend of Ecat fluidised dry gas factor vs equivalent nickel (ACE data)

catalyst microsphere is manufactured from kaolin clay and functional matrix raw materials. Then zeolite is grown within the microsphere. Nutrients for zeolite growth are provided by the microsphere itself, giving rise to the term *in situ*. Because the zeolite is grown directly on the microsphere, an epitaxial layer is formed, eliminating the need for a separate binder. By using the *in situ* process, higher levels of zeolite can be included in the catalyst. Additionally, the process leads to a more open pore architecture, allowing for improved metals tolerance.

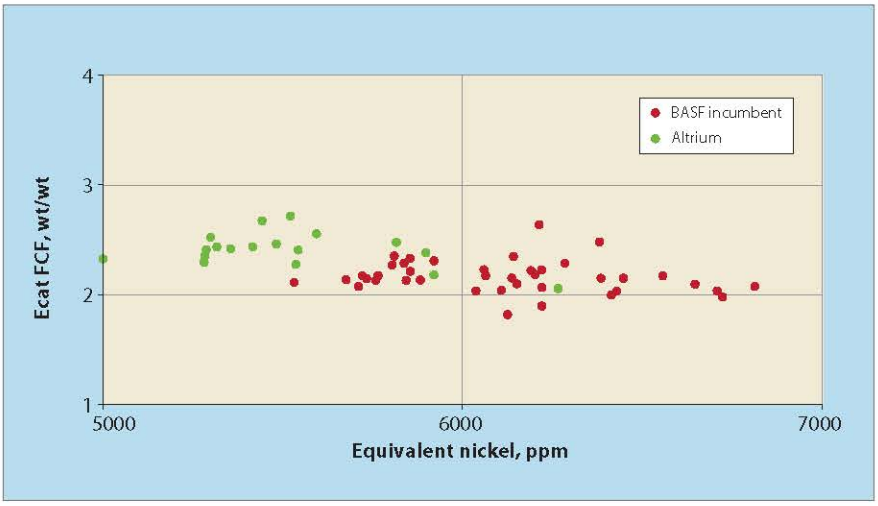

Figure 3 Trend of Ecat fluidised coke factor vs equivalent nickel (ACE data)

Commercial trial

Bayernoil Refinery GmbH is a refinery group of Varo Energy GmbH, Rosneft Deutschland GmbH, and Eni Deutschland GmbH. The company operates the largest refinery in the Bavarian region, ensuring security of supply in the region.

Production at Bayernoil has been running since 1964 on an area of about 300 ha southwest of the city of Neustadt. The refinery is supplied with crude oil from Trieste via the Transalpine Pipeline, producing propane and butane, refining gas, all types of gasoline, diesel, and light and heavy fuel oil.

Through continuous modernisation of the process plants and integration of the latest process technologies, it is one of the most productive refineries in the region with a Nelson Complexity Index of 8.1.

Operational background

The FCC unit at Bayernoil Neustadt is a UOP stacked design with 30 000 b/d processing capacity, operating in deep partial burn using a catalyst from BASF (the "incumbent"). Resid feedstock with high metals and Concarbon is converted to valuable products.

Due to changes in the market environment, increasing the LCO output as well as gasoline and LPG volumes has become more attractive for refineries. Altrium was introduced to increase yields of transportation fuels and to improve the overall profitability of the operation.

To maximise the profitability of the refinery, the FCC catalyst is designed to meet the specific requirements of the unit by means of its metals tolerance, surface area, rare earth on zeolite, matrix type, and pore architecture. Firstly, the pore architecture requires optimisation to facilitate the diffusion of heavy feed molecules and to help improve heavy molecule (bottoms) cracking. Secondly, the relative zeolite and matrix content requires optimisation to prioritise conversion or distillate yield.[4]

Altrium FCC catalyst has been fine-tuned and customised to achieve new operating targets for Bayernoil. To that end, the catalyst's design features include:

- A lower zeolite to matrix ratio (Z/M)

- Good metals tolerance, to maximise bottoms upgrading whilst maintaining low dry gas
- Ensuring that carbon on regenerated catalyst (CRC) is maintained at a low level to avoid disruption of the partial burn regime.

Figure 1 shows the trend of Ecat Z/M values while the unit was changing from the incumbent BASF catalyst to Altrium. A catalyst with lower Z/M will improve conversion of bottoms since the matrix surface area has been optimised to promote the cracking of heavy molecules and for pre-cracking oil to 'feed' the zeolite.

The regenerator temperature is influenced by many factors including operating conditions, catalyst activity, feed qualities, and more

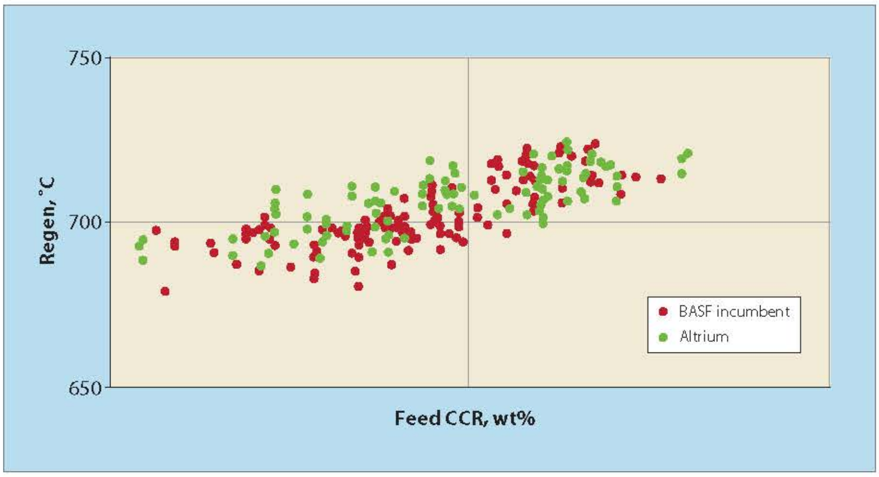

Figure 4 Trend of regenerator temperature vs feed Conradson carbon residue

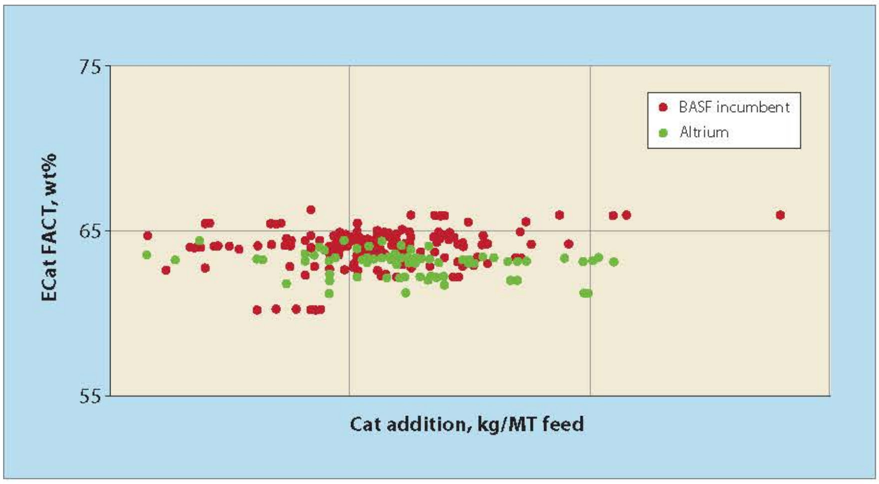

Figure 5 Trend of Ecat activity vs specific catalyst addition rate

Ecat comparison

The progress of the commercial trial has been monitored with regular evaluation of Ecat in the Advanced Cracking Evaluation (ACE) unit. The fluidised dry gas factor (FDGF) is the dry gas production (C_2 and lighter) adjusted for conversion. Hydrogen product, and therefore FDGF, is strongly influenced by metals contamination. With Altrium, the FDGF has been maintained through the full range of typical metals levels (see **Figure 2**). This means reliable operation of a wet gas compressor that has not been impacted by changes in dry gas yields.

In the same way, the fluidised coke factor (FCF) provides a measure of the coke of the equilibrium catalyst adjusted for conversion (see **Figure 3**). In this case, the performance has been maintained constant over a broad range of metals levels, normalised to nickel equivalent. This trend is particularly important to deliver a stable regenerator temperature and delta coke during the operation whilst improved conversion is achieved.

FCC operating conditions during the trial

The regenerator temperature is influenced by many factors including operating conditions, catalyst activity, feed qualities, and more. **Figure 4** shows that similar regenerator temperatures were maintained with the new catalyst while processing feeds in the typical Conradson carbon residue (CCR) range.

The reported Ecat activity, known as FACT (fluidised activity test), is the weight percent conver-

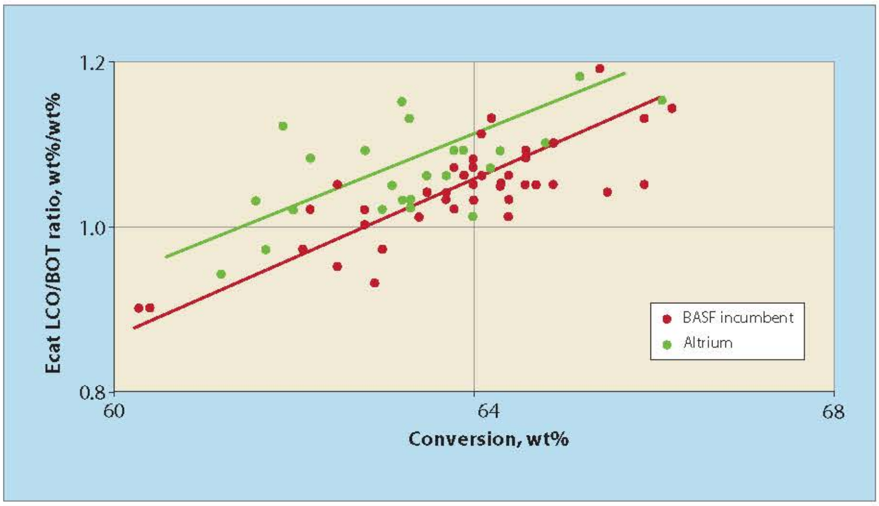

Figure 6 Comparison of Ecat LCO/BOT vs conversion (ACE data)

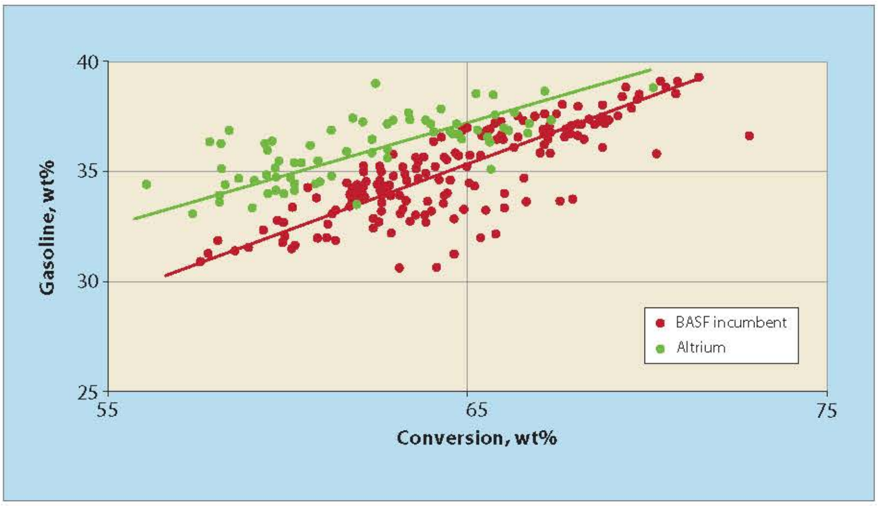

Figure 7 Comparison of gasoline yields vs conversion in the FCC unit

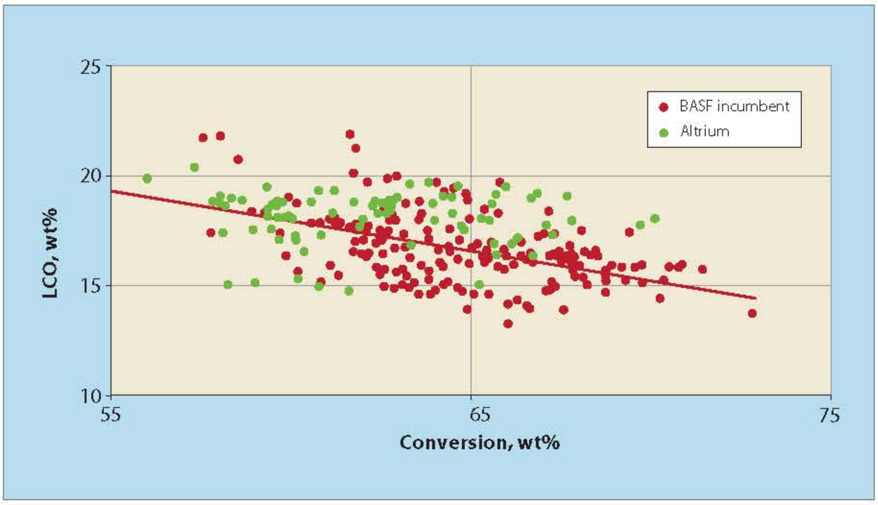

Figure 8 Comparison of LCO yields vs conversion in the FCC unit

sion obtained for a catalyst sample in an ACE unit run with a standard feedstock. It has been constant at the specific catalyst addition rates range used for the operation (see **Figure 5**). Since in-unit conversion is a function of FCC process conditions, feedstock properties, and catalyst properties, FACT activity provides a separate evaluation of the catalyst's contribution to unit conversion. With Altrium, the Ecat activity of the inventory was stable within the typical range of specific catalyst addition rates used at Bayernoil.

FCC unit performance

With Altrium, the light cycle oil to bottoms ratio (LCO/BOT) improved (see the Ecat comparison data (ACE) in **Figure 6**). This improved performance led to increased conversion to valuable products. This has been achieved thanks to the conversion of big molecules. With the new catalyst, the highly dispersed zeolite crystals on the surface of the stable, proprietary matrix provide access for feed cracking. The feed then cracks on active material, rather than on an amorphous matrix, thereby improving selectivity and reducing formation of coke. At the same time, over-cracking is minimised due to a reduction of secondary diffusion of cracked products to the zeolite residing internally. The net result is high bottoms conversion with low coke, and higher yields of valuable liquid products during the operation.

The contribution of the new catalyst to product yields can be seen in **Figures 7** and **8**. Overall, Altrium contributed to improved bottoms upgrading, resulting in less slurry (reduced by approximately 2.5-3.0 wt%, see **Figure 9**), and more valuable products, gasoline, and LCO.

Improvement in profitability

The economic performance delivered by Altrium was estimated based on the normalised yields

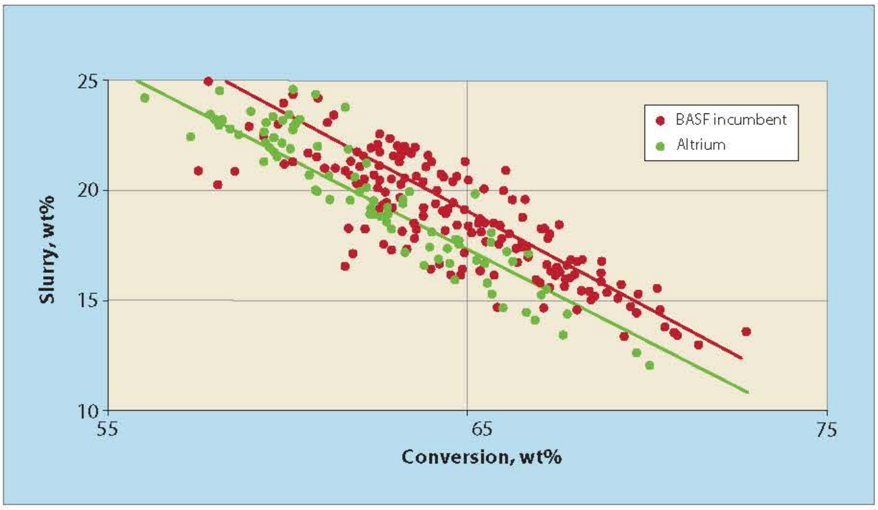

Figure 9 Comparison of slurry yields vs conversion in the FCC unit

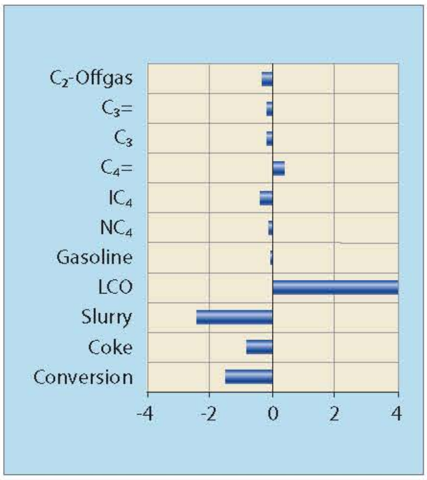

Figure 10 Comparison of performance based on normalised yields

shown in **Figure 10**. The normalised values show that gasoline yields were preserved while coke and slurry yields were reduced. The conversion was calculated as:

100 – light cycle oil (LCO wt%) – Bottoms (BOT wt%)

Thus the conversion obtained decreased in favour of more valuable LCO yields.

Under these conditions and using standard refinery product prices, an improvement in profitability of $0.50-0.60/bbl was achieved. Nevertheless, during actual operation the product slate was further optimised to take advantage of market conditions.

Conclusion

A combination of the latest BASF matrix technologies in the new Altrium FCC catalyst demonstrated superior performance and delivered additional benefits to Bayernoil Neustadt's FCC unit operation. While maintaining reliable and stable operation, the refiner increased bottoms upgrading of residual feeds into more valuable products.

Strong collaboration between Bayernoil Neustadt and BASF Refinery Catalysts enabled a better understanding of the refiner's needs, enabling BASF to deliver a customised solution and to secure successful performance in the unit.

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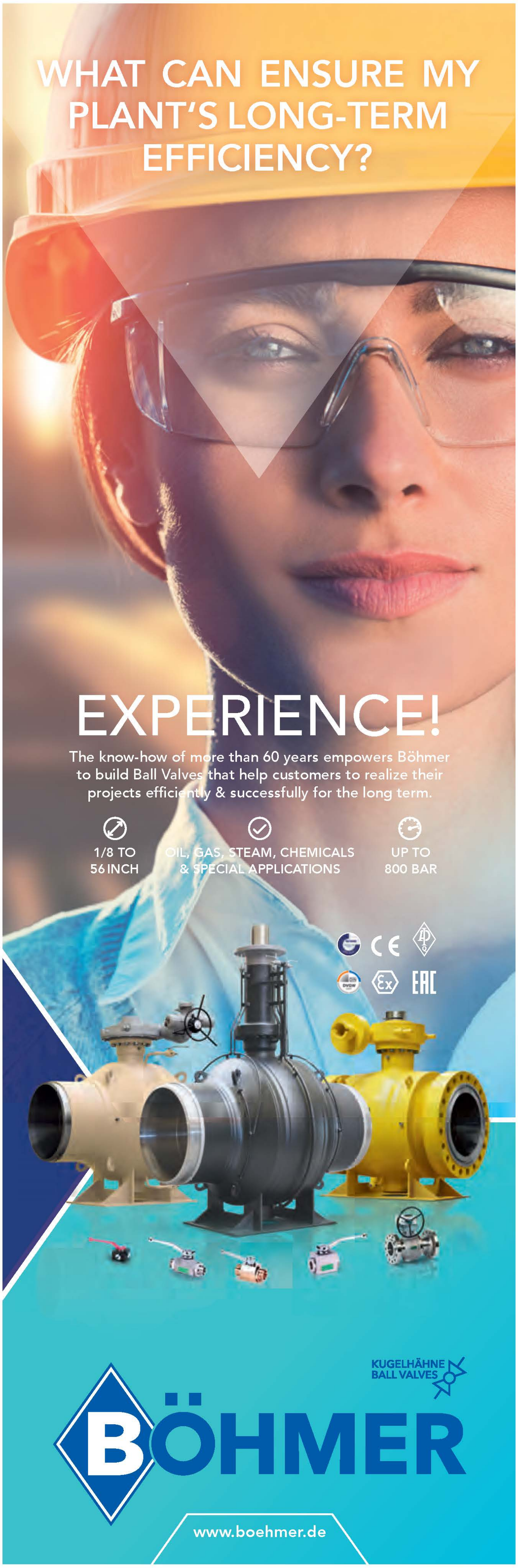

Halide corrosion in hydroprocessing

Changing process conditions in hydroprocessing affect the risk of halide corrosion, but proposed process design and operational solutions can mitigate the risk

BEN LEVITON, HARRY Z HA and MORGAN RODWELL *Fluor Canada*
CATHLEEN SHARGAY *Fluor Enterprises*

Opportunity crudes, changes in upstream production methods, changes in crude slate, and advances in catalyst technology can contribute to an increased risk of halide corrosion in the reactor effluent systems of a hydroprocessing unit wherever there is a risk of liquid water being present. The primary halide corrosion concern is with ammonium chloride (NH_4Cl) salts, and the plant location with these concerns includes both upstream and downstream of the water injection point upstream of the reactor effluent air cooler (REAC). A brief description of the corrosion mechanisms and a survey showing an increase in the instances of this corrosion are discussed. A simulation study is presented to demonstrate the relationship between changing conditions and the risk of halide corrosion, and a review of the possible process design and operational solutions to mitigate these risks are presented.

Although the global refining market will be challenged in the future as more and more jurisdictions promote replacing fossil fuel powered vehicles with alternative energy sources (primarily electric batteries), the demand for diesel and jet fuel remains strong in the near decades.[1] At the same time, stricter product specifications have been implemented due to global environmental concerns. Currently, many areas require 10 ppm sulphur content limits both for gasoline and diesel products and inclusion of bio-sourced materials. Hydroprocessing technology plays an important role in meeting market demand and environmental requirements. These units also tend to be important for refinery profitability as they convert low value streams like vacuum gasoil (VGO), coker gasoil (CGO), and light cycle oil (LCO) into high value fuel products.

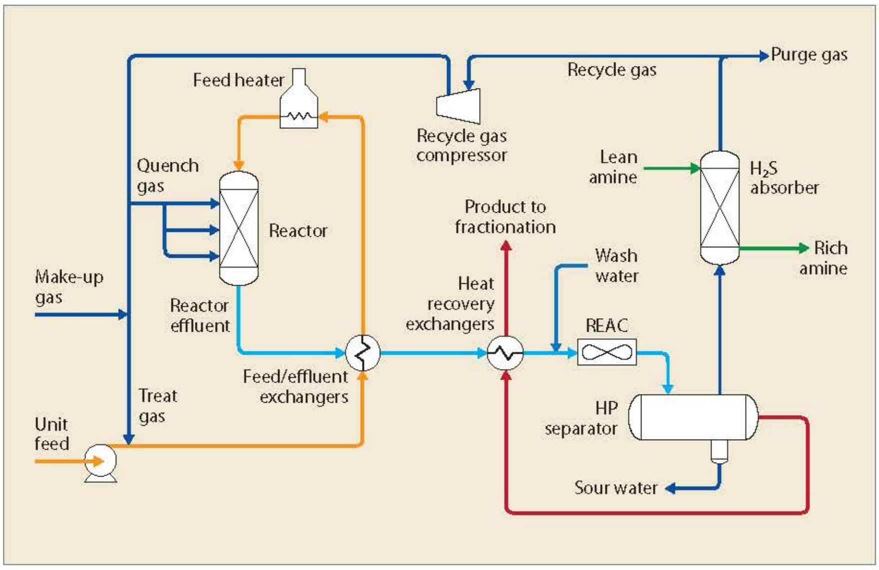

Figure 1 Generic distillate hydroprocessing unit flowsheet

In order to maximise profit, refiners look to a number of strategies, such as:
- Buying lower cost opportunity crudes
- Extending run lengths between catalyst changes and turnarounds through the use of improved catalyst offerings
- Increasing the energy efficiency of units
- Increasing throughput to better utilise the capital asset

Each of these measures, especially in combination, can increase the risk of halide corrosion in a hydroprocessing unit. This article investigates halide corrosion issues in a generic hydroprocessing unit using high activity catalysts; addresses potential issues and challenges associated with NH_4Cl corrosion; and proposes mitigations for the problems.

Ammonium salt corrosion

Corrosion in the REAC area of hydroprocessing units is considered one of the most complex and high-consequence reliability issues in refineries, especially since there are multiple possible corrodents. Hence, it is the topic of an API Recommended Practice, RP 932-B, which is an excellent resource on mechanisms and solutions.[2] This article expands on the process design impacts of implementing these solutions.

Figure 1 shows a typical hydroprocessing unit flowsheet. The reactor effluent streams are primarily hydrocarbons and hydrogen, but also contain corrodents of H_2O, H_2S, NH_3, and possible HCl (and, more rarely, HF or HBr). Wash water is injected to help in avoiding salt deposition (which can cause both plugging and corrosion if the deposits are wet), and to reduce the salt concentration in aqueous streams.

Corrosion due to ammonium bisulphide (NH_4HS) is a major

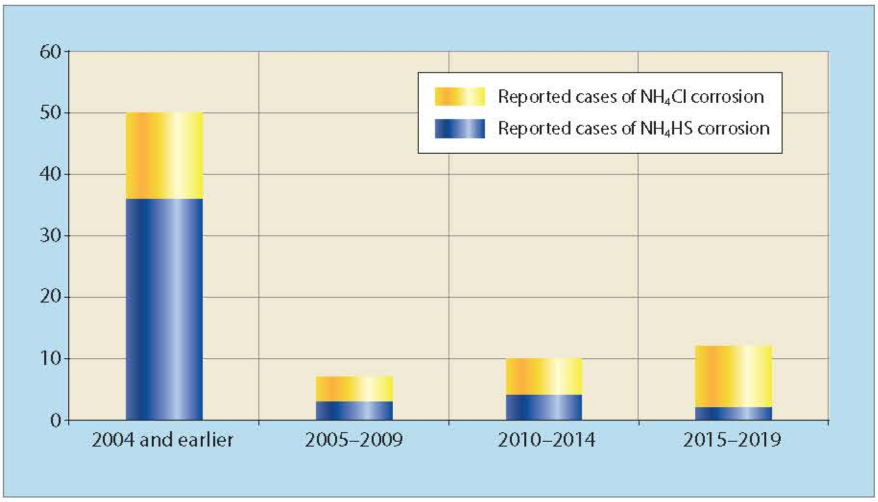

Figure 2 Reported REAC failures in hydroprocessing units

concern, but with proper water injection or use of appropriate materials, this corrosion can be avoided. The predicted corrosion rates from NH_4HS in the aqueous phase are primarily a function of the NH_4HS concentration, flow regime, wall shear stress, and H_2S partial pressure. A software tool called Predict-SW is widely used to predict corrosion rates and, when carbon steel is deemed to be at risk of high NH_4HS corrosion rates, a corrosion resistant alloy such as Alloy 825 is used for the piping and equipment.

The mechanism of corrosion due to ammonium halide salts, such as NH_4Cl, is somewhat different. These salts are generally at such low concentrations in the aqueous phase they do not cause corrosion in the areas seeing bulk liquid water. However, there are numerous cases of the reactor effluent having an NH_4Cl salt deposition temperature higher than both the water dew point and the temperature at the wash water injection point. The salts which deposit are not corrosive as long as they are 'dry', but they are hygroscopic and can absorb moisture (without dissolving), and then form an extremely corrosive, hot HCl environment under the deposits. These 'wet' deposits have corroded carbon steel, stainless steels, and nickel based alloys very rapidly, so there is no materials solution for this type of corrosion. There are papers which help in predicting whether process conditions will lead to wet or dry deposits,[3,4,5] however it can be difficult to stay consistently at dry conditions. The risk of changing conditions giving wet deposits and severe corrosion which can cause leaks over short term exposures may be considered too high for many operators. The safest path is to strive to avoid deposition of NH_4Cl and other halide salts.

This article focuses on the presence of chlorine atoms as this is the most common halide species found in hydroprocessing units. However, a mention should be made of fluoride and bromide. As shown in API RP 932-B,[2] the salt deposition curves for NH_4F and NH4Br lie above and below the NH_4Cl curve, respectively.

Incidence of ammonium salt corrosion

In recent years, refiners have seen an increase in the frequency of NH_4Cl induced corrosion failures in hydroprocessing units. A recent survey[6] provided the data that shows how reported cases of NH_4Cl corrosion in REAC systems now outstrip the number of reported cases of NH_4HS corrosion, which is a change from the pre-2005 period (see **Figure 2**).

Chlorides in feedstocks

One effective approach to control chloride corrosion in the REAC system may be to identify and remove sources of chlorides entering the hydroprocessing unit. Chloride corrosion has been reported in REAC systems with as little as 2 ppm chlorides identified in the feed.[7] The chlorides in hydroprocessing units mainly enter via two routes: feedstocks and/or make-up hydrogen from a catalytic reformer.[2,4,8] Crude oil typically contains a certain amount of inorganic salts (30-1000 wtppm). Most of these salts can be removed by desalting in the preheat train of the crude distillation unit. The slipped salts, in the form of $MgCl_2$, $CaCl_2$, and NaCl, partially hydrolyse to HCl in heaters and columns, creating overhead corrosion issues in crude units. The residual inorganic chlorides usually end up in the resids, while organic chlorides typically end up in sidecuts, or naphtha. These streams often make up the hydroprocessing unit feed; hence, chloride contaminants can cause corrosion in the REAC system.

NACE has classified chlorides in crudes as "extractable chlorides" and "non-extractable chlorides".[7] Extractable chlorides refers to the inorganic chlorides which are dissolved in produced/connate water and can be removed by the desalter in the crude unit. Non-extractable chlorides refers to those which are not soluble in the aqueous phase and typically cannot be removed by desalters. Non-extractable chlorides are typically organic chlorides.

Organic chlorides are typically not present in crude in nature.[8] They often make their way into crude oil by contamination during exploration, production, or transportation processes. For example, organic chloride or fluoride solvents may be used for equipment cleaning in production fields. Chloride-containing compounds are also used in naphtha reforming and isomerisation units to maintain catalyst activity. The recovered oil and slops from these units may also contain a substantial amount of chloride solvents and contaminate the refinery feed when being reprocessed.

Make-up hydrogen can be a source of chlorides when it comes from catalytic reforming units. These units convert naphtha to high octane gasoline and utilise chlorinated catalysts. The hydrogen produced in the reforming process is inevitably going to contain trace amounts (1-3 volppm) of chlorides. The chloride level in the hydrogen stream is usually

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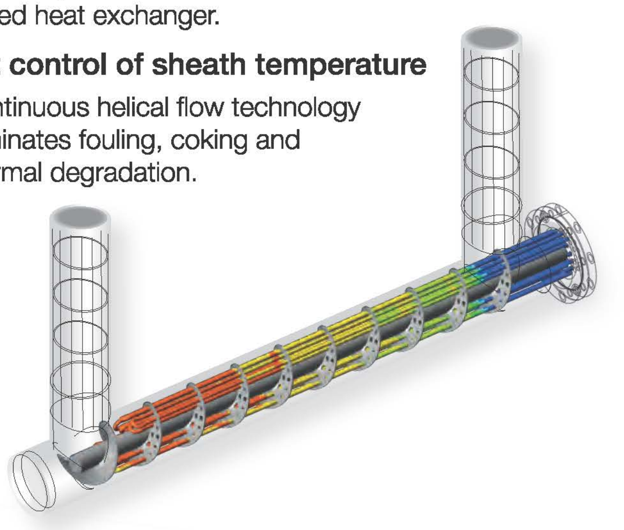

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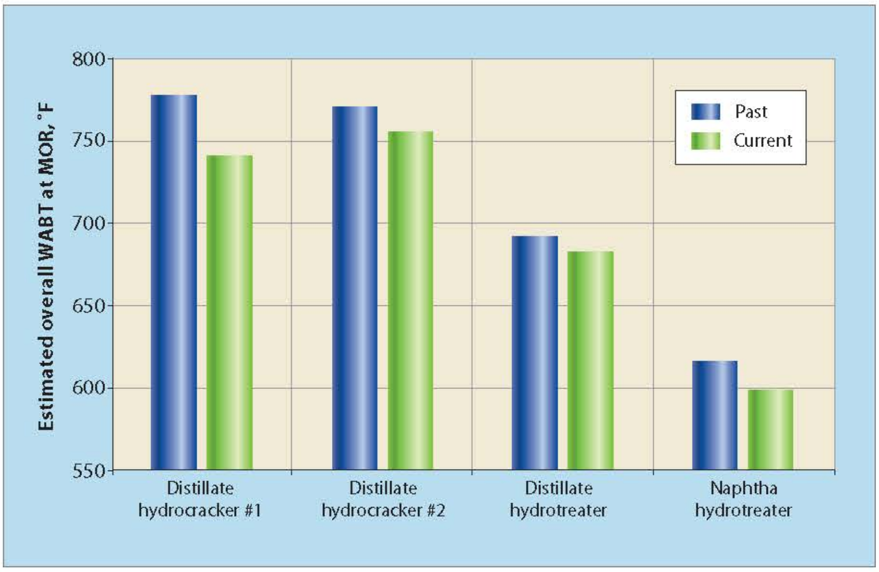

Figure 3 WABT changes with new hydroprocessing catalysts in existing units

Hypothetical catalyst parameters

	Start of run		End of run	
	Original	Updated	Original	Updated
Catalyst yields (wt% of feed)				
H_2O	0.3%	0.3%	0.3%	0.3%
NH_3	0.3%	0.3%	0.3%	0.3%
H_2S	2.7%	2.7%	2.7%	2.7%
C_1	0.3%	0.2%	0.4%	0.2%
C_2	0.4%	0.3%	0.5%	0.3%
C_3	1.0%	0.8%	1.3%	0.9%
C_4	2.1%	2.1%	2.6%	2.3%
C_5	2.2%	2.6%	2.6%	2.8%
C_6	3.3%	3.9%	3.8%	4.2%
C_7-350°F	17.9%	25.2%	19.0%	26.8%
350-650°F	45.9%	41.2%	43.2%	38.9%
650-850°F	15.3%	15.6%	14.9%	15.6%
850°F – FBP	11.5%	7.8%	11.5%	7.7%
Hydrogen consumption	3.0 %	3.0 %	3.0 %	3.0 %
Operating conditions				
Inlet temperature, °F	700	660	770	770
Outlet temperature, °F	775	715	820	795
WABT, °F	750	697	803	787
Heat of reaction, Btu/b	85 200	85 200	88 800	88 800

Table 1

controlled by sending it through a chloride absorber. However, when the chloride adsorbent becomes saturated, chloride slip occurs and high chloride content will be present in make-up hydrogen from the reformer.

A common approach for estimating chloride level in the hydroprocessing unit is to measure the chloride content in the cold separator sour water and wash water. The difference between the two is the total chloride level entering the unit (including chlorides in both fresh feed and make-up hydrogen). When chloride content in make-up hydrogen is also measured, the chloride level in the feed can be determined.

The chloride content in the feed can also be directly tested in the lab. For example, ASTM D32309 is a standard test method for salts in crude oil by electrometric method. NACE publications 2141510 and 341057 give details on test methods for organic chlorides. ASTM D492911 and ASTM D815012 also determine the organic chlorides (>1 μg/g) in crude oil using various methods; however, they assume all organic chlorides stay in the naphtha fraction which may not always be the case.

Other methods of avoiding NH_4Cl corrosion in units containing chlorides are discussed later in the article.

Impact of changes in operating conditions

Changes in operating conditions over time may contribute to the halide corrosion risk, and may do so in a gradual manner or with separate changes compounding each other such that the normal management of change process may not detect the risk. These changes may be the result of catalyst improvements implemented with the goal of increasing throughput, improving yield/selectivity (for gasoline or diesel), extending run lengths, or processing new crude slates.[13,14,15]

The operating conditions for new catalysts may differ from the original design. A key advance is that weighted average bed temperatures (WABT) are typically reduced due to the high activities of the new catalysts compared with prior generations of catalysts (see **Figure 3**).

Lower WABT values will prolong catalyst run lengths for a given unit feed rate. However, a lower WABT may also introduce the challenge of balancing higher furnace duty requirements against lower reactor effluent temperatures (which may result in increased halide corrosion risk), as illustrated in the next section.

Simulation study

A process simulation was developed for a generic distillate hydroprocessing unit to demonstrate some of the unforeseen challenges that may arise from catalyst improvements. While our model does not represent a specific site, its key parameters (catalyst yields, bed temperatures, and so on) are based on data collected from a number of operating plants. The generic unit configuration shown in **Figure 1** is used for this review. There are many possible variations, such as preheating recycle gas through a separate heater, or adding a hot, high pressure separator upstream of the REAC, but the design shown in **Figure 1** is quite common, especially for older units.

Table 1 compares key parameters from the hypothetical unit's original design against an updated catalyst with the same feedstock composition and unit throughput. The new catalyst is more active, allowing it to achieve higher conversion at lower WABT. The lower WABT limits the extent of undesirable thermal cracking reactions and thus the new catalyst achieves a high degree of selectivity.

By operating the reactor at lower bed temperatures, operators can expect to achieve a longer run life and improved yields with the new catalyst. Alternatively, they might choose to exploit the catalyst's increased activity to operate the unit at higher throughput. A third option is for the refiner to send a more challenging feedstock to the unit without increasing throughput. These competing advantages are illustrated in **Figure 4**.

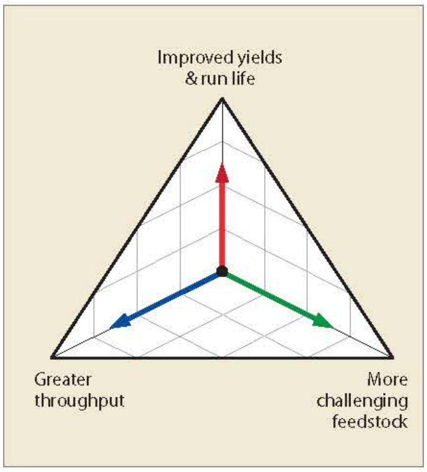

Figure 4 Potential benefits of catalyst improvements

Operators might take advantage of catalyst advances to realise any combination of the benefits shown in **Figure 4**, depending on refinery economics. Our generic process simulation was used to demonstrate the impact on the unit of each of three cases with respect to NH_4Cl corrosion. The results are summarised in the following sections.

Scenario 1: improved yield and run life and constant throughput and feedstock blend

The parameters in **Table 1** were used to complete a 'check rate' of the unit with the new yields and operating conditions, considering the feedstock composition and unit throughput are held constant. **Figure 5** compares the start of run simulation results for both the original operating conditions and updated conditions with the improved catalyst.

Simulation of the updated operating conditions makes it immediately clear that reduced bed temperatures do not translate to improvements in energy efficiency (see **Table 2** and **Figure 5**). In fact, the new catalyst conditions require either an increase in heater duty or a reduction in effluent temperature. This can be attributed to the following effects:

1. The lower reactor outlet temperature limits the amount of heat that can be recovered in the feed/effluent exchangers without reducing the effluent temperature downstream. Even if there is excess surface area available in these exchangers in the updated operating mode, the operator must shift duty (if bypass control is available) to the fired heater to avoid cooling the reactor effluent below the NH_4Cl deposition temperature.
2. The new catalyst may require more treat and/or quench gas, incurring more preheat duty. This occurs when the new catalyst requires a similar inlet temperature to the original design for catalyst activation, but a lower outlet temperature to achieve the reduced WABT. Since the heat of reaction has not been reduced based on the severity of reactions required and the inlet temperature is the same, the lower outlet temperature can only be achieved by circulating more hydrogen. In some instances, a shift of treat gas to quench gas is enough to achieve this, but in other cases it has not been.

For the purposes of this exercise, it is assumed that the available heater duty is limited to the original end of run required duty (26 400 Btu/b in this case), while the feed/effluent exchangers have excess area available due to their original fouling specification.

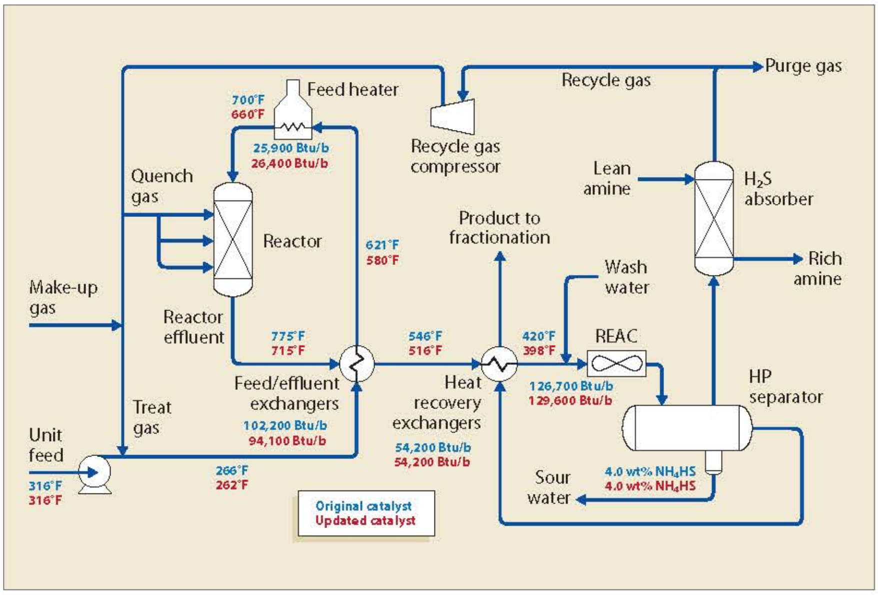

Figure 5 Scenario 1 simulation results

Scenario 1 simulation results

	Start of run		End of run	
	Original	Updated	Original	Updated
Heat exchanger duties				
Feed heater, Btu/b	25 900	26 400	26 400	26 400
Feed/effluent exchangers, Btu/b	102 200	94 100	128 600	136 800
Heat recovery exchangers, Btu/b	54 200	54 200	54 200	54 200
Temperature upstream of wash water, °F	420	398	420	398
Treat gas, scf/b	4000	4600	4200	4900
Quench gas, scf/b	6270	7410	6880	7840

Table 2


Repeat for each bolt in a criss-cross pattern
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Ultimately, the result is an effluent from the heat recovery exchangers that is colder by about 22°F. These exchangers cannot be bypassed further as they are relied upon to supply heat to the downstream stripper.

For this example, a 5 wtppm feed chloride content (23 wtppm measured chloride in the HPS sour water) translates to an NH_4Cl deposition temperature of approximately 408°F in the original operating mode and 401°F in the updated operating mode (due to the increase in recycle gas rates). Therefore, the installation of improved catalyst has moved operation from 12°F above to 3°F below the estimated chloride deposition temperature. The resulting NH_4Cl corrosion may lead to corrosion that – if not detected – could result in loss of containment.

Scenario 2: increased unit throughput

Scenario 2 considers that the refinery has chosen to increase throughput by 20%, which the upgraded catalyst can accommodate due to its increased activity. In this case, the reactor yields and conditions are assumed to match the original plant design. Results are listed in **Table 3**. SOR conditions before and after catalyst improvement are shown in **Figure 6**.

Scenario 2 simulation results

	Start of run		End of run	
	Original	Updated	Original	Updated
Heat exchanger duties				
Feed heater, Btu/b	25 900	26 400	26 400	26 400
Feed/effluent exchangers, Btu/b	102 200	127 200	128 600	159 800
Heat recovery exchangers, Btu/b	54 200	65 000	54 200	65 000
Temperature upstream of wash water, °F	420	411	420	409
Treat gas, scf/b	4000	4000	4200	4200
Quench gas, scf/b	6270	6270	6880	6880

Table 3

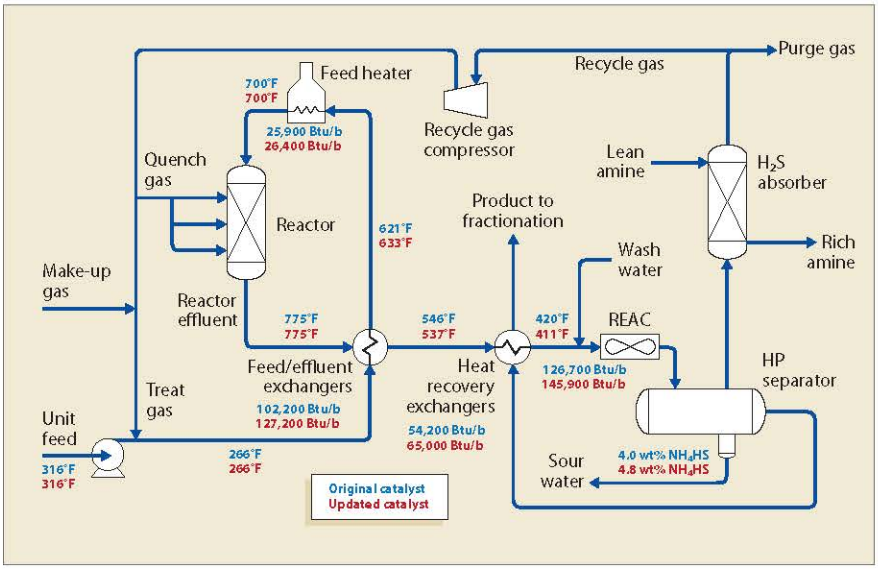

Figure 6 Scenario 2 simulation results (start of run)

In this case, the temperature upstream of wash water injection has been reduced by about 9°F as a result of increasing the unit throughput, despite no changes to the reactor bed temperatures. This change would reduce the margin between operating temperature and deposition temperature from 12°F to 3°F. This is attributed to heater limitations which force a higher duty across the feed/effluent heat exchangers at higher throughput.

Additionally, the concentration of NH_4HS at the REAC outlet has increased from 4 wt% to 4.8 wt%, assuming a constant wash water injection rate, reflecting the 20% increase in total nitrogen entering the unit.

Scenario 3: change to feedstock composition

A third way in which operators may benefit from catalyst improvements is to process more 'difficult' feedstocks in the hydroprocessing unit. These feeds, often characterised as bottom-of-the-barrel or refractory products like LCO from the FCC (fluid catalytic cracker), have potentially higher contents of heavy metals (Ni and V), sulphur, nitrogen, oxygen, and aromatics. New feed streams could also introduce more chloride to the unit depending on the sources of organic and inorganic chloride within the refinery.

The impact of feedstock compositional changes is assessed with the same baseline simulation assuming 5 wtppm chloride content in the feed.

Setting aside any potential increase in chloride, consider a 50% increase in feed nitrogen associated with processing a higher fraction of LCO in the feed, or just a higher-nitrogen crude oil charge. This change would increase the NH_4Cl deposition temperature by roughly 8°F from 408°F to 416°F, reducing the margin between operating temperature and deposition temperature from 12°F to 4°F. This would also increase the concentration of NH_4HS at the REAC outlet from 4 wt% to 6 wt%, assuming a constant wash water injection rate, which could dramatically increase corrosion rates due to that mechanism. A separate study should be done on whether the water rate should and/or could be increased.

Simulation study conclusions

The process simulation results presented in this section demonstrate that three common benefits of catalyst advancements – run life extension, throughput increase, and feedstock changes – may inadvertently contribute to an incremental increase in the risk of halide corrosion damage. This effect may be one factor contributing to the observed increase in halide corrosion incidents discussed earlier.

Mitigating ammonium chloride corrosion

When installing new catalysts, increasing unit throughput, or

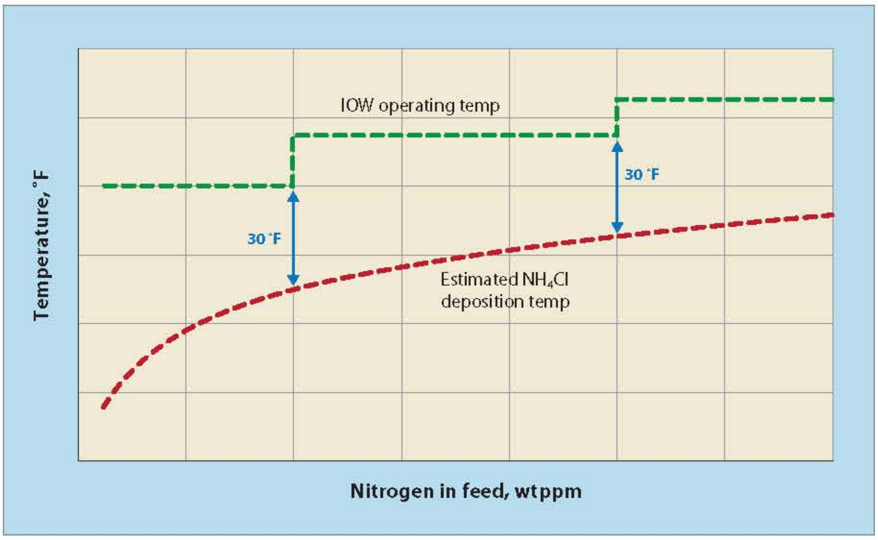

Figure 7 Integrity operating window for reactor effluent system

changing feedstocks, the first step in managing potential impacts should be to commission a new heat and material balance for the unit. A revised heat and material balance representing the new mode of operation can be used to:

- Predict the NH_4Cl deposition temperature in the reactor effluent train based on the guidelines in API RP 932-B, 3rd edition.[2]
- Determine if the desired reactor effluent temperature upstream of wash water injection can be achieved (the minimum temperature will be above the NH_4Cl deposition temperature), given the heat integration limitations of the existing equipment. This typically means maximising duty in the existing feed heater at EOR conditions to allow the feed/effluent exchangers to be bypassed as much as possible.
- Predict the NH_4HS concentration at the REAC inlet and outlet, and review the predicted corrosion rates using Predict-SW or similar tools.
- Check rate existing equipment for the new conditions to identify other bottlenecks and potential scope. This may include heat exchanger or recycle compressor limitations.

Preventing NH_4Cl deposition in an existing unit after the installation of new catalysts can be challenging. Several strategies that may be considered include:

Integrity operating window

API RP 584[16] presents a practice for setting integrity operating windows (IOW) for a process unit. A key aspect of this is to consider the possible range of operations and uncertainties in the available data. IOWs can be used to establish the process parameters for avoiding corrosion or other degradation mechanisms based on the design and materials of construction. It is typically recommended that a multi-disciplinary team from engineering (process, mechanical, and materials), inspection/reliability, and operations be involved in setting these thresholds.

For NH_4Cl deposition, one possible avoidance strategy is to use a 30°F margin between the minimum operating temperature and the predicted salt deposition temperature at points upstream of the wash water injection point. The logic of the 30°F margin is that an uncertainty analysis of thermodynamic predictions indicates there is 7-12°F uncertainty in the predicted values, which leaves 18-23°F for variability in operating conditions or measurement error. For units with a feed nitrogen content that is stable on a day-to-day basis, the IOW can be expressed as a function of feed nitrogen (see **Figure 7**). To avoid having to recalculate the IOW temperatures too frequently, a stepped model can be used to cover ranges of nitrogen in the feed safely.

Attention must be paid to potential cold spots in the piping that may be subject to NH_4Cl deposition and severe corrosion. Some units have a compressor spillback/anti-surge line that injects cold gas upstream of the REAC and can cause a significant local temperature drop when that valve is open.

Debottlenecking to achieve IOW targets

Implementation of the IOW described above can be challenging given the heat integration limitations of an existing plant. For Scenarios 1–3, the reactor effluent temperature cannot easily be raised because (a) the feed heater is already operating at maximum duty and (b) the duty in the heat recovery exchangers cannot be reduced without impacting the downstream H_2S stripper/fractionator.

A basic debottlenecking of these limitations might involve revamping the feed heater or the introduction of a new heating medium to the system such as an LP separator liquid preheater (see **Figure 8**). These

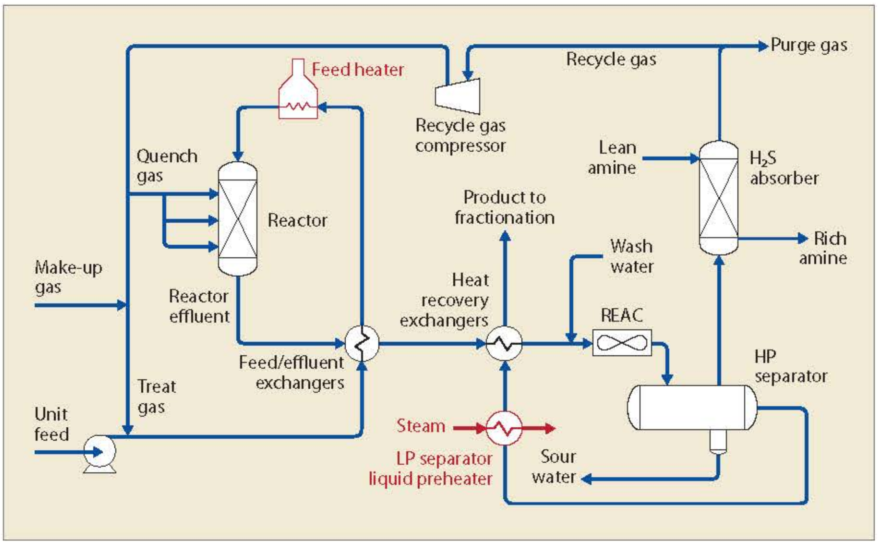

Figure 8 Debottlenecking heat integration limitations

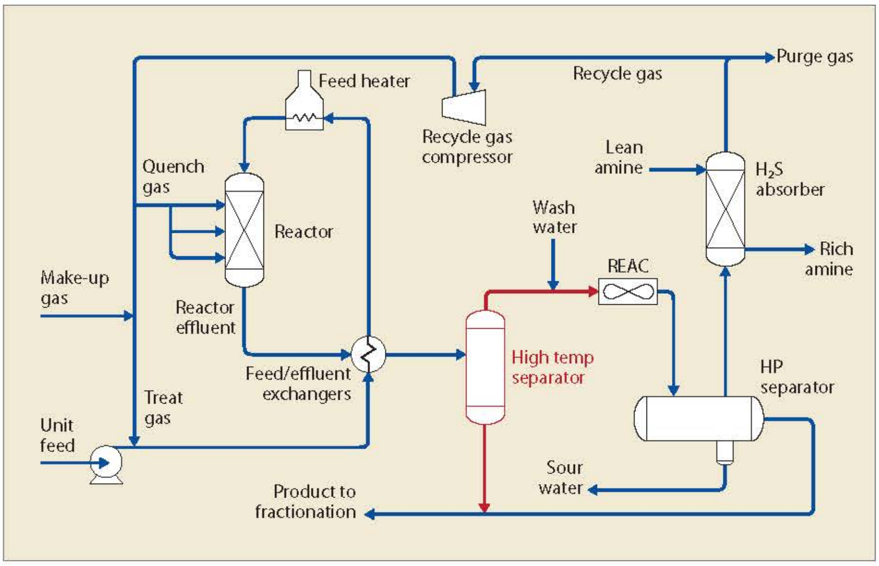

Figure 9 Unit with added high temperature separator

options increase the required REAC cooling duty as well as the required wash water flow rate.

Another alternative could be the installation of a high temperature separator (see **Figure 9**), which avoids cooling most of the effluent, negating the need for preheat of the LP separator liquid. This option is favourable for reducing operating cost, wash water rates, and REAC duty requirements; however, it may result in increased hydrogen losses to the H_2S stripper overhead via the high temperature separator liquids (especially for very high pressure units) which may be a challenge when revamping existing units.

Wash water injection

If the desired operating temperatures to avoid NH_4Cl deposition cannot be achieved economically, a second wash water injection point may be added upstream at a higher temperature location in the reactor effluent train (see **Figure 10**). High nitrogen and chloride levels may require this to be at a significantly higher temperature location, requiring considerably higher volumes of wash water to ensure at least 25% remains liquid upon injection according to API RP 932-B guidelines.[2] The addition of wash water will drop the temperature and reduce the heat available to be recovered in the downstream exchanger(s) so it is not always a feasible solution. There may also be problems with water maldistribution in the shell-and-tube heat exchanger.

Even with the normal injection point, which is upstream of the REAC, care must be taken to design an effective wash water injection system for mitigation of NH_4Cl corrosion. Three mass and heat transfer mechanisms occur when wash water is injected into the reactor effluent stream:

1. Mass transfer of HCl gas from the reactor effluent vapour into the aqueous wash water
2. Heat transfer from the hot effluent to the cold wash water
3. Mass transfer (evaporation) of wash water, leading to saturation of the effluent vapour with water, along with 25% of the injected water remaining unvaporised.

All three of the above processes are rated-limited, meaning equilibrium is not reached instantaneously upon mixing. The use of a static mixer to enhance contact between the gas and liquid phases prior to cooling the effluent is strongly recommended where NH_4Cl corrosion is a concern.

Recommendations

A summary of recommendations for assessing the operation of, or making any modifications to, a hydroprocessing unit, whether it be a catalyst change, feedstock change, capacity change, or equipment or control modification, includes:

1. When installing modified or upgraded catalysts in an existing hydroprocessing unit, commission a revised heat and material balance to assess the widespread impact on the unit.
2. Establish IOW to ensure that the reactor effluent temperature exceeds the NH_4Cl (or NH_4Br or NH_4F) deposition temperature by a reasonable margin upstream of wash water injection. Special attention must be paid to potential cold spots in the piping that may be subject to NH_4Cl deposition and severe corrosion.
3. Consider modifications to existing wash water injection systems to achieve adequate mixing of wash water and effluent in all hydroprocessing units where halides may be present. The use of a static mixer should be considered.
4. Measure and track chloride sources throughout the refinery to identify and mitigate sources of organic and inorganic chlorides.

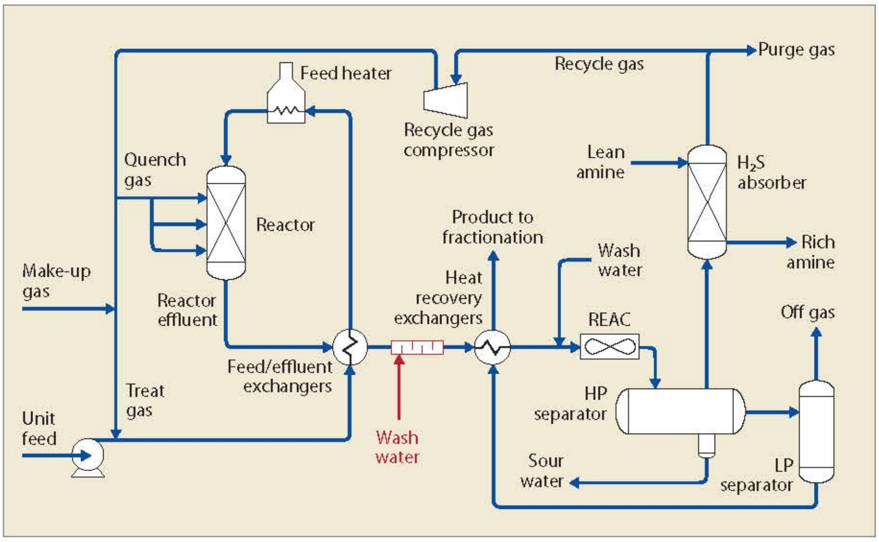

Figure 10 Alternative location for wash water injection

5. Measure and determine sources of bromides and fluorides and try to avoid using feedstocks containing these materials, or introducing them through any other routes.

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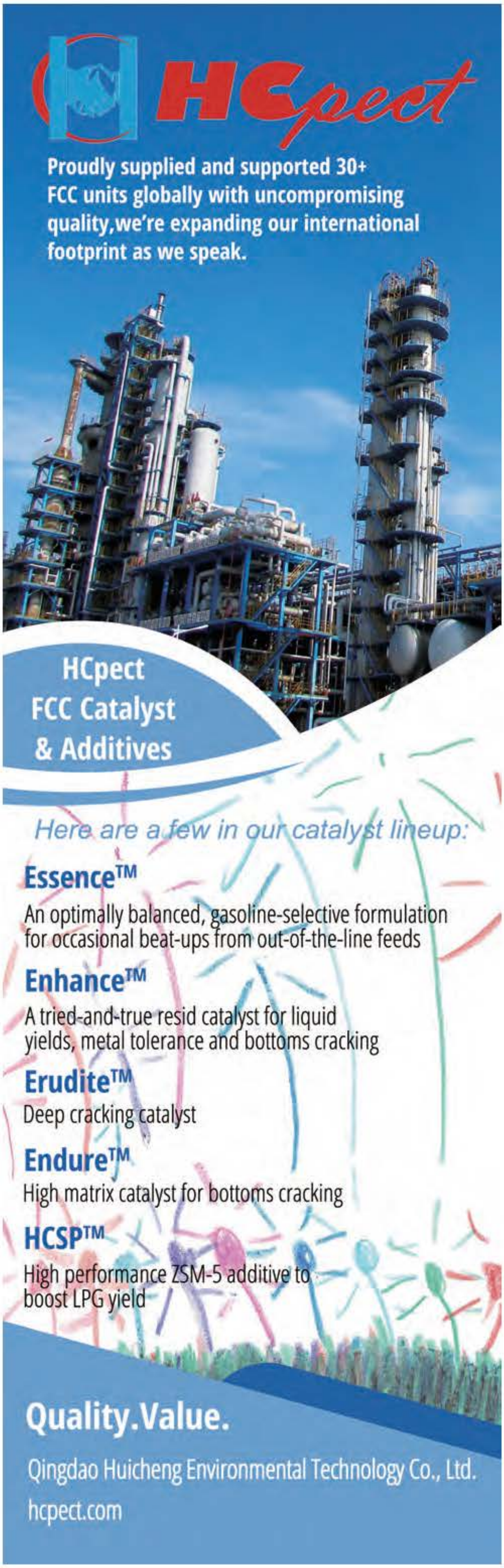

Mitigating corrosion with a digital twin

Data-driven engineering helps engineers to identify ways to improve predictions of corrosion

RODOLFO TELLEZ-SCHMILL *KBC (A Yokogawa Company)*
EZEQUIEL VICENT *OLI Systems, Inc.*

Processing plants depend on assorted metallic equipment and pipelines. However, like most things, metal does not last forever. It eventually dwindles through corrosion due to water, oxygen, extreme temperature changes, and acidity. It is necessary to take measures to manage corrosion or accept that whatever relies on the metal structure will eventually fail.

The total economic cost of corrosion is massive. NACE estimates the global cost to be 3.4% of global gross domestic product, or \$2.5 trillion.[1] Approximately 50% of this comprises the direct cost of corrosion – materials and equipment needing repair, maintenance, and replacement, and the services to deal with them. The remainder includes the effects of corrosion, such as environmental damage, waste of resources, loss of production, or personal injury.

Corrosion in oil refining

A typical oil refinery has several process vessels, fractionation towers, miles of horizontal and vertical pipelines, and a large number of shell/tube exchangers and air coolers. Many of these pipelines are inaccessible due to their height or coverings such as insulation, cement, soil, mud, or water. This makes corrosion a major consideration for safe, reliable, and profitable operations.

Controlling the corrosion of oil refining equipment and pipeline systems is complex. Key areas for anti-corrosion measures are composition and phase state, viscosity, flow regime, temperature, pressure, and proper equipment selection to mitigate risk.

In general, engineers can minimise corrosion if they limit variations in operating conditions. However, the industry's need to frequently change the crude oil or raw materials it processes makes this difficult, if not impossible. Changes in composition, processing, and flow rate through process equipment and piping lead to different distributions and varying degrees of corrosion.

Implementing a corrosion management plan can reduce operating costs and corrective measures. Proper corrosion control measures can help to improve the performance of many operating units (for instance, reducing atmospheric column operating pressures or increasing distillate yields) and possibly reduce the need for heat exchanger bundle changes. Reducing unexpected shutdowns during a refinery's turnaround schedule would allow the plant to meet and exceed targeted profits.

> **Proper corrosion control measures can help to improve the performance of many operating units and possibly reduce the need for heat exchanger bundle changes**

Embrace the science

KBC and OLI joined forces to create a solution that helps operators manage and mitigate corrosion risk. Combining the Petro-SIM process simulation platform with OLI Alliance Engine electrolyte and water chemistry simulation software creates a digital twin for a broad range of downstream applications to prevent and mitigate corrosion.

Creating a digital twin strengthens a plant's corrosion management plan by giving process and production engineers total stream properties at their fingertips, including pure as well as pseudo-stream components, covering both ionic and non-ionic systems.

Engineers can determine the current state of corrosion, manage chemical additives management, and assist in proper equipment selection. This delivers enhanced model fidelity and engineering efficiency for holistic measurement, prediction, and mitigation of corrosion, scaling, and fouling in aqueous environments.

Petro-SIM's open architecture collects real-time operations data from the site historian. It then delivers virtual representations of hydrocarbon molecule transformation and associated plant operating conditions. The digital twin provides a single source of the truth for what is going on inside the plant at a molecular and asset level.

Distillation units and the preheat train

The presence of acids and chlorides in the atmospheric distillation unit (CDU) and vacuum distillation unit (VDU) overhead systems can cause corrosion. Some crude oil physical properties, such as total acid number (TAN), total sulphur content, water, and chlorides are carefully monitored. If they exceed allowable limits, corrosion can be a problem.

The concept of scaling tendency

Scaling tendency	Result
< 1.0	The solid is under-saturated and is not expected to form
= 1.0	The solid is saturated and is expected to form
> 1.0	The solid is over-saturated and may or may not form

Table 1

With changeable crude diets and throughput rates, corrosion in the CDU and VDU vary over time. This can create overhead corrosion hot spots, changing their severity and location. As increased equipment replacement and repairs become necessary, reliability and availability decrease.

To counter this, chemical injection may be effective. Corrosion inhibitors, neutraliser chemicals, or in some instances wash water are useful in controlling corrosion. However, engineers must avoid over-dosing.

Corrosion inhibitor injections can result in sodium contamination of heavier products from the distillation unit. In addition, excess injection of inhibitor may cause formation of inhibitor-related salts on the overhead section of the column.This can affect downstream units such as the coker and visbreaker. Other mitigation measures might also include material selection, protective coating, and cathodic protection.

Hydrotreating units

The primary objective of hydrotreating processes is to remove sulphur and other impurities, such as nitrogen, oxygen, halides, and trace metals. These impurities may contribute toward regulatory emissions, catalyst deactivation, or product specification limits. These processes can take the form of a naphtha hydrotreater, middle distillate hydrotreater, diesel oil deep desulphurisation (hydrofining), or residue hydrotreating. However, proper functioning of hydrotreating units depends on the unit's feed/effluent exchangers, reactor effluent air cooler (REAC), and associated downstream units. Reactors convert sulphur, chloride, and nitrogen compounds in feedstock to hydrogen sulphide, hydrogen chloride, and ammonia, respectively.

When operating at high pressures and low temperatures, the precipitation of ammonium bisulphide (NH_4HS) and ammonium chloride (NH_4Cl) in the reactor effluent stream occurs. This results in accelerated corrosion processes around the feed/effluent exchangers and REAC welds, leading to loss of primary containment and, potentially, fires. Hence, water injection upstream from the REAC is necessary to avoid NH_4HS and NH_4Cl condensation and formation of crystalline solids, which can corrode the REAC. As a result, the hydrotreater REAC is a corrosion hotspot. Several corrosion-related incidents have occurred across the refining industry involving the rupture of air cooler tubes.

Simulation case studies of corrosion analysis

The following simulation case studies demonstrate how Petro-SIM with the OLI Engine can provide corrosion analyses for a gasoil hydrocracker and a diesel hydrotreater, both high risk units.

Flow rate and wash water quality affect the probability of corrosion in both instances. High flow rates increase shear stress at the internal pipe surface which causes excessive corrosion. Deposition of solid NH_4HS and NH_4Cl in wash water can increase corrosion risk as well.

Our analysis of these two variables in avoiding corrosion are shown in these studies. The predisposition of NH_4HS and NH_4Cl towards precipitation as a solid was calculated and reported as scaling tendency. Scaling is a result of supersaturation of mineral ions in the process fluid. The precipitation of solids occurs due to changes in temperature or solvent liquid evaporation so that the concentration of salts may exceed the saturation level (see **Table 1**).

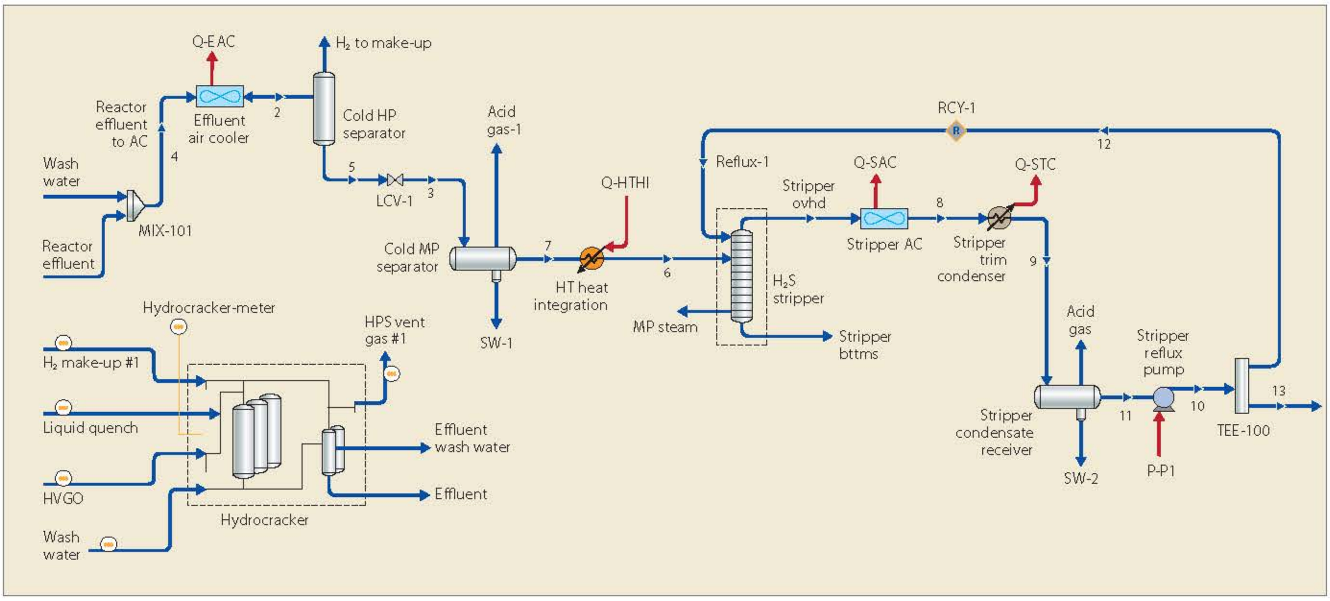

Figure 1 PFD of the gasoil hydrocracker

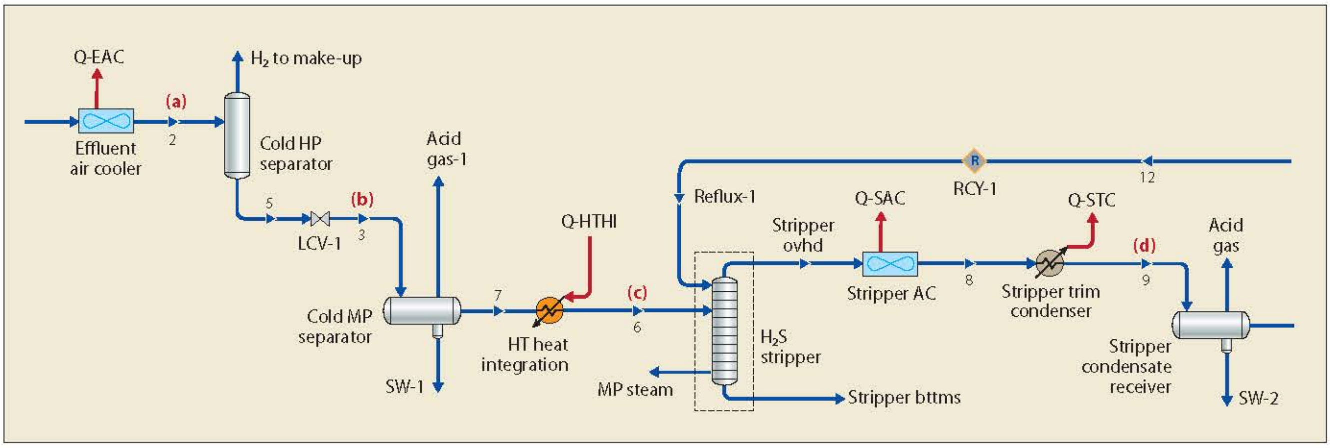

Figure 2 Gasoil hydrocracker streams

Case study 1: gasoil hydrocracker

The hydrocracker has two hydrotreating sections processing light vacuum and heavy coker gasoil. Products from the hydrocracker include light and heavy naphthas, kerosene, diesel, and unconverted oil (see **Figure 1**).

The effluent from the hydrocracker reactor had concentrations of H_2S and ammonia of 3.95 and 0.46 mass%, respectively. A heat exchanger train cooled down the reactor effluent, recovering heat to the reactor feed stream.

From the exchanger train, the reactor effluent emerged at 410°F (210°C) and 2320 psig. This stream mixed with wash water at a flow of 93 t/h prior to reaching the REAC in order to control the precipitation of solid NH_4HS. The wash water contained stripped sour water with a maximum content of H_2S and NH_3 of 300 ppm-mol and 50 ppm-mol, respectively.

The temperature of the outlet stream from the air cooler was 104°F (40°C). It led to the cold HP separator to remove unused hydrogen which recycled back to the hydrocracker reactors. The remaining liquid was then sent to the cold MP separator, where the sour water produced was removed from the process, and the hydrocarbon liquid was sent to a H_2S stripper. It was then preheated with the effluent from the second hydrotreating section.

The stripper used medium pressure steam to remove H_2S from the main product stream. The purpose of stripping steam injections was to achieve a bottoms product with less than 15 wtppm of H_2S. The overhead stream from the stripper was condensed with an air cooler and a trim condenser, cooled to 86°F (30°C) at a pressure of 99 psig. The condensate was received by a three-phase separator to remove sour water from the produced overhead light naphthas.

Two possible operational changes to save wash water were investigated:

1. Reduce the flow rate of wash water by 20%. Before implementing such a change, confirm whether this could lead to accelerated corrosion due to the presence of NH_4HS.
2. Use produced sour water to make up 50% of the wash water. Determine the possibility of a corrosion problem due to the quality of the wash water.

The following streams were analysed for both scenarios (see **Figure 2**):

a) Effluent cooler outlet – Stream 2
b) Cold MP separator inlet – Stream 3
c) H_2S stripper inlet – Stream 6

NH_4SH scaling tendencies in selected streams of the gasoil hydrocracker

Stream	Scaling tendency		
	Original wash water flow rate	Reduced wash water flow rate	Sour water + wash water
Effluent cooler outlet	0.0009	0.0013	0.0028
Cold MP Sep. inlet	0.0009	0.0013	0.0028
H_2S stripper inlet	0.0000	0.0000	0.0000
Stripper trim condenser outlet	0.0001	0.0001	0.0005

Table 2

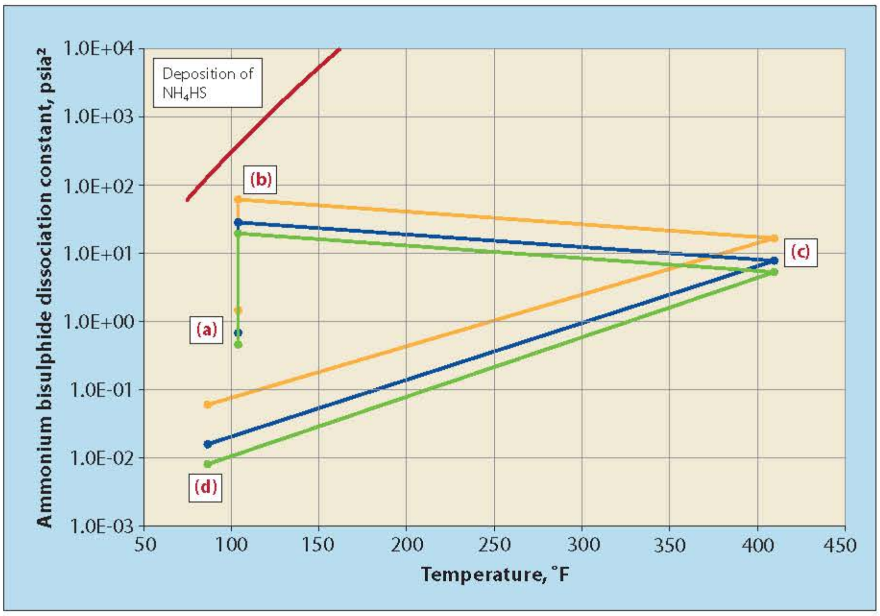

Figure 3 Deposition of NH_4HS in gasoil hydrocracking

Corrosion rates, pH, and NH_4^+/HS^- concentrations in selected streams of a gasoil hydrocracker

Stream		Effluent cooler outlet	Cold MP Sep. outlet	Stripper trim condenser outlet
Original wash water flow rate	Corrosion rate, mm/y	0.173	0.167	0.315
	pH	7.17	7.20	6.45
	$NH_4^+ + HS^-$ conc.	4.73	4.72	1.03
Reduced wash water flow rate	Corrosion rate, mm/y	0.165	0.156	0.297
	pH	7.25	7.28	6.60
	$NH_4^+ + HS^-$ conc.	5.82	5.81	1.50
Sour water + wash water	Corrosion rate, mm/y	0.147	0.297	0.257
	pH	7.41	7.44	6.89
	$NH_4^+ + HS^-$ conc.	8.60	8.57	3.13

Table 3

d) Stripper trim condenser outlet – Stream 9

After reviewing the composition of all of the streams for both scenarios, we found that no NH_4SH was predicted to occur. The scaling tendencies of NH_4HS in selected streams are presented in **Table 2**. For the purposes of corrosion analysis, we want to avoid the >1 tendency.

A reduction of the wash water flow rate by 20% or the use of stripped sour water as 50% of the total wash water will not promote the presence of NH_4SH. This can be graphically represented (see **Figure 3** where the critical stream is 'b').

The absence of solid NH_4HS does not guarantee that no corrosion is occurring. The presence of H_2S and NH_3 dissolved in the produced sour water can promote corrosion at a very low but important rate. Information from the simulation on stream concentration is useful for predicting the general corrosion rate in carbon steel from the sour water pH and its chemical composition. See **Table 3** for the predicted corrosion rate in selected streams.

The corrosion rates predicted by OLI Studio are acceptable. The streams have concentrations of NH_4^+ and HS^- lower than the industry's upper limit of 8 wt% with stream velocity control.[2] With Petro-SIM we can analyse the ideal line internal diameter to ensure a stream velocity less than 20 ft/s (6.1 m/s)[2] and avoid erosional corrosion. The pipe-sizing function in Petro-SIM can determine the best line diameter to meet erosional corrosion, depending on specific stream flow rates (see **Figure 4**).

In the simulation cases, the produced sour water dissolved nearly all the ammonia in the reactor effluent. It then dissolved more H_2S when the wash water flow rate increased. Therefore, the corrosion rate is calculated to be larger in the original wash water flow rate case than in the other two cases with a slower wash water flow rate.

Petro-SIM with the OLI Engine confirmed with confidence the operating integrity window for the gasoil hydrocracker, allowing the planning and executing of robust operating strategies.

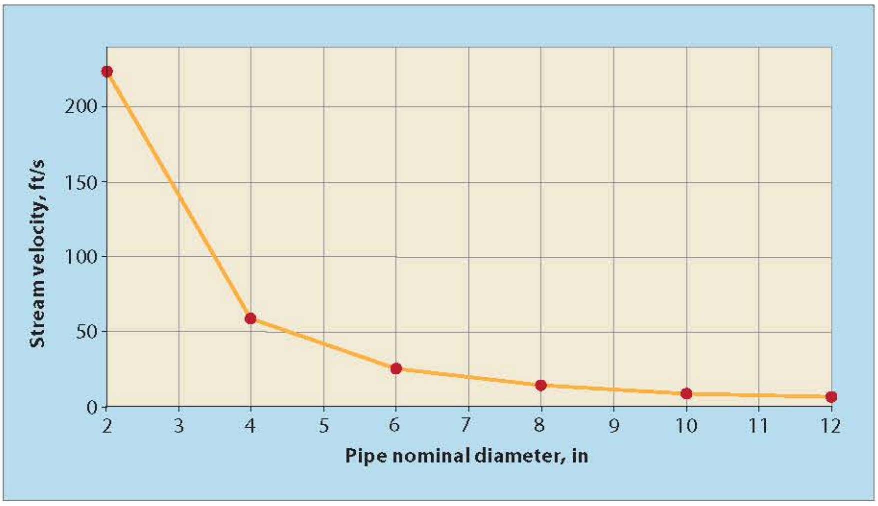

Figure 4 Erosional corrosion analysis tools in Petro-SIM

Case study 2: diesel hydrotreater

Effluent from the diesel hydrotreater had a H_2S concentration of 2 mass%, NH_3 0.23 mass%, and HCl 4 ppm-mol. The effluent was cooled in a heat exchanger train (feed/effluent exchanger), recovering energy to heat up the reactor feed. The reactor effluent from this exchanger train emerged at 313°F (156°C) and 1140 psig. This stream was mixed with wash water with a flow rate of 3.3 t/h (stripper sour water), then sent to the REAC. The outlet stream from the REAC was then sent to a condensate receiver in which the produced sour water was separated from the hydrotreated diesel, unreacted hydrogen, and other side products.

The flashed gas was sent to an air cooler condenser and most of the unreacted hydrogen was separated in the acid gas knockout drum in order to be recirculated back to the hydrotreating reactors. The liquid from the acid gas knockout drum was mixed with the liquid from the condensate receiver and sent to a stripping column. Stripping steam was used to remove the remaining H_2S from the hydrotreated diesel. A concentration of less than 1.5 wtppm of H_2S was maintained in the stripped diesel.

Critical streams analysed for both scenarios were (see **Figure 5**):
a) Warm reactor effluent
b) Effluent air cooler outlet
c) Acid gas condenser outlet
d) Condensate receiver liquid outlet
e) Stripper feed
f) Diesel stripper condenser outlet

In this case study, NH_4Cl solid formation was observed in the feed/effluent exchangers' outlet stream. Almost all of the hydrogen chloride in the reactor effluent reacts with ammonia. The formation of NH_4Cl occurs inside the feed/effluent exchanger and starts at about 438°F (226°C, see **Figure 6**).

Precious Metals

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Dragoceni metali
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Mahalagang Metals
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Métaux Précieux
Edelmetalen
Metais preciosos
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Metali presye
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Nā Metala kūpono
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Logam Berharga
Metalli preziosi
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Metals Logam
귀금속
Metayên hêja
nobilis metalli
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Taurieji metalai
Metaly sarobidy
Logam Berharga
Metalli prezzjużi
Metara Raraemi
Edelmetaller
Drogocenne metale
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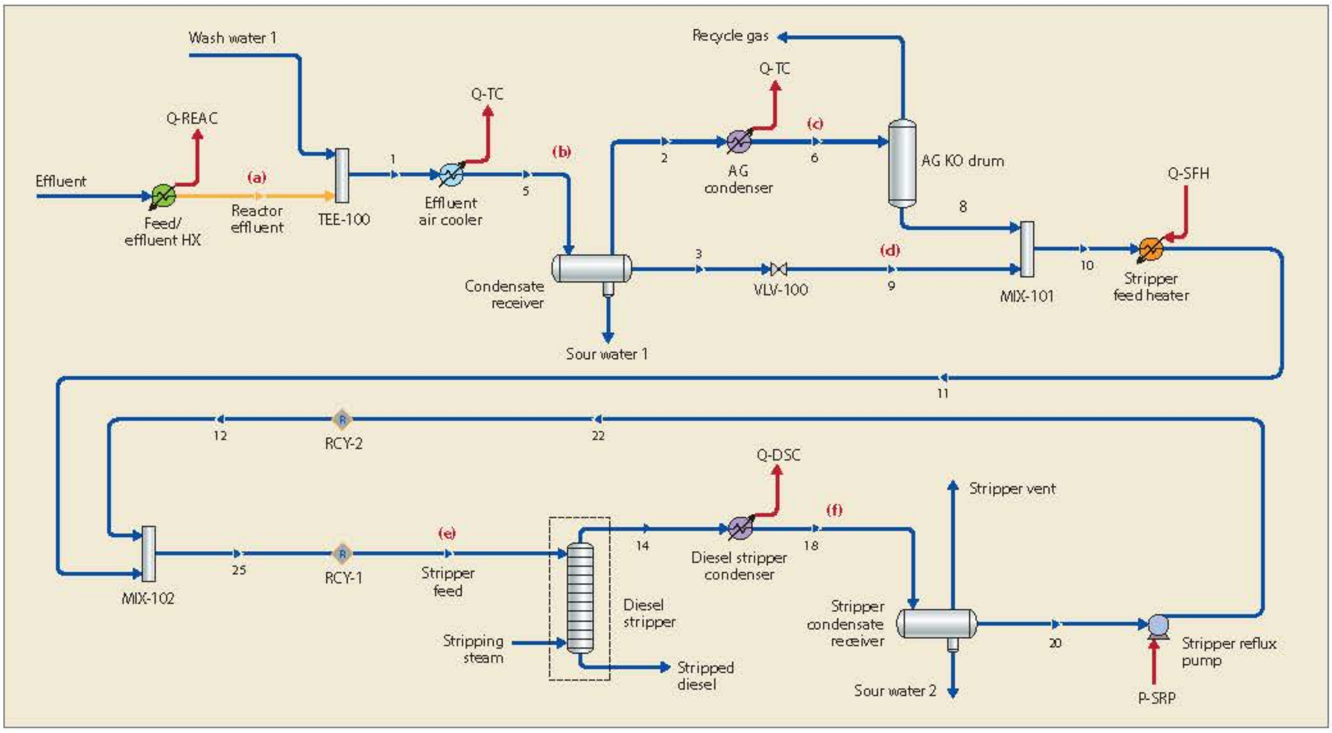

Figure 5 Diesel hydrotreater streams (effluent cooling, separation and stripper systems)

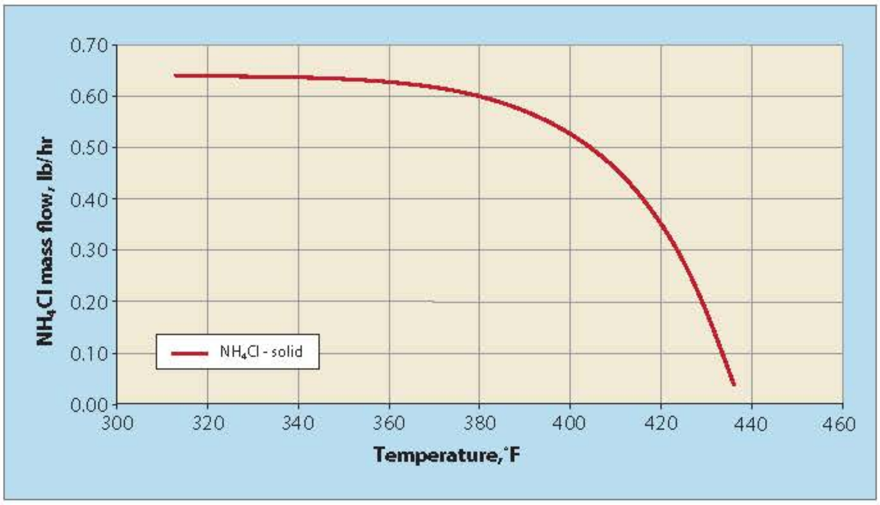

Figure 6 NH_4Cl formation temperature

NH_4HS and NH_4Cl scaling tendencies in a diesel hydrotreater

	NH_4SH	NH_4Cl
Effluent air cooler outlet	0.0026	3.5×10^{-5}
AG condenser outlet	0.011	0.0
Condenser receiver liquid outlet	0.0026	0.0
Stripper feed	0.0	0.0
Stripper condensate outlet	1.1×10^{-4}	0.0

Table 4

This suggests that corrosion occurs inside this exchanger the moment the temperature falls below 438°F. However, the addition of wash water dissolves the NH_4Cl ahead of the REAC and disappears from the process in the sour water produced by the condensate receiver separator.

We can pinpoint with precision which shells in the feed/effluent train will suffer desublimation of NH_4Cl (see **Figure 6**). The use of dispersants to facilitate its solution in wash water can prevent the deposition of NH_4Cl. Dispersants also serve for online chemical cleaning to prevent potential shutdowns and improve heat recovery in the heat exchanger network. The scaling tendency of NH_4HS and NH_4Cl was checked to verify there were no additional problems of corrosion downstream of the REAC (see **Table 4**).

The Petro-SIM with OLI Engine simulation results proved the effectiveness of the amount and quality of wash water in the control of corrosion. Both variables were critical in controlling the deposition of NH_4HS and NH_4Cl (when chlorides are present) in the reactor effluent system (see **Figure 7**).

Petro-SIM predictions using the OLI Engine were consistent with API RP 932-B recommendations. This reinforced confidence that the computer models are reliable and applicable to different hydroprocessing procedures.

Conclusion

The energy and chemical industries can reduce financial losses due to corrosion by using the proper tools to monitor and improve corrosion prediction. Data-driven engineering strengthens corrosion management systems. It helps engineers to identify corrosion issues to improve predictions of corrosion.

The Petro-SIM digital twin reflects real systems. It accommodates real constraints and physics in a seamless manner in the design or operations phases, optimising the total cost and ownership value of process simulation models.

The Petro-SIM digital twin with OLI Engine provides the necessary capabilities for engineers to design facilities and predict process performance to ensure a strong corrosion management system.

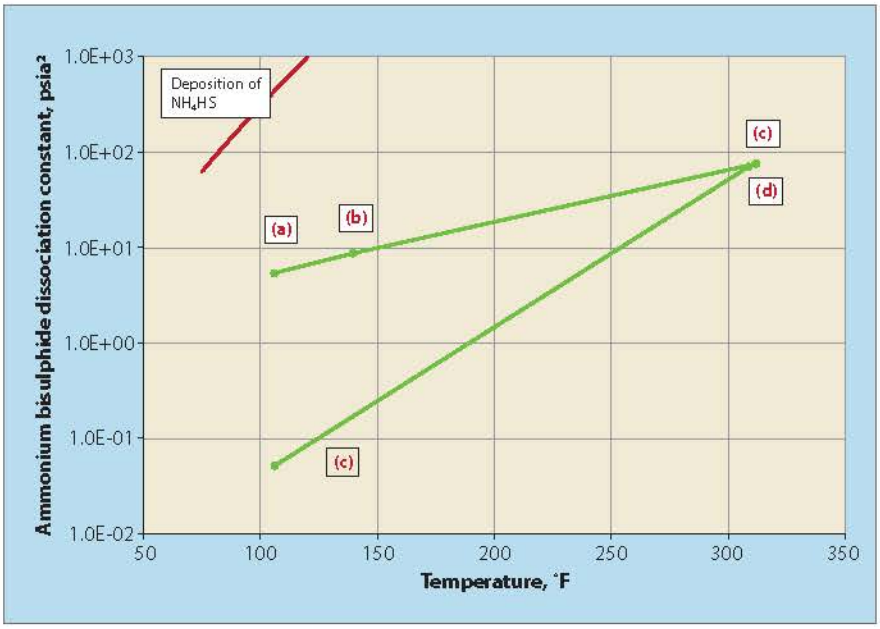

Figure 7 Deposition of NH_4HS in a diesel hydrotreating process

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Should you rely on your simulation results?

Avoiding some of the pitfalls of process simulation

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Tata Consulting Engineers

Process simulation is a useful and powerful tool to model chemical process flowsheets of varying complexities. Modern day simulators are built with a comprehensive, pure component databank, an exhaustive library of thermodynamic systems, physical property estimation methods, initial estimate generators, and inbuilt algorithms for every unit operation with a user-friendly graphical interface. These simulators can solve and optimise virtually any flowsheet synthesis problem. However, despite the simulator's sophisticated and rigorous modelling techniques, process simulations at times fail to represent real life plant data. In most cases, the user shows blind faith in the inbuilt configurations and default selection of methods in simulators, which can introduce erroneous results for specific systems. Since simulators can generate multiple and, at times, conflicting solutions for the same set of external input data parameters, this raises doubts about their effectiveness and reliability. There are a number of reasons for simulation failure. This article discusses various issues that may help users to derive meaningful results from simulation and thus enhance the reliability of their simulations.

Elements of process simulators

With advances in computer technology and the availability of modern tools, commercial steady state simulation software packages have become an integral part of process design practices. Process simulation is utilised in all stages of process plants, from concept and feasibility, to basic design, to detail design, even extending to commissioning and revamps. Process flowsheet synthesis using simulation software yields a heat and mass balance that is consistent with thermodynamics. This heat and mass balance is a firm basis for all downstream process design activities including preparation of equipment and instrument specifications.

Mathematical simulation models offer a drag-drop type of graphical interface for setting up process flowsheet configurations. Graphical user interfaces have matured to the extent that they make it easy to build large and complex models; they also provide a step-wise menu and online help to enable users to define input parameter specifications easily.

Simulators serve a wide variety of unit operations in refining and include mathematical solver algorithms specific to every unit operation model. For example, distillation columns can be solved by selecting any of the suitable prebuilt algorithms like Inside Out or chemdist. In short, virtually all unit operations are well supported and can be easily defined using a typical simulation suite. These mathematical models are supported with internal databases covering physical and thermodynamic property databanks. In a bid to enhance the capability of the software, these simulation packages present multiple choices for the user to configure and then to solve the flowsheet. A few of the important user choices include selection of thermodynamic methods (for calculating pure component and mixture physical properties) and/or specific algorithms for solving individual unit operations, deciding calculation sequences, methods for generating initial estimates, methods for defining a non-library component, and so on.

More choice, more confusion?

As more options become available, it is expected and assumed that the user is knowledgeable enough to select appropriate methods and employ correct choices to solve the flowsheet. Since simulation software uses advanced high-end computer hardware for such sophisticated and advanced simulation programs, there is no programming limit with respect to presenting multiple choices to the user. In fact, they are increasingly interpreted, falsely, as 'more choice, more capability' products. However, so many choices surely pose a challenge for process simulation engineers to check the applicability and suitability of every choice to model a given process, verify the advantage or disadvantage of the selection, and determine its effectiveness over the operating range. Thus, to utilise the capability of the simulation software, adequate knowledge and specific process experience become a prerequisite. However, this basic and fundamental issue could affect the quality of simulation output results.

With increased availability of simulation models, it has become easier for users to study various design cases. Normally, these design cases include modelling the same flowsheet for various case studies, for instance the effect of processing different feedstocks, or checking performance under different operating conditions. In today's world of high computing speeds, computation time is no longer a constraint while selecting or adding as many check cases as required. The user can check performance for multiple cases, conduct what-if analysis, perform sensitivity studies, and optimise process designs.

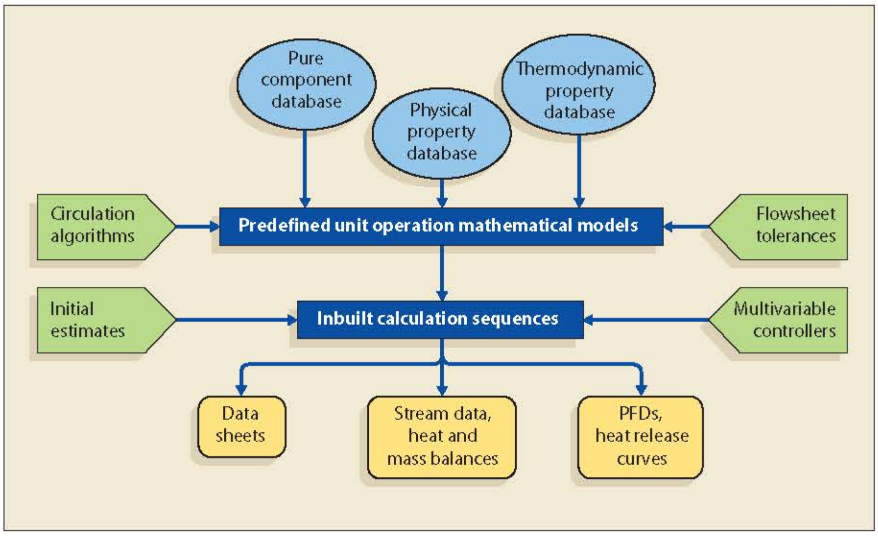

Figure 1 General architecture of a typical commercial steady state simulator

Using a simulation tool, one can significantly increase the profitability of a process by optimising design and operating parameters. Thus, simulators provide a reliable platform by solving any process flowsheet using an inbuilt modelling approach. However, a few problems still exist with respect to multiple solutions that can be generated for the same flowsheet by different users using the same simulator and using the same set of input data. Multiple solutions are possible as multiple choices are available to users while configuring the flowsheet. As an example from experience, a typical glycol dehydration tower for the same input and output specifications will require eight theoretical stages if an equation of state based thermodynamic model is selected against 12 theoretical stages if a liquid activity coefficient based thermodynamic model is selected. In both cases, the simulator will converge but will yield two different hardware configurations for the same mass balance.

Blind faith by inexperienced engineers

Knowing how to configure a flowsheet in a simulation environment and familiarity operating the simulator does not necessarily confirm the availability of skills required to effectively solve and analyse flowsheet synthesis results. Here is the main hitch. Although simulator programs provide early warnings for missing input data or inadequate input data, there may be no warning if the user selects an inappropriate calculation method. This is especially true when blind faith is exhibited by users on the applicability of various choices such as selection of a thermodynamic system. As **Figure 1** shows, modern day simulators carry a wide variety of unit operation libraries, expanded thermodynamic data libraries, comprehensive pure component and binary interaction parameter databases, initial estimate generators, and so on. Looking at these capabilities, it seems that most chemical plant modelling problems or process design and optimisation problems can be dealt with accurately and reliably. Unfortunately, this is not a reality.

Accuracy of simulation output is critical, irrespective of the reputation of the simulation package deployed, or the speed to obtain a solution. Unless the simulation model accurately describes the interaction of different components at varying temperatures or pressures using reliable methods, simulation results will not represent reality. Simulators are just automated mathematical model solvers based on inputs provided by users. Therefore, simulation input parameters require skilful scrutiny. Also, the results need to be carefully analysed based on fundamental principles and the specific objectives of a simulation.

Differences in simulation and design

It is now widespread practice to employ process simulators to solve design cases. Although a simulator can be configured to provide solutions to a design problem, there is a difference in approach and method using simulators to arrive at a solution. In order to obtain a uniform solution, any design problem is solved in a step-wise manner utilising a fixed and defined method or procedure for every step. However, when it comes to solving the same design problem using a simulator, an iterative or case study type of approach has to be adopted. Before dealing with a simulation's pitfalls, it is important to understand the differences between a design problem and a simulation problem.

As **Figure 2** shows, a design problem can be defined with a known or given set of input parameters; the objective of a design problem is to obtain design variables for an already known set of performance parameters. For example, a simplified problem statement can be: "Design a heat exchanger to cool water from 60°C to 50°C." In this simple problem the set of input parameters is known. These are the component (water), its physical properties, and initial conditions (60°C). The desired output performance parameter (50°C) is also known. With input and output per-

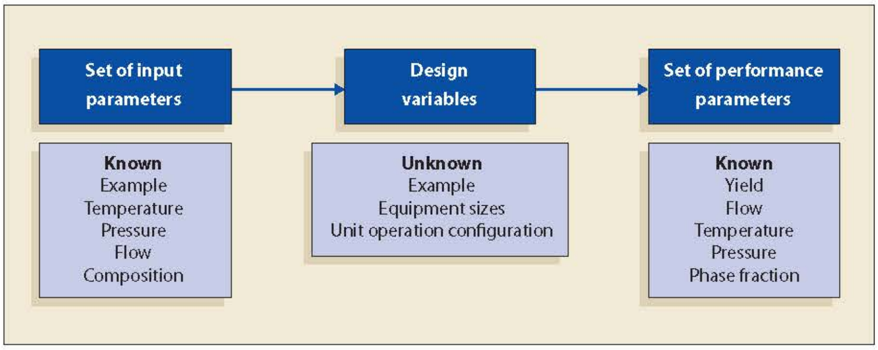

Figure 2 Definition of a design problem

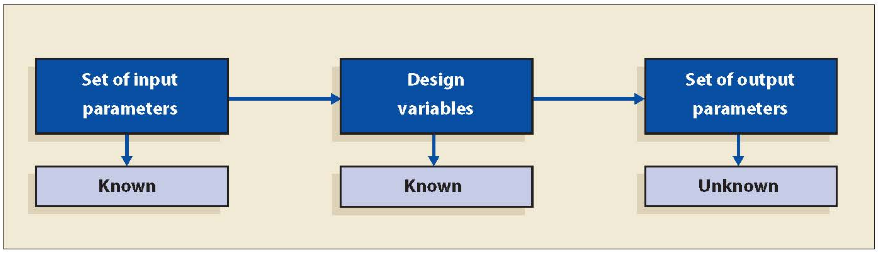

Figure 3 Definition of a simulation problem

formance parameters known, the objective is to find design variables (heat exchanger geometry) to satisfy the desired output parameters. This design problem is then systematically solved in a stepwise manner so as to obtain the outlet temperature.

As **Figure 3** shows, a simulation problem can be defined with a known or given set of input parameters. The objective of a simulation problem is to obtain output (or performance) parameters for predefined design variables. In the above example, the simulator will use a set of available input parameters. The user needs to define a design variable (the exchanger geometry) so that the simulator can check the suitability of the exchanger geometry to obtain the desired output (50°C) parameter. In every subsequent run, the exchanger geometry can be readjusted by the user until the desired output is obtained.

This means that when a simulator is to be used for designing an exchanger, a user should first assume a suitable design geometry and then check if the assumed geometry satisfies the output requirements. The user thus needs to follow an iterative or 'trial and error' approach to solve the problem statement. Unlike the design case, a good approximation for the most suitable exchanger geometry as a starting point is essential in solving a design problem using a simulator. The solution and number of cycles for convergence depend on the user's ability to assume a configuration close to a reasonable design. Analysis of the convergence history of each cycle provides a direction for the user to decide which design parameters in subsequent runs need to be adjusted to obtain the desired output. Lack of proper understanding will lead to solution failure and divergence may be observed instead of convergence.

Result validation

The user can select a particular calculation method from a variety of options offered by the simulator. Simulators also provide multiple choices of design variables for configuring the given problem. Depending on the user's selection of design methods, it is possible to generate multiple solutions for the same set of input parameters.

Arriving at the most appropriate, most suitable or most optimised solution can then be a dilemma.

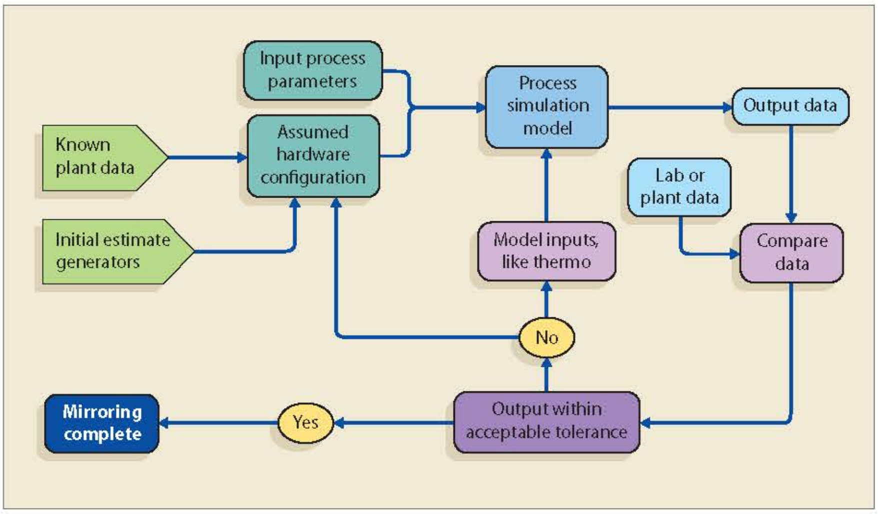

Figure 4 Simplified procedural overview for plant mirroring

This issue can become very subjective. Therefore, it is necessary to verify the simulation results with some baseline data. Preferably, the simulation results are compared with actual plant operating data and/or proven baseline design data supplied by technology suppliers. Matching the data for the operating case enriches the designer's experience and understanding to perform similar designs effectively. In the absence of verification against such baseline reference data, the simulation results cannot be fully trusted. Their accuracy remain unverified. Simulation of grassroots design cases can be based on careful analysis of laboratory data or from simulation experience for similar operating units/operations or pilot scale/laboratory scale setups. When any of the reference data is somehow not available for new designs, then the user must be expert in modelling the problem with experience in selecting the most suitable methods to represent the system. However, ignoring the validation exercise and opting to go ahead with the simulation results based on the user's gut feeling may result in unreliable simulation results.

Concept of mirroring

An operating plant provides realistic and true data for various operating variables that need to be reflected in a mathematical simulation model. This is the concept of plant mirroring.

As previous discussion points out, process simulation results can vary for every user based on the inputs specified. Even for the same set of input data, various simulators will predict somewhat different results depending on the source of thermophysical or other data in its internal databases. The accuracy and correctness of output data depends on various modelling techniques. Chemical engineering's empirical correlations pose a challenge in representing the true nature of many processes and applications. Therefore, it is imperative that any simulation model must be calibrated based on representation of true laboratory or plant operating data.

Initially, a simulation model must be checked to reflect true and real-life conditions for comparison, either from the plant or from the laboratory. Simulation results for the base case must be compared to verify and validate their close resemblance to actual plant or laboratory data. Once it has been verified that the simulation results match closely with benchmark or real-life data, further studies such as process performance predictions with separate sets of operating conditions, different capacities, different feedstock conditions, and so on can be simulated. Even in such cases, the extent of extrapolation of the operating envelope may matter.

This works for building simulation models of operating facilities. However, it is not a fool proof method; gathering error-free, consistent data from an operating plant and laboratory data (which is discrete data) is not easy. Even with the right data and with the validation exercise completed, fundamental mistakes in selecting thermodynamic methods (for instance) cannot be eliminated. In any case, this may not help in new designs other than that the user's understanding is enhanced. Thus, for effective representation/mirroring one must have:

- Good understanding of the unit/operations to be simulated
- Error-free data from various sources (DCS, equipment specifications, lab analysis) which is also consistent with respect to time
- Correct selection of options in simulation – thermo, component data banks, solving options, and so on
- Correct interpretation of deviations/results

Figure 4 shows a procedural overview of plant mirroring when using a simulation model. This exercise in verifying simulation results with available plant or laboratory data to reflect the real world is commonly termed mirroring the plant.

Many engineers struggle to fix an acceptable degree of accuracy when comparing simulated data with plant data. While it is desirable to match the data as closely as possible, there are no fixed rules for accepting or rejecting the simulation data. The results must be analysed and compared considering the simulation objective of the application. For example, if the objective of the simulation is to calculate the heat of mixing of, say, caustic dilution in water, then temperature data at the mixer outlet is compared with information from the operating plant. As long as this temperature comparison matches with an acceptable degree of accuracy, the model can be accepted. In this example, while comparing the data, even if a large deviation is noticed in the transport properties of the mixer outlet stream, the simulation model can be accepted with respect to its main objective of predicting the heat of mixing.

The user should be aware of the limitations and capabilities of a selected method or a selected equation. For example, a simulation model is set up to calculate pressure drop in a cross-country pipeline. Initially, in the absence of any data for comparison, the user may provide some design margins based on sound engineering practices and may decide to trust the simulation results. On commissioning, the user notes that the actual pressure drop calculated by the simulator turned out to be 10% higher. In an assignment involving exactly the same service conditions, should the user reject the previous simulation model because of its large deviation from reality? It is important to know the extent of deviation and possible reasons for such deviation, and thus determine the applicability of a given method. Many times, the properties of an actual fluid may be different from the design fluid, or the roughness factor used in designs could be different from the actual. It really does not matter, even though there are deviations. As long as the user is aware of the limitations of the selected design options, the simulation results can be accepted with work-around adjustments. In this example of pressure drop calculation, the user can accept the simulation model by derating the calculated pressure drop values by 10%. However, for another case involving close boiling point component separations, a deviation in vapour pressure of 10% between simulated and plant data will be unacceptable. There are no fixed rules for an acceptable degree of deviation. It depends on the application, hence a user must cautiously compare results while mirroring the process plant.

Pitfalls in process simulation

Process simulation enables experimentation with predictions in the form of what-if scenarios for a real process plant. The success of a simulation model depends on design techniques applied while modelling the problem. It is common belief that simulators can provide sophisticated and accurate results in the shortest time. However, the truth is that simulations can fail badly. They can fail in all the ways that theories can fail, and in all the ways that experiments can fail as well. An understanding of the many ways in which simulations can fail offers better clarity on the reasons for failure and, in a way, helps the user to be cautious. Some pitfalls of simulation can be categorised as follows:

Data entry

This is very common and the simplest source of simulation error. A decimal shift error has serious consequences. For example, a decimal level error in specifying the wash water flow rate injected on a column overhead stream, say inflating it, will result in multiple errors in hardware design including an increase in condenser heat duty, an increase in cooling media consumption, oversized pipes, an oversized reflux drum with boot for water separation, and so on.

Incorrect units of measurement

Although simulators have an automatic feature for converting units of measurement, there is potential for wrong selection from the graphic interface menu. As an example, entering the feed stream data in molar flows instead of mass flows will lead to erroneous results.

Data reconciliation

Operating plant data obtained from a plant's DCS system are rarely constant. Depending on the relative mode of operation and position of other control variables, the results and trend line for the same controller vary with respect to time. There are typically no unique single fixed-point data for any given variable. For example, a simple one feed, two product stream binary distillation column with flow and composition measurement on feed and both products lines will not perfectly satisfy a feed flow = products flow mass balance rule. Bigger errors may crop up as feed and product analysis timing may not be consistent with each other or other operating data. Therefore, data reconciliation must be done carefully for obtaining satisfactory representative data which is consistent and satisfies heat and material balances. Even with correct modelling techniques and appropriate choice of equations to represent the system, data reconciliation if not done properly results in horrendous results.

Ignoring warning messages

A fully converged complex flow sheet using rigorous procedures is no guarantee of dependable results. Modern simulators can display the results for a selected unit operation or selected stream with a click of the mouse. The detailed simulation text report runs to several pages; most of the time, such a detailed report is not generated while converging the simulation model. A detailed text report contains warnings and messages which if ignored can lead to an erroneous simulation. For example, the report may highlight a warning about unavailability of binary interaction parameters for certain pairs. Such pairs are defaulted to 'ideal behaviour' in the absence of any other user supplied data. If a detailed report is not generated and all warnings are not analysed correctly, simulation failures can occur.

Physical and thermodynamic property model

The user needs to have adequate knowledge of the suitability of thermodynamic methods for various components/situations. The user also needs to be familiar with the specific methods/guidance available from the simulation software guide. Selection of a suitable thermodynamic model and physical property model is crucial to the success of any simulation problem.

Missing, inaccurate or inadequate physical and thermodynamic properties compromise accuracy of results. Most inbuilt properties have a predefined applicability range. The user needs to verify and confirm that the inbuilt databases associated with the selected thermodynamic methods cover the operating range required for a given process. Estimation of missing parameters using various techniques (the UNIFAC method, or data regression, for instance) must be done carefully. Estimated data must be validated before its use in simulation.

Too much faith in input data

The quality of input data clearly influences the quality of output results. Any data used without proper analysis for any discontinuity in material and heat balances or plant data used without reconciliation may provide unexpected results. Negligence in mirroring of plant or laboratory data will result in an inaccurate simulation model.

Configuration of simulation defaults

Every simulation model has default configuration values for many parameters. These include initial estimation generation methods, selection of a minimum tear stream algorithm to decide a calculation sequence, flow sheet tolerance values, water decant options, and methods for estimating missing data. These defaults need to be reviewed and accepted consciously and may need to be modified as and when necessary.

Apparent accuracy

Engineers sometimes feel obliged to use simulation tools to solve optimisation problems. There is no point in investing effort in optimising a process based on the heat exchangers' small temperature approaches, when the enthalpy model itself is only ±20% accurate. It is important to apply cause and effect type of error analysis skills. The user should have a fair understanding of the impact of one variable on the entire flow sheet. Process engineering knowledge cannot be replaced by a process simulator.

Conclusion

A process simulator is one of the most powerful tools for modelling a process flow sheet. It is highly flexible when applied to the design and analysis of many simple or complex systems. At the same time, its results can be misleading and prone to generating multiple, conflicting results if proper modelling techniques are not understood and followed. The fundamental understanding of thermodynamics, engineering principles and unit operations, cause and effect type of error analysis skills, the ability to understand variability and consistency gaps in input data, the degree of sensitivity of performance parameters to the variable parameters, and so on, play a vital role in successful simulation. Validation of a simulation model by mirroring actual operational performance in a plant/unit or pilot/laboratory scale equipment can provide confidence of reliable results. It is crucial that simulation results are not blindly accepted. The success of a simulation depends on the user's ability to interpret input and output data. The onus of accuracy, reliability and relevance never lies with the simulator.

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Process safety time for fired heaters

Cases illustrate the actions needed to avoid hazards occurring when the supply to a fired heater is disturbed

CHRIS STEVES, RICHARD TODD, JAMES NORTON and JERRY ZHANG
Norton Engineering Consultants

The fired heater is a common unit operation in the refining and petrochemical industries that is used to increase the temperature of a process fluid. Fired heaters are required when a process-to-process heat exchanger or a utility exchanger (steam condenser, hot oil heater) cannot provide sufficient driving force to raise the temperature of a process fluid for downstream processing. There are numerous applications for fired heaters, from preheating feed to process units to reboiling distillation towers.

During the course of normal operation a fired heater will be exposed to disturbances in the supply of fuel, combustion air, or process fluid that may lead to a potentially hazardous condition developing. To manage these disturbances and take appropriate action to safely operate and control the fired heater, several layers of protective systems are normally provided.[1] These protective systems are designed to take independent action that will prevent the fired heater from reaching a hazardous condition. Protective actions can include:

- Operator intervention based on alarms or other indication of a process upset; typically this intervention can only be effective for slow responding systems that have extended times to reach a hazardous condition
- The basic process control system (BPCS), typically a DCS, which automatically responds to process conditions to maintain stable and safe operation
- A fault-tolerant PLC is also commonly used on fired heaters. The independence of the PLC system allows actions to be taken in cases where components of the BPCS are not functioning correctly. These safety instrumented systems (SIS) are critical components in maintaining the safe operation of the fired heater

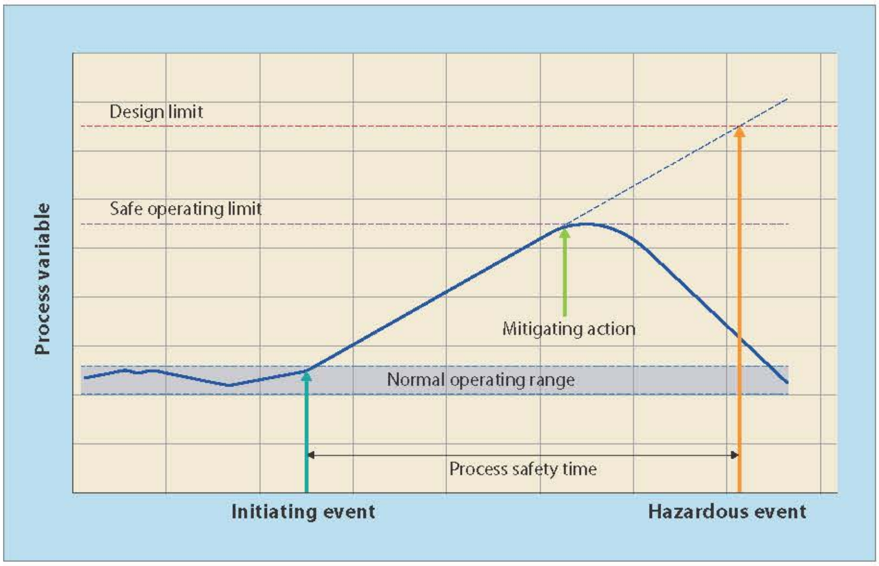


Figure 1 Illustration of process safety time[3]

The combination of protective systems on a fired heater ensures that the unit can be safely started up and operated within its safe operating limits (SOLs). The design of these systems can vary depending on the process fluids passing through the heater, the specific safety concerns that are present due to these services, and the configuration of the heater, along with any design standards or guidelines that are applied by the owner. For the protective systems to be effective in protecting the fired heater and preventing a catastrophic failure, the process safety time for various hazardous events must be calculated and used to ensure the systems offer adequate protection.

Process safety time is defined as the time period between a failure occurring in the process or its control system and the occurrence of the hazardous event.[2] Process safety times are functions of equipment design and operating parameters, and can be estimated for various failures and resulting hazardous events based on modelling of system dynamics. Estimates of process safety time do not take into account any mitigating action that would be performed to protect the heater. **Figure 1** illustrates a fired heater response to an initiating event and the resulting process safety time. Several commonly used terms for process safety time analysis are also shown in the figure.

Process safety times should be defined and calculated for different initiating events, usually based on input from a multi-functional team participating in a process hazard analysis (PHA) or HazOp study. As the PHA team reviews potential hazards associated with process equipment and the different modes of operation (start-up,

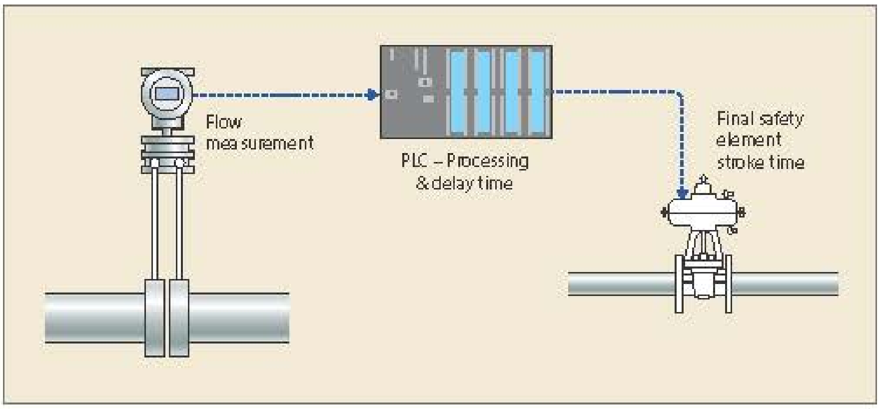


Figure 2 SIF to shut off fuel to a fired heater on loss of process flow to the coil

shutdown, normal operation, operational upset, and so on), the severity of the potential consequence and likelihood of occurrence will then be used to define which type of mitigating action should be taken to prevent the negative consequence from occurring (for instance, is an automated safety system required or can manual operator response be utilised). An understanding of the process safety time is critical in deciding on the best hazard mitigation strategy.

In order to evaluate and determine the process safety time for a particular scenario, several simplifying, conservative assumptions about operation prior to the initiating event must be made. Critical review by the multi-disciplined PHA team, including subject matter experts, to verify these assumptions is good practice to improve the efficacy of the process safety time estimation process. For example, it is common to assume that a fired heater is operating at design fired duty prior to any 'initiating' event, but if the unit is often operated at firing rates above design then this should be considered when developing the conditions to be used to initiate the static and/or dynamic simulations of the event necessary to determine the process safety time.

Some initiating causes and their resulting hazardous events that may need to be considered and evaluated for a fired heater include:

- Loss of process flow to one or more passes, causing the tubes to overheat and rupture
- Gas burner fuel block valves open before light-off, or a flameout at the burners occurs due to a disturbance in the fuel supply during normal operation, causing an accumulation of unburned fuel in the firebox which can lead to an explosion
- Damper closed in a natural draft heater, causing an accumulation of unburned fuel in the firebox which can lead to an explosion
- Loss of combustion air from a forced draft fan, causing an accumulation of unburned fuel in the firebox which can lead to an explosion

After all process safety times for a particular piece of equipment like a fired heater have been determined, the SIS can be designed to ensure that it will successfully keep the hazardous event (the consequence) from occurring after the initiating event (the cause) has started. The SIS will usually incorporate multiple safety instrumented functions (SIF), each of which may be considered as an independent protection layer (IPL) for mitigating the hazard and usually evaluated as part of a PHA and layer of protection analysis (LOPA).

The total response time for the SIF is composed of the detection time (based on instrumentation used to detect the initiating event), any process delay built into the SIF to filter out spurious instrument or process issues, the time for the SIF to complete its action (logic controller time and valve closure time), and any process lag present in the system

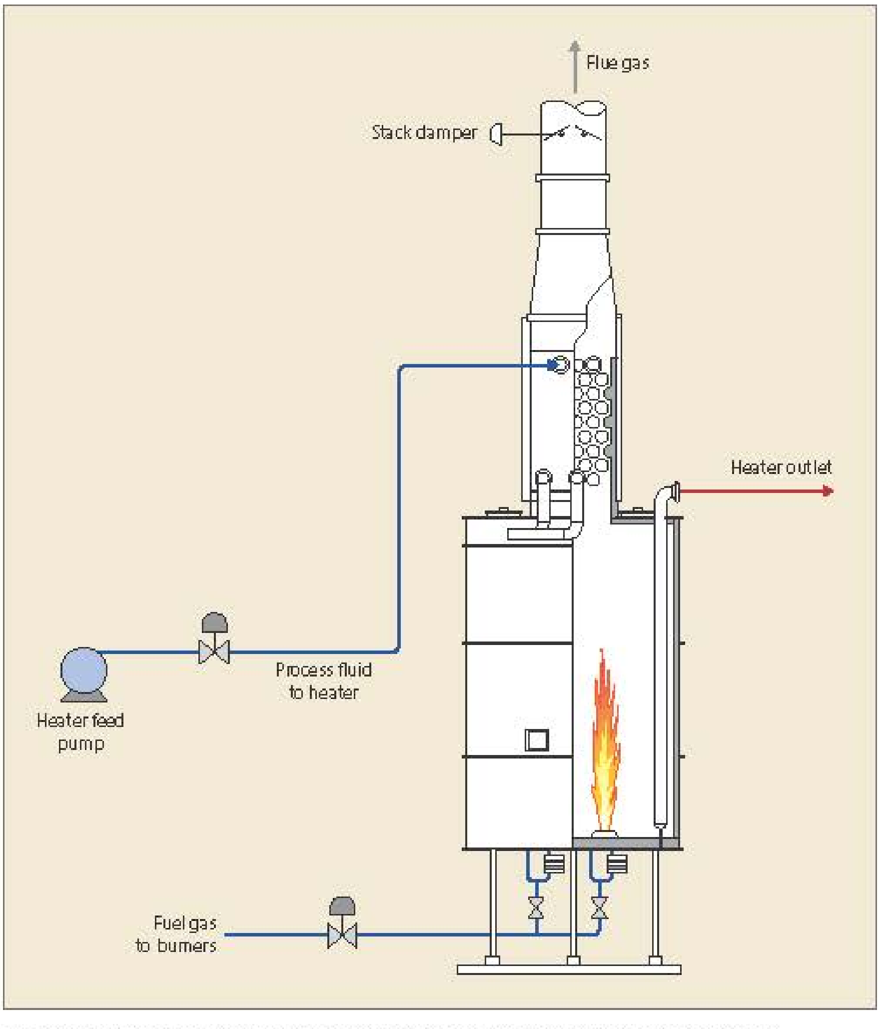


Figure 3 Arrangement of the fired heater used to determine process safety time

after the SIF has completed its action. An example of a SIF to close the fuel shut-off valve upon a loss of process flow to the heat transfer coil is shown in **Figure 2**.

In order for the SIF to be successful in preventing the hazardous event from occurring, the total response time for the SIF must be less than the process safety time. In many cases, owners will choose to incorporate some conservatism into the design of the SIF, and many will specify that the total response time must be less than one half of the process safety time.[2]

The following examples illustrate the steps involved when evaluating process safety times for a fired heater. These examples will focus on a vertical-cylindrical, natural draft heater that is in the reboiler circuit of a distillation column (see **Figure 3**). The fired heater has four burners installed in the floor for a combined design firing rate of 60 MMBtu/h. The fired heater is burning a refinery fuel gas that is a mixture of light, paraffinic hydrocarbon species along with hydrogen, while the process fluid entering the convection coil is an oil stream characterised by a true boiling point curve.

Case 1: Accumulation of combustible species in the firebox during light-off

The first case study considers the scenario where the fired heater has been steam purged to remove any hydrocarbons and prepare the firebox for burner light-off. The following conditions are assumed:

- The heater is at 250°F (120°C)
- All pilots on the burners are lit
- O_2 concentration in the firebox is equal to that of ambient air
- The stack damper is in light-off position
- The air registers were inadvertently closed following the purge

With these assumptions, the primary source of O_2 for combustion comes from the initial concentration of air in the firebox. At time zero, two of the four burners are lit at their minimum firing rate, which represents the lowest firing rate that can be sustained for start-up. As time progresses, combustion is maintained on the two lit burners while O_2 is still available in the firebox. Once O_2 is exhausted, the flame goes out and combustion is extinguished. Although the pilots on the burners remain lit, flame instability at the burners under sub-stoichiometric combustion in a cold firebox results in loss of flame. Hence the operating point at 0% O_2 results in a transition where the two lit burners flame out and unburned fuel now starts to accumulate rapidly in the firebox. **Figure 4** shows the trend in firebox fuel composition with time from the onset of the initiating event, which was when the two burners were lit with the air registers closed. Although the firebox is depleted in O_2 and there is no O_2 available to burn the fuel, the condition in the firebox at times greater than 120 seconds presents a very dangerous situation. If the air registers were suddenly opened and air was allowed to enter the firebox, the potential exists for a rapid and uncontrolled detonation of the combustible mixture. The fact that the pilots are lit and will continue to run with the air registers closed means there is always a source of ignition in the firebox. Another potential detonation event may arise if the heater is old and is known to leak tramp air into the firebox.

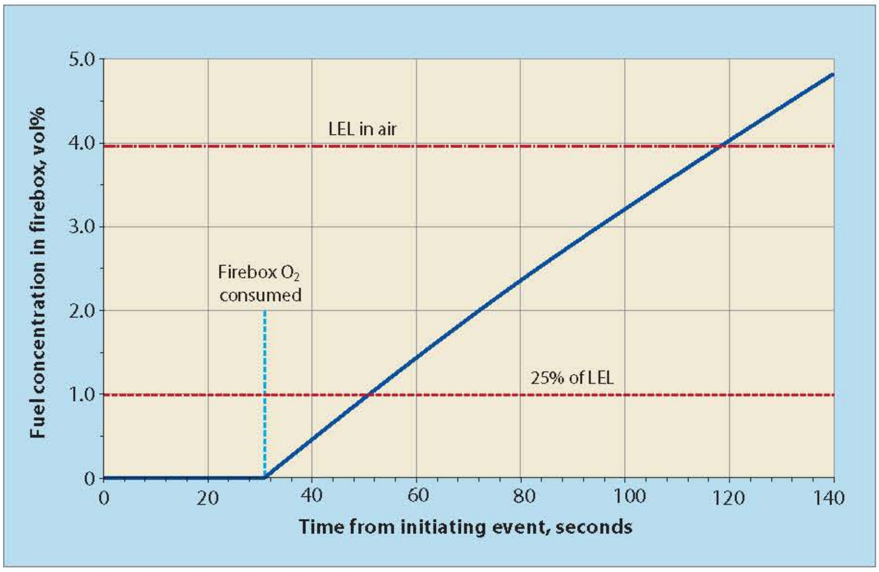


Figure 4 Fuel concentration in the firebox for Case 1 used to determine process safety time

For this case, the process safety time is the difference in time between the burners being lit (initiating event) and the point where the fuel concentration in the firebox crosses the LEL for the refinery fuel gas mixture (consequence), which is around 120 seconds. According to API 556, "The accumulation of combustibles within the firebox should not be permitted to exceed 25% of the LEL before corrective action is initiated".[1] This will set the practical limit on any delay times that are applied. In **Figure 4**, 25% of the LEL is reached approximately 50 seconds after the initiating event. The SIF needs to be designed to identify the failure (gas detector that samples flue gas at the bridgewall in the heater) and initiate the action necessary to mitigate the event (shut the fuel gas emergency shut-off valve to the burners), including any delay, within 50 seconds. When the process safety time is relatively short like the case calculated here, the gas detector response time and accuracy at the low end of the concentration range will be important factors in the design of this SIF. In this case, the delay time that is applied in the logic solver to avoid a spurious trip may be very short given that the response time of the gas detector may be a significant fraction of the available process safety time (catalytic bead detectors may have a 20-30 second response time).

Case 2: Loss of process fluid flow during normal operation

The second case study addresses a disturbance during normal operation at the fired heater. Process fluid is flowing through the tubes,

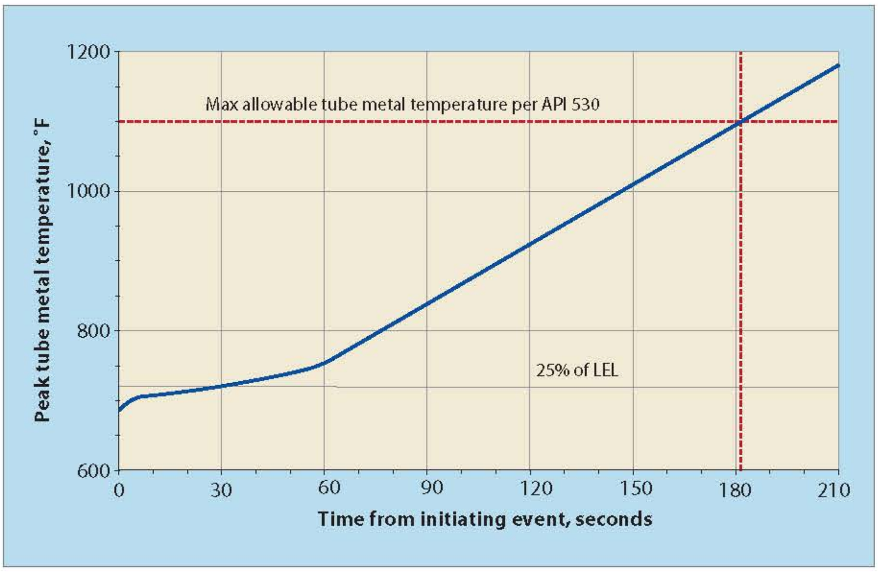


Figure 5 Tube metal temperature in Case 2 used to determine process safety time

originating from an upstream pump that is connected to the bottom of the distillation column. If the pump were to trip while the heater was firing at design rate, then oil flow through the tubes will stop. In this scenario, the process fluid is no longer carrying the heat that is released from the flue gas inside the firebox out of the heater at the same rate it would do otherwise, and tube metal temperatures will start to increase. While most fired heaters include outlet thermocouples to alert the operators of a high coil outlet temperature, with the loss of flow through the tubes due to the pump trip these outlet thermocouples are in a stagnant region and will not provide an accurate indication of the process fluid temperature inside the heater. The process safety time for this scenario can be determined once initial and short term boundary conditions are established.

The following operating conditions and design information were validated for this case:

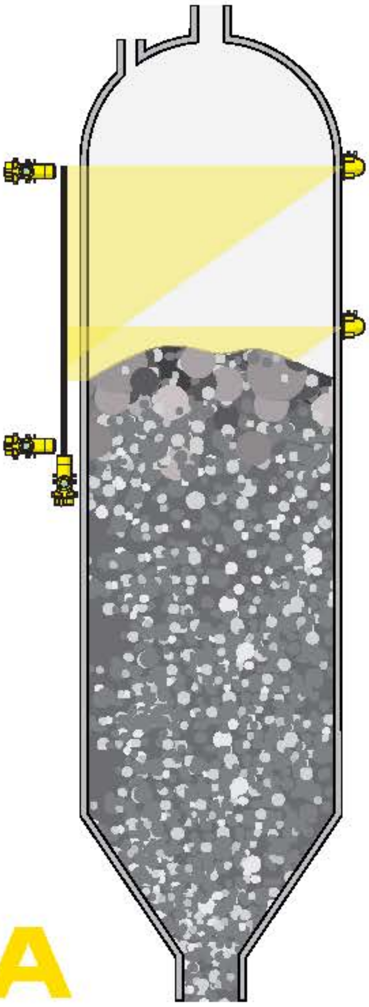
- **Heater firing rate**: all four burners are assumed to be in service and firing at the design rate of 60 MMBtu/h.
- **Tube metallurgy in the firebox**: ASTM P9 (9%Cr-1%Mo)
- **Maximum allowable tube metal temperature**: based on the design pressure, tube outside diameter, and minimum wall thickness (using design corrosion allowance), the stress for this material can be calculated using procedures outlined in API 530.[4] Once stress has been calculated, then the curves in API 530 are utilised to determine the maximum tube metal temperature, which for this example is 1100°F (590°C).
- **Heater geometry**: determine volume, tube surface area, and cold plane surface area within the firebox. Shield tubes located in the convection coil are also included in this analysis as they can 'see' the radiating flue gas and provide an additional sink for heat that is released in the firebox.

The complicating factor with this analysis is tube metal temperatures are changing with time. Radiant heat transfer in the firebox is a complex function of heater geometry and the difference in the fourth power of radiating flue gas temperature and tube metal temperature. As the tube metal temperature increases, the amount of incident radiation absorbed by the tubes will decrease, which means the bridgewall temperature increases. Being able to characterise the radiant heat transfer characteristics of the firebox and incorporate this into the transient analysis is an important aspect when evaluating process safety time. Proprietary models have been developed for determining both bridgewall and tube metal temperatures in the short time periods of interest in this analysis. The trend in **Figure 5** shows the dynamic response of tube metal temperature to the initiating event. The change in the slope of the curve for tube metal temperature at times greater than 60 seconds is the result of the liquid boiling away inside the tubes and vapour being left behind. Once the inside of the tube is blanketed with vapour that is not flowing, the ability to absorb the heat released from the flue gas rapidly decreases and tube metal temperature rapidly increases.

The process safety time for this case is the time difference between the initiating event (pump trip) and the resulting consequence (tube failure and release of hydrocarbon into the firebox). **Figure 5** shows that the process safety time is around 180 seconds. If conservatism is applied (using the recommendation of less than half of the calculated process safety time), then the total response time of a SIF to mitigate this hazard must be less than 90 seconds. The SIF will need to be designed to detect the failure (typically via flow measurement of the process fluid), and take mitigating action (closing the emergency shut-off valve in the fuel supply), including any delay, in less than 90 seconds. Since detection time and mitigation time for this example would be typically an order of magnitude faster than the process safety time, a fairly long delay time could be incorporated into the design of the SIF to avoid a spurious fired heater trip.

Case 3: Inadvertent closure of the stack damper during normal operation

The third case study addresses the scenario where a malfunction or mis-operation results in the stack damper going to its minimum open position at design firing rate. Most stack dampers will not completely close but instead will be limited in how far closed they can go before reaching a hard mechanical stop that prevents the damper from totally closing the flow path for flue gas. The minimum stop is generally set to maintain some measure of flue gas control at minimum turndown. At design firing rate, a 'closed' (pinched or throttled) damper will limit the amount of air that can be drawn through the



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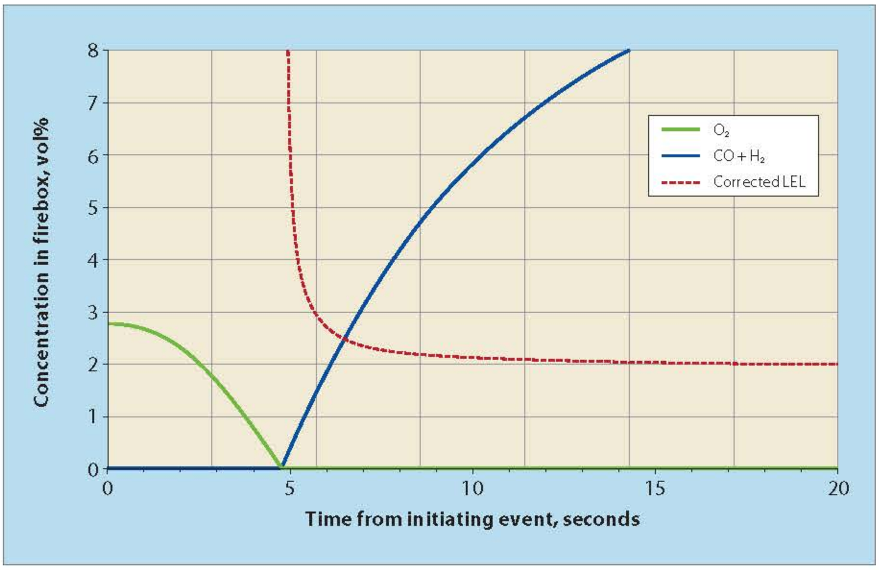

Figure 6 Firebox concentrations in Case 3 used to determine process safety time

burners, which in extreme cases can cause sub-stoichiometric combustion to occur.

The following operating conditions and design information were validated for this case:

- **Heater firing rate**: All four burners are assumed to be in service and firing at the design rate of 60 MMBtu/h
- **Stack damper travel**: It takes four seconds for the stack damper to reach the minimum stop position from its initial position
- **Stoichiometric ratio**: when the stack damper fails at its minimum position, hydraulic analysis of the flue gas circuit determines that the estimated equilibrium stoichiometric ratio is 85% of the theoretical stoichiometric air required for complete combustion

It is assumed that combustion continues in the firebox. Although combustion becomes sub-stoichiometric, the assumption is made that the firebox is hot enough to maintain combustion in a fuel-rich environment for relatively short periods of time (less than five minutes). For extended periods of time this assumption will breakdown.

Closure of the stack damper reduces the available draft at the heater floor which in turn reduces the amount of combustion air that can be drawn through each burner to support combustion of the fuel. Prior to closure of the stack damper, the firebox is hot with average gas temperature well above the auto-ignition temperature of the refinery fuel gas and pilots are lit providing an ignition source at each burner. Under these conditions, the fuel that enters the firebox through all burners will continue to burn to the limit of available O_2. Immediately after the initiating event (normally the first several seconds), unburned fuel from the burners will consume all the available O_2 in the firebox (the firebox has excess O_2 at time = 0) and the firebox will then enter sub-stoichiometric combustion. For typical burners, volppm levels of CO will be observed in the flue gas as the O_2 concentration approaches 0%. Once conditions at the burners become sub-stoichiometric, the combustion products will contain increasing levels of CO and H_2. The combination of high temperature and high CO and H_2 concentrations creates a very dangerous situation that can result in an explosion in the firebox.

The combination of high temperature and high CO and H_2 concentrations creates a very dangerous situation that can result in an explosion in the firebox

Determining the concentration of flammable species in the flue gas as the burners consume the available O_2 and combustion becomes sub-stoichiometric requires a dynamic analysis of the chemical equilibrium between CO, CO_2, H_2 and H_2O formation as a function of firebox temperature. This requires the combustion algorithm in the firebox chamber to be modelled using a Gibbs free energy analysis. The necessary piece of information that is required to model Gibbs free energy reactions in a firebox is provided through the chemical equilibrium for the water gas shift reaction:[5]

$$K_{WCS} = \frac{p_{CO_2}\, p_{H_2}}{p_{CO}\, p_{H_2O}} = \exp(\tau(\tau(\tau(0.63508 - 0.29353\tau) + 4.1778) + 0.31688)$$

where τ=(1000/T-1), T is in Kelvin and p_i represents the partial pressure of species i in the flue gas.

The resulting composition profiles for O_2 and CO+H_2 that are produced from the burners are shown in **Figure 6**. The red dashed line on this same figure shows the corrected LEL for the resulting flue gas mixture at firebox temperature, which rapidly approaches the 2 vol% range as sub-stoichiometric combustion continues. Once the combustion becomes sub-stoichiometric, which occurs approximately five seconds after the initiating event, the combined concentration of CO and H_2 passes the corrected LEL approximately six seconds after the initiating event.

The process safety time for this case is the time difference between the initiating event (stack damper starts to close) and the resulting consequence (CO + H_2 concentration in the flue gas crosses the LEL). In this case, the process safety time is very short, just six seconds after the initiating event, which means the ability to detect high CO levels at the bridgewall via a gas detector and take the appropriate action to close the emergency shut-off valve will be very difficult to achieve with a dedicated SIF. In cases like this, further analysis of the stack damper hard stop is often required to determine if a higher position should be considered to maintain adequate O_2 in the firebox to minimise the level of sub-stoichiometric combustion that is achieved at design firing rate or provide additional time for the SIF to detect and respond to the conditions in the firebox. This will require additional heater modelling to determine the achievable turndown capability of the heater under these conditions.

Conclusion

This analysis has presented three cases that vary in their calculated process safety time for various initiating events on a fired heater. The outcome from this analysis will play a key role in the determination of appropriate SIFs that should be applied to the fired heater in order to prevent the hazardous event from occurring. In some cases, for instance stack damper failing in the closed position, more analysis is warranted to determine an appropriate course of action to mitigate the hazardous event, as a dedicated SIF is unlikely to provide adequate protection. In most cases, the end user will choose a smaller SIF delay time than needed, and may standardise the delay time for similar types of SIFs in the facility in order to simplify operator training. It is always recommended to thoroughly evaluate each initiating cause when operating a fired heater to verify that the SIFs in place are suitably designed to mitigate the event. This requires expert analysis along with the input of a multi-disciplinary team to generate the appropriate data.

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The hazards of fired heater flooding

Heater flooding is a serious and potentially dangerous condition which must be dealt with properly and quickly

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DOUG BASQUEZ *Consultant*

Heater flooding incidents continue to happen. This has resulted in increased requests for the John Zink Institute to include fired heater flooding in its training classes. There is also increased interest in burner management systems (BMS) which are designed, among many other things, to help prevent such incidents. Currently, most fired heaters do not have a BMS and are manually operated. An informal industry survey has shown that about three quarters of fired heater incidents occur at start-up which is generally considered to be the most dangerous time in fired heater operation. For burners that must be manually lit at start-up, this exposes the operators to potential hazards including heater flooding. Since flooding incidents continue to occur, more training and information are needed to prevent them.

Definitions

According to API 535, fired heater flooding is defined in section 14.2 as "operation with insufficient combustion air, resulting in unburned fuel or combustibles in the firebox and/or flue gas". It further notes that the temperature typically decreases when a heater is flooded because not all of the fuel is combusted. Fuel flow is normally controlled based on the process fluid outlet temperature. If that temperature begins to drop, the control system calls for more fuel. In a flooded heater, this exacerbates the problem. If this continues, the heater can become bogged, where the flames are extinguished due to lack of oxygen because they exceed the upper flammability limit for the fuel. This is very dangerous if the heater is above the autoignition temperature because any sudden introduction of oxygen can lead to a re-ignition of the fuel, potentially leading to an incident.

Figure 1a Small tube leak

1b Cause found to be snuffing steam condensate dripping on the tube over time

Causes

Fired heater flooding is simply too much fuel going to the heater for the available combustion air. It is possible for the excess oxygen sensor, which should be located at the bridgewall of the heater, to indicate sufficient O_2 levels and yet the burners can be unstable for lack of air because of too much tramp air leakage into the heater. That tramp air is not going through the burners which are designed to have all the combustion air come through them. Depending on the tramp air source, the flames may be very long. There could even be afterburning in the convection section; depending on where the fuel finds the rest of the air it needs to complete combustion.

There are two basic causes for heater flooding: too much fuel flow to the heater or too little air flow through the burners. Too much fuel flow could occur if, for example, the process feed rate increases beyond the design rate which would cause the fuel flow to increase to try to keep up with the increased feed rate. Too much fuel flow could also occur if there is a sudden change in fuel composition where significantly more air is required for complete combustion. For example, if the fuel suddenly contains components with a much higher heating value (Btu/ft^3), much more air would be needed, assuming there is no change in the fuel pressure. A related problem is a sudden loss of hydrogen in the fuel which requires less air for combustion compared to other fuels, or switching to natural gas/methane which requires more air than many other hydrocarbons. Liquid fuel carryover in a gaseous fuel could send significantly more fuel to the burners than desired. The fuel control system would eventually correct this situation by reducing the fuel flow rate to maintain a certain heat rate. However, the initial surge of higher heating value fuel could put a heater into a flooded condition. Assuming the process fluid is some type of hydrocarbon, a tube failure leading to process fluid leaking into the heater (see **Figure 1**) could also cause a heater to flood due to the addition of flammable process fluid. Fuel control valve problems could cause

Figure 2a Refractory fallen onto burners

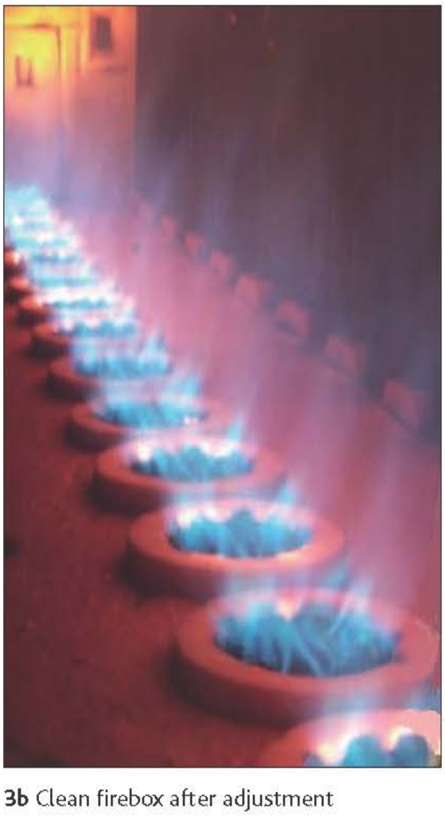
2b After removing the refractory

flooding. This could be a valve that is stuck open or one that opens too rapidly before the combustion air has a chance to catch up to the fuel flow.

Another possible cause could be improper settings on the burner dampers/registers so that insufficient air is flowing through the burners. A related problem is something blocking the air flow to the burners, such as a plastic bag sucked into a burner air inlet. While that would not likely be a significant problem on a large heater with many burners, it could be a serious problem on a smaller heater with few burners. For a forced or induced draft heater, the combustion air fan or induced draft fan, respectively, could be improperly set. A related problem is inadequate draft at the burners which could be caused by an improperly set stack damper or a plugged convection section.

Significant changes in ambient conditions could also cause a heater to run out of air if no adjustments are made to compensate for the changes. When the air temperature increases, the humidity increases, or the barometric pressure decreases, there is less oxygen per cubic foot of air. Higher temperature and lower pressure reduce the air density, while higher humidity causes water to displace some oxygen. Since process burners are volume flow devices, the air flow to the burners would need to be increased to compensate for reduced oxygen per unit volume of air.

Figure 3a Hazy firebox before adjustment



3b Clean firebox after adjustment

Indication

One possible indication of a flooded heater is firebox pressure pulsations sometimes referred to as huffing or panting. This may be caused by lack of combustion air to the burners which causes them to become unstable because they are searching for air to complete combustion. The flames may bounce up and down or pulse. This is caused by rapidly changing combustion dynamics where the flames first lift off while searching for air and then burn back toward the burner when they find some air. However, because that reburn air is not coming through the burners, the flames again lift, searching for air, and the cycle is repeated. These pulsing flames are usually at a low enough frequency they can be seen with the naked eye. The pulsations may also cause the draft gauge to swing back and forth. Very severe pulsing of large burners can cause the heater walls to flex and damage brick and castable refractory because of the vibrations. Refractory falling from the roof can damage and block burners (see **Figure 2**). Severe pulsations can also cause sight ports and explosion doors to flap open and close.

If the flooding is severe enough, some flames may be extinguished. While burners that have flamed out may no longer have attached flames, there may be flames elsewhere in the heater such as higher in the radiant section or afterburning in the convection section. The flooding could be severe enough that all burners have flamed out. There may or may not be flames elsewhere in the heater depending on how fuel rich the conditions are and the amount of tramp air leaking into the heater.

There may be a hazy appearance in the firebox caused by large quantities of unburned fuel in the heater (see **Figure 3**). The haze includes smoke from soot produced by incomplete combustion. The flame lengths may be much longer and brighter than normal as they search for air (see **Figure 4**). There could be flame impingement caused by these long flames (see **Figure 5**).

Other indications of flooding may be seen by changes in sensor readings. There could be a reduction in the bridgewall or process fluid outlet temperatures due to incomplete combustion. The stack gas temperature could decrease or increase, depending on whether or not there is afterburning in the convection section. If the heater is equipped with O_2 and combustible/CO sensors, the O_2 will likely read very low and the combustibles/CO will likely read high. The draft may decrease due to reduced temperatures in the firebox.

Response

All personnel should be removed from near a heater suspected of being flooded. If possible, all actions should be done remotely from the control room. No sight ports should be opened to look into the heater as that could provide air to combust unburned fuel in the firebox. Heater flooding is a serious condition that must be dealt with immediately.

The proper response to heater flooding is to reduce the fuel flow. This should be done as smoothly as possible, because quick and jerky changes could cause unstable flames to go out. The reduction should be done incrementally until the conditions have been corrected back to normal operation. The specific reduction amounts and pattern should be done according to the procedures set for the given heater.

There are some responses that could make the situation worse. Obviously, adding more fuel or reducing the air flow would exacerbate the problem. While it might seem that adding more air would be recommended to catch up with the fuel, this is not the proper response for a couple of reasons. If the fuel flow is too high due to over-firing or a sudden increase in the higher heating value of the fuel, increasing the air flow to the burners could cause the burners to be over-fired, leading to unstable flames including lift-off and even flame-out. Another reason not to add air is that this could cause unburned gases in the heater to suddenly start burning. Depending on where and how rapidly that occurs, this could lead to an incident.

Figure 4a Flooded, fuel rich firebox

4b Clean firebox after adjustment

Figure 5 Fuel rich flame impinging on convection section tubes

Other actions could be problematic. One is immediately shutting down a flooded heater where some burners have flamed out. While that would remove the source of the fuel, it also means that, as air continues to enter a natural draft heater, the fuel gases that were not burning may now find the air they need for combustion which could produce an undesirable incident assuming something in the heater is above the autoignition temperature for the air/fuel mixture. The stack damper and burner air registers/dampers should also not be adjusted because of the possibility of suddenly providing air to the heater.

Examples

Many flooded heater incidents have happened at start-up. In one of these incidents, a heater tripped due to flame scanner problems. The operators had difficulty relighting the burners and manually bypassed the fuel block valves without following the proper procedures because the heater temperature was dropping rapidly. Multiple relights were attempted unsuccessfully. Since the steam purge permissive was already satisfied, no steam purging was done on the last relight attempt which left the heater in a flooded condition. This led to a heater over-pressure incident. There were no injuries but significant equipment damage.

In another start-up incident, unburned fuel accumulated in a heater due to a burner flame-out which caused the heater to flood. That excess fuel was ignited during an attempt to light another burner just being brought on. There were no injuries but significant heater damage.

In another start-up incident after a routine shutdown, burners were being brought on but the air registers were not properly adjusted

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as the firing rate increased. This caused the burners to huff and the heater to be flooded with fuel. An operator suddenly opened an air register that provided air needed to combust unburned fuel in the heater. This caused an overpressure incident that included a fatality, injuries, and significant equipment damage.

In still another start-up flooding incident, the fuel gas quality varied significantly during start-up which caused both the pilots and the burners to be extinguished, filling the heater with unburned fuel. The heater was improperly purged before attempting to relight the pilots. Flammable gases in the flooded heater were ignited by a torch used to relight the pilots. There were some minor injuries and very significant equipment damage from the resulting over-pressure incident.

In an incident during normal operation, a furnace huffed so loudly that operators could hear it from some distance away. They were approaching the heater when it suddenly over-pressured. No persons were injured but one side wall of the cabin heater blew out. It was determined the burners were starved for air and became unstable. Not enough air was provided for the given fuel flow which caused the coil outlet temperature to drop. This caused the fuel control system to increase the fuel flow which worsened the problem. The heater had both O_2 and CO sensors on it which both read low. However, the previous shift failed to notify the operators the CO sensor was malfunctioning and needed repairs. The operators unknowingly relied on that false low reading, otherwise they may have diagnosed that the heater was flooded and not approached it under those conditions.

Figure 6 shows the results of an incident in a vertical cylindrical furnace which had a transient increase in fuel heating value, causing the heater to run out of air and become flooded. This led to an over-pressure incident where four people were injured and the equipment was significantly damaged.

Figure 6 Heater incident resulting from flooding (*Courtesy of NOWnews*)

There are some conditions that make heater flooding more likely. Large and regular swings in fired heater duty increase the odds of flooding. Significant variations in fuel heating value make it more likely that a heater will run out of air. Stack dampers and burner air dampers/registers that are fixed or manually operated make it more difficult to keep up with rapidly changing conditions. Air-limited heaters are more susceptible to flooding. Delayed sensor response times for measurements such as excess O_2 and combustibles make it more difficult to correct for conditions that could lead to flooding.

Prevention

There are many things that can be done to minimise the chances of flooding a heater. Heaters should be adjusted in advance of major fuel changes such as spikes in the heating value. Instruments should be properly calibrated and maintained to ensure accurate measurements. BMSs include flame detection devices to shut down heaters automatically during flame-outs. Alarms may be added to warn of potential flooding conditions such as high fuel pressure, low excess O_2, high combustibles, or a sudden drop in coil outlet temperature.

Heater flooding is a very serious condition that must be dealt with properly and quickly. Suitable procedures must be in place and followed. Operator training is critical to ensure appropriate actions are taken to prevent flooding and to respond to a flooding condition.

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Realities of heat flux in fired heaters

Uneven radiant heat flux distribution is a major cause of poor reliability in refinery fired heaters

GRANT NICCUM and STEVE WHITE
Process Consulting Services

Fired heaters in refinery heavy oil service are common limits to unit throughput and run length. Aside from cases where a heater is simply at maximum firing, many units are limited by poor heater reliability. Unreliable heaters tend to begin coking rapidly at start-up and require frequent decoking to lower pressure drop and tube metal temperatures. In crude/vacuum, FCC, delayed coker, and many other units, maximising heater reliability extends run length and increases profitability.

Fired heaters coke due to high oil temperature and residence time. Reliable heaters that meet run length expectations are designed by optimising the heater layout and the process side mass velocity. When it comes to heater sizing and layout, radiant section heat flux is one of the most important parameters. Excessive radiant tube peak heat flux is a common cause of radiant tube coking. Peak radiant heat flux is listed on the API heater datasheet, but does the datasheet number really reflect reality? Specific heater layout parameters can heavily influence the answer to this question, and analytical tools are available to explore the question during the design process to avoid surprises at start-up. These same design parameters and analytical tools also provide critical insights into practical revamp solutions for existing problem heaters.

Definition of heat flux

In the context of fired process heaters, heat flux is the amount of heat absorbed through the heater tubes per unit outside surface area. Heat flux is typically expressed in units of kcal/h-m^2 (BTU/h-ft^2). For fired heater design and evaluation, it is typical to discuss the heat flux for a specific section rather than for the heater as a whole. For example, the radiant section average heat flux is the total duty absorbed in the radiant section divided by the total radiant tube outside surface area.

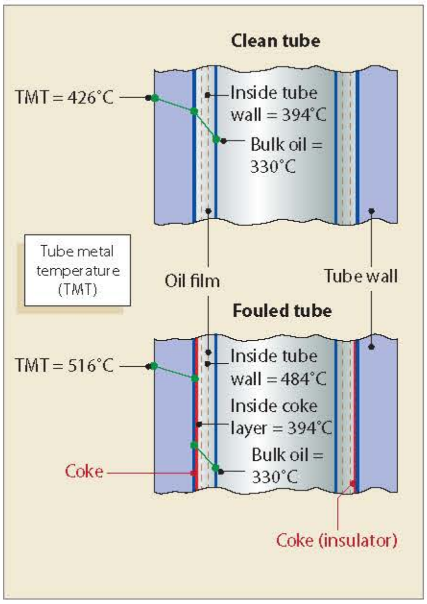

Figure 1 Clean and fouled heater tube cross-sections

While average heat flux is a useful concept for high level heater design and evaluation, it does not capture the harshest conditions, which are better represented by 'peak' heat flux. Peak heat flux represents the maximum heat flux in a specific heater section and can be used to calculate maximum expected oil film and tube metal temperatures (TMT).

Many heaters are specified with a maximum allowable radiant section average heat flux. Average heat flux specifications are useful because the calculation is simple and, for a given heater design, peak flux varies proportionally with average flux. For well-designed heaters, average heat flux is a good gauge of likely reliability, along with process side mass velocity (not discussed here). However, in some cases the specific heater design (geometry, burner selection, and so on) leads to peak heat fluxes that are significantly higher than expected. When this happens, heaters can have severe reliability problems at average fluxes that might normally be considered safe.

Consequences of high heat flux

Two major crude heater problems associated with high oil temperatures are cracking and coking. As oil temperature increases, the oil tends to crack and produce light ends and off-gas, and it can also form hard coke attached to the inside tube walls. The highest oil temperatures in a fired heater occur in the oil film at the inner wall of the tubes (see **Figure 1**). The temperature at the inner tube wall, $t_{w,i}$, can be calculated using **Equations 1** and **4. Equation 4** shows that the temperature rise across the oil film is directly proportional to the heat flux. As heat flux increases, so does the likelihood of coking and cracking:

Tube inside wall temperature

$$t_{w,i} = t_b + \Delta t_f \qquad [1]$$

Tube outside wall temperature (clean)

$$t_{w,o} = t_b + \Delta t_f + \Delta t_w \qquad [2]$$

Tube outside wall temperature (fouled)

$$t_{w,o} = t_b + \Delta t_f + \Delta t_c + \Delta t_w \qquad [3]$$

Oil film temperature rise

$$\Delta t_f = \frac{q * D_o}{D_i * h} \qquad [4]$$

Tube wall temperature rise

$$\Delta t_w = \frac{D_o * q}{2 * k_w} * \ln\left(\frac{D_o}{D_i}\right) \qquad [5]$$

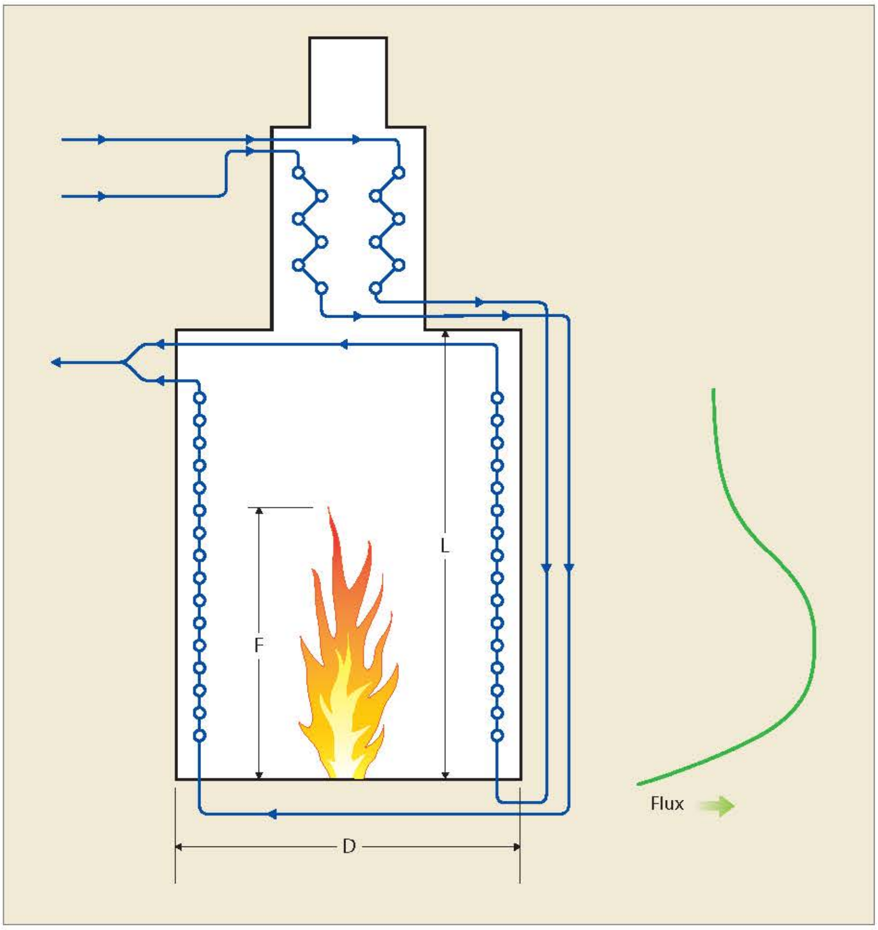

Figure 2 Heat flux distribution and firebox dimensions

Coke layer (fouling) temperature rise

$$\Delta t_c = \frac{D_o * q * f_c}{D_i} \quad [6]$$

Many refinery heaters operate against limits on maximum TMT in the radiant tubes. Building on the equation for the inside wall temperature, **Equations 2** and **5** allow for the calculation of the outside tube metal temperature for a clean tube. Adding a term to incorporate a fouling factor allows for calculation of the outside metal temperature of a fouled tube (**Equations 3** and **6**). For crude heaters, typical design fouling factors are in the range 0.0012-0.0020 h-m^2-°C/kcal (0.006-0.010 h-ft^2-°F/BTU) which roughly corresponds to the thermal resistance of 3-6 mm (⅛-¼ in) of coke thickness.

Determining maximum heat flux

Most commercial fired heater modelling software is based on the assumption of a 'well-stirred' firebox, meaning that the flue gas temperature is uniform throughout. Well-stirred firebox models do not account for firebox/burner geometry or flame characteristics. By assuming a constant flue gas temperature and calculating the heat transfer to each radiant tube in one or more segments, these programs iteratively solve for the average heat flux of each tube. In the process, they must also solve for the process side bulk temperature, internal heat transfer coefficient, film temperature, fouling ΔT, and outside tube metal temperature for each tube segment.

Once the average heat flux for a radiant tube in a well-stirred firebox is known, the ratio of peak radiant heat flux to average radiant heat flux around the circumference of the tube, F_c, is a geometric function of the tube layout and the tube centreline spacing. For a single row of tubes with typical tube spacing of twice the tube outside diameter, F_c is about 1.8 for single fired tubes and 1.2 for double fired tubes. This implies that, for the same peak heat flux, double fired heaters can be designed for 1.8/1.2 = 1.5 times the average heat flux and thus less radiant tube surface area.

In reality, flue gas temperature is never uniform throughout the fire box. Hot flue gas tends to flow upwards in between the tubes while colder flue gas flows downward between the tubes and refractory. The recirculating flue gas at the heater floor may be only 535°C (1000°F) while the flue gas entering the convection section (bridgewall) is over 790°C (1450°F). Burner heat release is not instant and occurs over the length and volume of the flame. In addition to the circumferential heat flux distribution around the tubes (F_c), there is in reality a further ratio of peak-to-average heat flux along the height of the firebox (F_L), with the peak heat fluxes typically occurring near the middle of the burner flame height (see **Figure 2**). Many software programs fail to account for longitudinal peak heat flux, which can result in under-prediction of actual peak heat flux by 50% or more.

Given the reality of non-ideal firebox conditions, actually achieving peak heat fluxes (and film temperatures, and tube metal temperatures) near those predicted by commercial heater software requires designing heaters within a proven envelope. Some simple rules of thumb for heater design help to keep heaters in a range where well-stirred firebox models provide good predictions of overall heat transfer and peak heat flux. **Table 1** presents several critical design parameters and approximate limits to stay within the bounds of the well-stirred firebox assumption in standard heater models.

L/D is essentially the firebox aspect ratio. L can be taken as the firebox height, and typically refers to the length of tubes in a vertical cylindrical heater. D can be taken as the heater cell width, and typically refers to the diameter of the tube circle in a vertical cylindrical heater.

F/L is a ratio of the flame height to the firebox height. Many refiners have had problems with high F/L ratios (approaching 1) when they transition to low-NOx and ultra-low NOx burners with longer flames. As F/L approaches 1, flame impingement at roof tubes or shock tubes becomes likely. Very low values for

F/L can result in an over-concentration of heat at the bottom of the heater with short, wide flames that may impinge upon the tubes.

Floor flux is the total heater floor burner heat release divided by the heater floor area. High floor flux can result in poor flue gas recirculation in the firebox and cause high NOx and flame impingement problems.

Burner-to-tube spacing can be defined in several ways, but here it refers to the distance from the burner centreline to the centreline of the nearest tube divided by the burner's design heat release. Having burners too close to the tubes increases the likelihood of radiant hot spots on the tubes.

When heaters operate outside of the bounds established in **Table 1**, the peak-to-average heat flux ratio can increase rapidly. If actual peak heat flux is higher than the predicted peak heat flux, then oil film temperatures and tube metal temperatures will be higher too. Furthermore, higher peak heat flux also means that the ΔT across any coke layer will be higher than predicted.

The guidelines presented in **Table 1** are not a guarantee; *every* new heater should be checked to ensure that peak fluxes are not much higher than expected due to final heater layout details. In cases where a heater is suspected of operating with uneven firebox flue gas temperature distribution, several tools exist to better predict the actual peak heat flux, TMTs, and film temperatures. One tool is a computationally simple method published by E. Talmor in the 1980s. Talmor's Hot Spot Analysis considers actual burner geometry and flame characteristics to find the maximum flux at the heater tubes. Coupled with heat transfer coefficients and bulk temperatures from a commercial heater program, accurate maximum oil film and tube metal temperatures can be calculated from the Talmor peak heat flux values.

An increasingly practical tool for evaluating non-ideal heaters is computational fluid dynamics (CFD). CFD is much more computationally intensive and time consuming than Talmor calculations, but it is quickly becoming more common and accessible. CFD has progressed to the point that it should be standard to include a full CFD model by the heater vendor, burner vendor, or a third party in the procurement cycle for every new heater.

Heater layout parameters

	Recommended minimum	Recommended maximum
L/D	1.5	2.75
F/L	0.4	0.75
Floor flux, kcal/h-m^2 (BTU/h-ft^2)	-	675 000 (250 000)
Burner-to-tube spacing	Per API	API + 0.5 m (API + 1.5 ft)

Table 1

Comparison of two crude heaters

	Heater 1	Heater 2
L/D	2.28	4.54
F/L	0.40	0.18
Floor flux, kcal/h-m^2 (BTU/h-ft^2)	871 700 (321 200)	662 600 (244 100)
Burner-to-tube spacing, mm-h/MM kcal (ft-h/MMBTU)	570 (0.47)	730 (0.60)

Table 2

Case study: coking crude heater

Two North American crude heaters processing a high percentage of Canadian bitumen provide an example of the factors discussed above. Heater 1 followed the typical design rules outlined in **Table 1** and was found to adhere to the well-stirred model assumptions and operate reliably. Heater 2 violated the rules, had extremely high peak heat fluxes that were not accounted for in the heater design, and suffered from rapid coking and very high tube metal temperatures.

Table 2 compares the design parameters for the two heaters, and **Figure 3** provides a representational comparison of the two heaters' firebox dimensions.

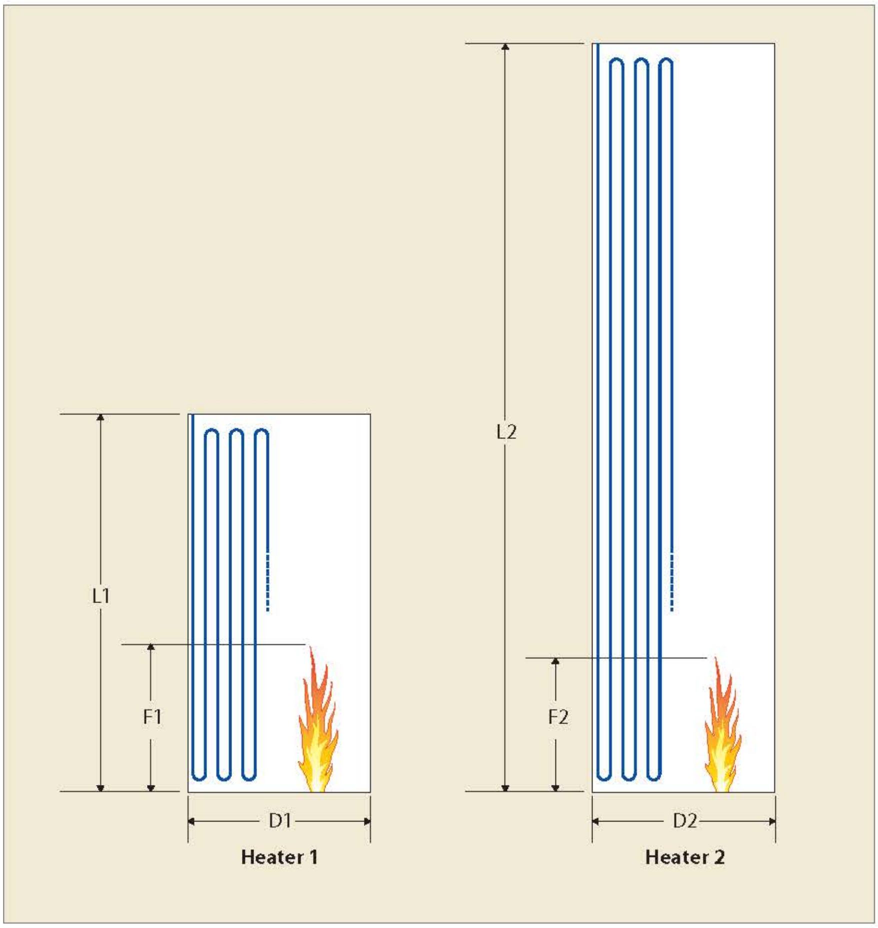

Figure 3 Illustration of heater geometry

Heat flux and temperature comparison

	Heater 1	Heater 2 Well-stirred	Heater 2 Non-ideal
Average radiant flux, kcal/h-m^2 (BTU/h-ft^2)	37 300 (13 750)	53 800 (19 830)	53 800 (19 830)
Peak radiant heat flux, kcal/h-m^2 (BTU/h-ft^2)	67 600 (24 920)	68 200 (25 140)	132 400 (48 800)
Peak inside film T, °C (°F)	394 (741)	402 (756)	463 (865)
Peak tube wall T (clean), °C (°F)	426 (799)	434 (813)	526 (979)
Peak tube wall T (fouled) fs = 0.0012 h-m^2-°C/kcal (0.006 h-ft^2-°F/BTU), °C (°F)	516 (961)	525 (977)	702 (1296)
Peak tube wall T fs = 0.0020 h-m^2-°C/kcal (0.010 h-ft^2-°F/BTU), °C (°F)	576 (1069)	585 (1085)	819 (1506)

Table 3

In Heater 2, high L/D and low F/L are the result of a narrow firebox with very long vertical tubes and relatively short flames. Simply based on inspection of **Figure 3** and the numbers in **Table 2**, it seems reasonable to expect that Heater 2 will be very hot in the bottom and much colder at the top of the firebox. This was confirmed by visual field observations and quantitative measurements such as IR scans.

Somewhat counter-intuitively, floor flux is higher in Heater 1 even though Heater 2 has a much taller firebox. In general, for similar layouts, increasing heater L/D increases the floor flux because there is less floor area per tube area. In this case, the general burner and tube arrangements of Heaters 1 and 2 are so dissimilar that a direct comparison of floor flux is difficult. However, it should be noted that floor flux for both heaters is high, which should invite scrutiny during the design process. For reference, modifying the design of Heater 2 to lower L/D to 2.75 while maintaining the general tube and burner layout would result in a floor flux of less than 450 000 kcal/h-m^2.

Table 3 compares the peak heat flux and tube metal temperatures for Heater 1 and Heater 2. Note that Heater 1 uses single fired tubes and Heater 2 has double fired tubes, so the design average heat flux for Heater 2 is about 1.5 times that for Heater 1. Two columns are included for Heater 2: one for the well-stirred 'expected' values, and a second column based on the non-ideal peak heat fluxes calculated by Talmor and CFD. Heater 1 oil and metal temperatures are also shown in **Figure 1** for reference.

Based on the calculated peak heat flux of 132 400 kcal/h-m^2 (48 800 BTU/h-ft^2), the heater tube design metal temperature would have to be in the region of 720°C (1330°F) minimum, which is not a practical target for design. Furthermore, a calculated oil film temperature of 463°C (865°F) is unacceptable for Canadian bitumens, which require oil film temperatures to be minimised to avoid excessive cracking and coking.

It seems clear that Heater 2 would not have been built as designed if a more detailed peak heat flux analysis were performed during the detailed engineering phase of the project. In fact, the unusual values in **Table 2** should have triggered a detailed review during the early stages of the heater design.

In operation, brand new Heater 2 was a disaster. In less than a year, tube skin temperatures began to exceed the tube design temperature of 600°C. Additionally, tubes bowed due to uneven heating, and supports in the bottom of the heater failed due to extremely high temperatures. Without major modifications, Heater 2 would not run more than about six months between shutdowns for decoking and repairs.

Conclusion

Uneven radiant heat flux distribution is a major cause of poor reliability in refinery fired heaters. The simple guidelines presented here can help heater designers avoid excessive peak heat flux that leads to rapid coking and high tube metal temperatures. For troubleshooting purposes, some simple equations (**Equations 1-6**) can be used to estimate the actual peak heat flux as a 'sanity check' against complex CFD evaluations that can seem inscrutable. Understanding the importance of firebox geometry and actual tube and burner configurations should foster intuitive operations, design, and troubleshooting of fired heaters to maximise reliability. Finally, although this paper has focused on the flue gas side, do not forget the process side. Process side mass velocity, residence time, and film temperatures are all critically important variables that are not covered here.

Glossary

Symbol	Term
D	Firebox cell width, m (ft)
D_i	Tube inner diameter, m (ft)
D_o	Tube outer diameter, m (ft)
F	Flame height, m (ft)
f_c	Fouling factor (coke), h-m^2-°C/kcal (h-ft^2-°F/BTU)
F_c	Circumferential peak-to-average heat flux ratio
F_L	Longitudinal peak-to-average heat flux ratio
h	Heat transfer coefficient, kcal/h-m^2-°C (BTU/h-ft^2-°F)
k_w	Tube wall thermal conductivity, kcal/h-m-°C (BTU/h-ft-°F)
L	Firebox height (tube length), m (ft)
q	Heat flux, kcal/h-m^2 (BTU/h-ft^2)
T_b	Bulk fluid temperature, °C (°F)
$T_{w,i}$	Inner tube wall temperature, °C (°F)
$T_{w,o}$	Outer tube wall temperature, °C (°F)
Δt_c	Fouling factor (coke) temperature rise, °C (°F)
Δt_f	Film temperature rise, °C (°F)
Δt_w	Tube wall temperature rise, °C (°F)

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Recovering hydrogen and LPG from off-gases

A practical investigation devised the most effective combination of available separation technologies to recover valuable products from refinery off-gases

MARCELO TAGLIABUE
Air Liquide

Some 66% of world production of hydrogen, estimated at 70 million tonnes, is used as an input to oil refining, ammonia production, methanol and, in recent years, in the development of engines that run on hydrogen. In the last case, the use of fuel cells completely eliminates polluting emissions. This circumstance makes hydrogen the cleanest existing fuel.

Currently, the best known and developed production methods are:

- **Electrolysis of water**: currently limited to 5% of hydrogen production. It is achieved by dissociating the water molecule into its components (hydrogen and oxygen) using electricity and is known as green hydrogen.
- **Reformed with water steam from natural gas**: this represents 95% of current production worldwide. It is a thermochemical process which requires high temperatures and subsequent purification of the final stream obtaining the so-called grey hydrogen. If the CO_2 produced is captured, you are in the presence of blue hydrogen.

Hydrogen is an important and expensive utility in oil refining and petrochemicals processing. It is required for many operations such as hydrotreating (where it is used to remove impurities such as sulphur from streams and to hydrogenate aromatics and olefins) and hydrocracking (where it breaks down large hydrocarbons into smaller, higher value molecules). The main consumers are the refinery processes that consume H_2 such as hydrotreaters and hydrocrackers.

As refinery product specifications become stricter to meet environmental requirements, demand for hydrogen from the refinery has continuously increased to supply hydroprocessing units. Further improvements in combustion qualities, such as cetane, also require more hydrogen.

Typical conditions of refinery off-gases

Typical ROG source	Pressure, barg	vol% H_2
Delayed coker off-gas	~10	15-30
Hydrocracking HP off-gas	40-125	60-85
Hydrodealkylation off-gas	25-28	50-75
Catalytic reforming	20-30	68-88
Catalytic cracking off-gas	~20	~18
Hydrotreater off-gas	20-50	60-80

Table 1

Global economic trends toward the use of heavier crudes results in a higher need for hydroprocessing and thus a higher need for hydrogen.[1]

Global economic trends toward the use of heavier crudes results in a higher need for hydroprocessing and thus a higher need for hydrogen

For many refineries, the hydrogen byproduct produced by gasoline reforming has been able to supply enough, but restrictions to the addition of BTX to gasoline hydrogen mean that production by reforming gasoline has diminished.

Nowadays, full conversion refineries generally require more hydrogen.

This article explores processes used to recover hydrogen and hydrocarbons in refineries and petrochemical processes, and how these techniques can be optimised and adapted to different circumstances. In addition, some innovative techniques to improve recovery and increase the capacity of the units mentioned are described.

There are several possible sources of hydrogen. Typically, most make-up hydrogen in refineries is supplied from gasoline catalytic reforming. Catalytic reforming produces aromatic compounds from the cyclisation and dehydrogenation of hydrocarbon molecules and is used to increase the octane number of gasoline. At the same time, large amounts of hydrogen are produced as a byproduct. Since the amount of BTX added to gasoline is limited, the charges to these units are decreased in the same way that hydrogen production is decreased.

If the hydrogen from catalytic reforming is insufficient, additional hydrogen may be supplied by building a hydrogen plant that produces the gas either by steam reforming or partial oxidation of hydrocarbons. Alternatively, hydrogen may be imported via pipeline.

Finally, the most economical option and the one we are going to

Overview of hydrogen recovery systems

Parameter	PSA	Membrane	Cryogenic
Min. % H_2 in feed	~50	15	15
H_2 capacity, kNm^3/h	0.1-100	0.5-70	5-1000
Feed pressure, bar	10-65	15-120	10-80
H_2 prod. pressure, bar	Close to feed pressure	< 1/3 of feed pressure	Close to feed pressure
Feed pretreatment	No	Yes	Yes
H_2 purity, vol%	~99.999	98	97
H_2 recovery, %	~90	95	98
Ease of expansion	++	+++	+
Economy of scale	Moderate	Small	Large

Table 2

explore in depth is hydrogen recovery from the off-gas currents of refineries (ROG). These techniques provide the ability to recover hydrogen from streams that would otherwise end up in the fuel gas system or in the flare. And in the event that this recovered H_2 is still insufficient to meet a refinery's needs, the investment necessary for the acquisition of a steam methane reformer (SMR), a partial oxidation process (POX) or an over-the-fence contract with a third party would be considerably less.[2]

The amount of hydrogen from the main ROG stream in a refinery may be seen in **Table 1**. The remaining streams are hydrocarbons ranging from CH_4 to C_{6+}, some of which represent a benefit to the refinery and can also be recovered.

The amount of hydrogen in the fuel gas system of a refinery can reach 40%. In this way ,the recovery of hydrogen also contributes to a fuel gas with more kcal/Nm^3, which enables better furnace operation.

Units used to recover hydrogen and LPG

Membrane and pressure swing adsorption (PSA) units are mainly used to recover H_2 from the various waste gases in the refinery. Cryogenic recovery is also feasible, but high complexity in the operation of cryogenic units makes them less desirable, unless recovery of light hydrocarbons (ethane, ethylene) is also desired.

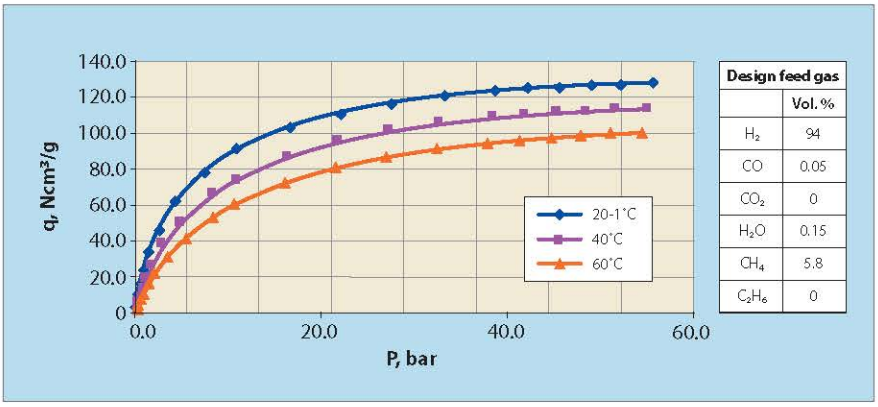
Table 2 shows the factors and criteria that affect the selection of one technique or another.

As we can see, many factors influence the decision-making process. Without underestimating other factors, the pressure of the ROG, the percentage of hydrogen it contains, the need for pretreatment, and the pressure of the recovered hydrogen are the most significant.

PSA – adsorption mechanisms

Three mechanisms are used to carry out mixture separations in PSA. They are selective speed, particle size, and selective balance.

In the first case, the force that drives separation is the difference in the rate of adsorption, desorption, and diffusion of the components to be separated. In this way, the flow of the adsorbate inside and outside the adsorbent controls the process.



Design feed gas	
	Vol. %
H_2	94
CO	0.05
CO_2	0
H_2O	0.15
CH_4	5.8
C_2H_6	0

Figure 1 Adsorption isotherms/design feed composition

In the second mechanism, separation of the feed gas is based on the size of the molecular component relative to the pore of the adsorbent. Large molecules are simply excluded from the adsorbent, while small or narrow ones are adsorbed. The pore size is what determines which molecules are adsorbed and which are not.

In the last model, the affinity for the adsorbent or the greater or lesser adsorption force of one component with respect to another is what controls the separation.

To determine the efficiency of a PSA system, in addition to the mechanisms seen, the following aspects, among others, must be taken into account: installation capacity, cycling time, loss of charge, pressure ratio, adsorber geometry, and so on. It is clear that the optimal performance of a PSA does not obey a simple work guide or predetermined recipe.

PSA – innovation and optimisation

One of our jobs was to optimise a PSA to increase its capacity and hydrogen recovery under conditions close to design. Then, because of significant changes in the feed composition, other existing assets were incorporated in order to increase hydrogen recovery.

The mechanisms that regulate the adsorption process are strongly influenced by temperature, and its variation can significantly alter product purity and process recovery. The installed PSA operates with the feed (impure hydrogen stream) at room temperature, typically 25°C, but in summer this temperature can reach 40°C.

Figure 1 shows that, because of the composition of the impurities to be separated (light hydrocarbons such as CH_4, C_2H_6), the adsorption isotherms show a strong increase in adsorption of impurities as the temperature diminishes.

A reduction in temperature causes a significant increase in purity, with a small increase in recovery.

Intending to increase the production capacity of our facility, we decided to reduce the supply temperature as much as possible within safe working values, and

Figure 2 LIN/H_2 exchanger

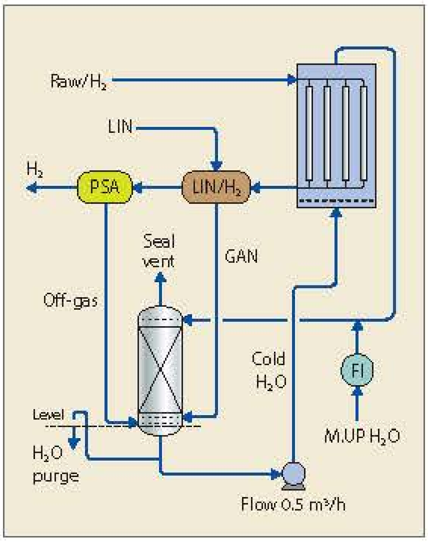


Figure 3 Optimisation of liquid nitrogen consumption

to keep it constant over time. With these measures, the purity of the hydrogen would increase and more charge could be processed.

Taking advantage of the availability of an unconventional source of refrigeration in the area (liquid nitrogen – LIN), a H_2/LIN exchanger was designed (see **Figure 2**). It was built entirely in aluminum with the purpose of maintaining the inlet temperature of the PSA at 5°C, having a nitrogen gas stream at room temperature that is used for inerting gas.

It can be concluded that with the stream quality conditions of the raw material, it has been possible to increase the processing flow of impure H_2 by around 25%, maintaining the purity conditions of the final product, and its recovery increased by 2%. Process stability noticeably improved also.

In order to optimise LIN consumption, a water recirculation system was designed, taking advantage of the particularity of dry gas from the PSA off-gas. In this way, the cold water obtained exchanges with the raw hydrogen before its exchange with LIN (see **Figure 3**).

Change of feed composition/incorporation of a membrane

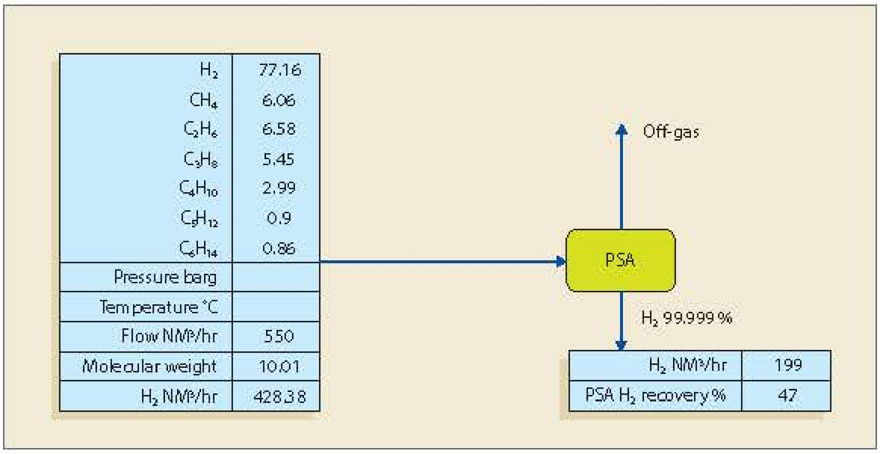
As we have previously mentioned, the present technologies for H_2 separation include PSA, cryogenic condensation, and membrane. All three processes are efficient for high hydrogen content and high pressure feeds, but are not efficient for low hydrogen content and low pressure feeds. For PSA, the inefficiency arises partly because the absorbents, including molecular sieves and activated carbons, preferentially adsorb heavy impurities. This is good if the heavy impurities are less than 50%, but not as good otherwise. When the hydrogen content in a gas mixture is less than about 50%, it is more efficient to use an adsorbent that adsorbs hydrogen instead of the heavier components. A hydrogen adsorbent that can be used in a practical separation process is not available today.

In the case of PSA systems, C_{5+} hydrocarbons and other contaminants may sorb preferentially onto the bed, both reducing the capacity of the beds to sorb the light hydrocarbons that they are intended to remove, and giving rise to serious regeneration difficulties.

This was just the second problem we had to solve in maintaining hydrogen production for our customers. The ROG available as PSA feed on heavy oil content was far from design values.

Due to important changes in the concentration of the feed to the PSA, it was not possible to maintain production of hydrogen. For this reason, we incorporated an unused membrane into the process, placing it before the PSA, in order to generate a stream that was poorer in heavy hydrocarbons that were strongly adsorbed in the PSA, making it difficult to desorb and reducing production.

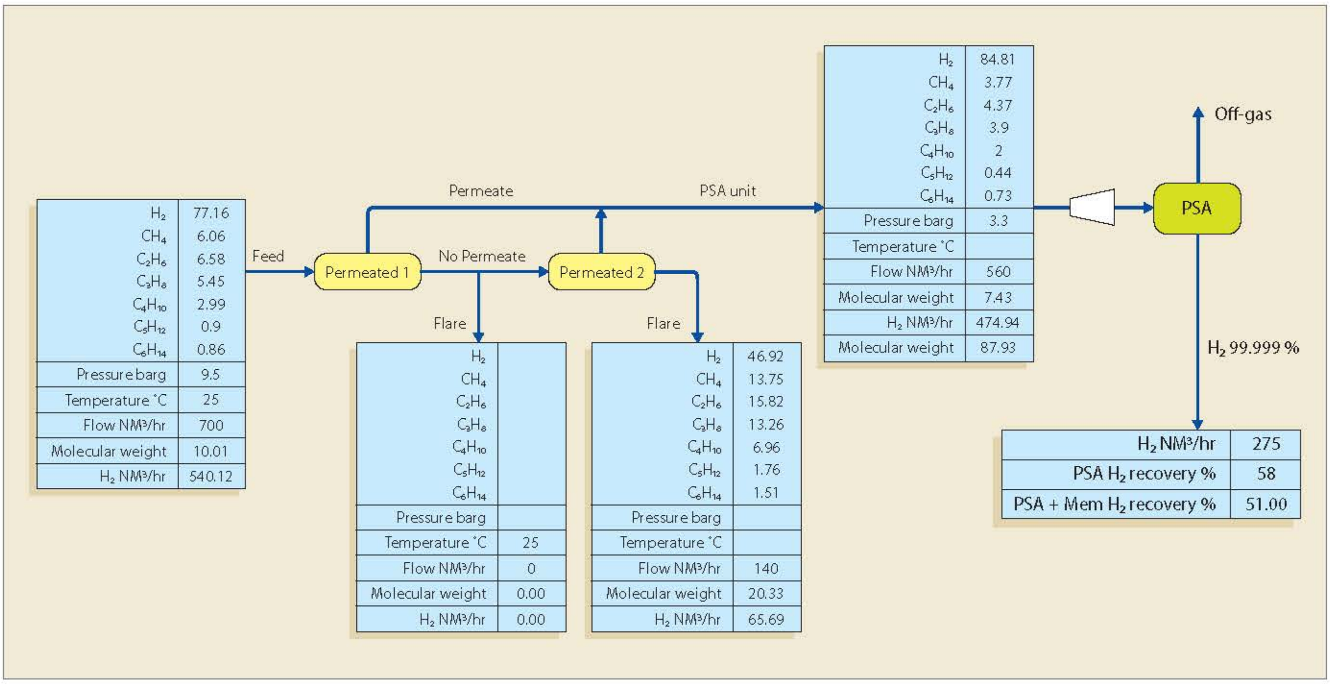
Figure 4 shows the initial conditions of the PSA with the new feed. **Figure 5** shows the improvements obtained by placing the membrane in series with the PSA. Finally, in **Figure 6** the final optimisation can be seen with cooling of the PSA supply.



H_2	77.16
CH_4	6.06
C_2H_6	6.58
C_3H_8	5.45
C_4H_{10}	2.99
C_5H_{12}	0.9
C_6H_{14}	0.86
Pressure barg	
Temperature °C	
Flow NM³/hr	550
Molecular weight	10.01
H_2 NM³/hr	428.38

H_2 NM³/hr	199
PSA H_2 recovery %	47

Figure 4 PSA recovery with heavy hydrocarbons in the feed



H_2	77.16
CH_4	6.06
C_2H_6	6.58
C_3H_8	5.45
C_4H_{10}	2.99
C_5H_{12}	0.9
C_6H_{14}	0.86
Pressure barg	9.5
Temperature °C	25
Flow NM^3/hr	700
Molecular weight	10.01
H_2 NM^3/hr	540.12

H_2	
CH_4	
C_2H_6	
C_3H_8	
C_4H_{10}	
C_5H_{12}	
C_6H_{14}	
Pressure barg	
Temperature °C	25
Flow NM^3/hr	0
Molecular weight	0.00
H_2 NM^3/hr	0.00

H_2	46.92
CH_4	13.75
C_2H_6	15.82
C_3H_8	13.26
C_4H_{10}	6.96
C_5H_{12}	1.76
C_6H_{14}	1.51
Pressure barg	
Temperature °C	
Flow NM^3/hr	140
Molecular weight	20.33
H_2 NM^3/hr	65.69

H_2	84.81
CH_4	3.77
C_2H_6	4.37
C_3H_8	3.9
C_4H_{10}	2
C_5H_{12}	0.44
C_6H_{14}	0.73
Pressure barg	3.3
Temperature °C	
Flow NM^3/hr	560
Molecular weight	7.43
H_2 NM^3/hr	474.94
Molecular weight	87.93

H_2 NM^3/hr	275
PSA H_2 recovery %	58
PSA + Mem H_2 recovery %	51.00

Figure 5 PSA recovery when adding a membrane unit

Hence it may be concluded that a PSA membrane tandem offers the possibility of obtaining satisfactory hydrogen recovery when currents with a high level of impurities are processed, mainly heavy hydrocarbons, for which the installed PSA is inadequate.[3]

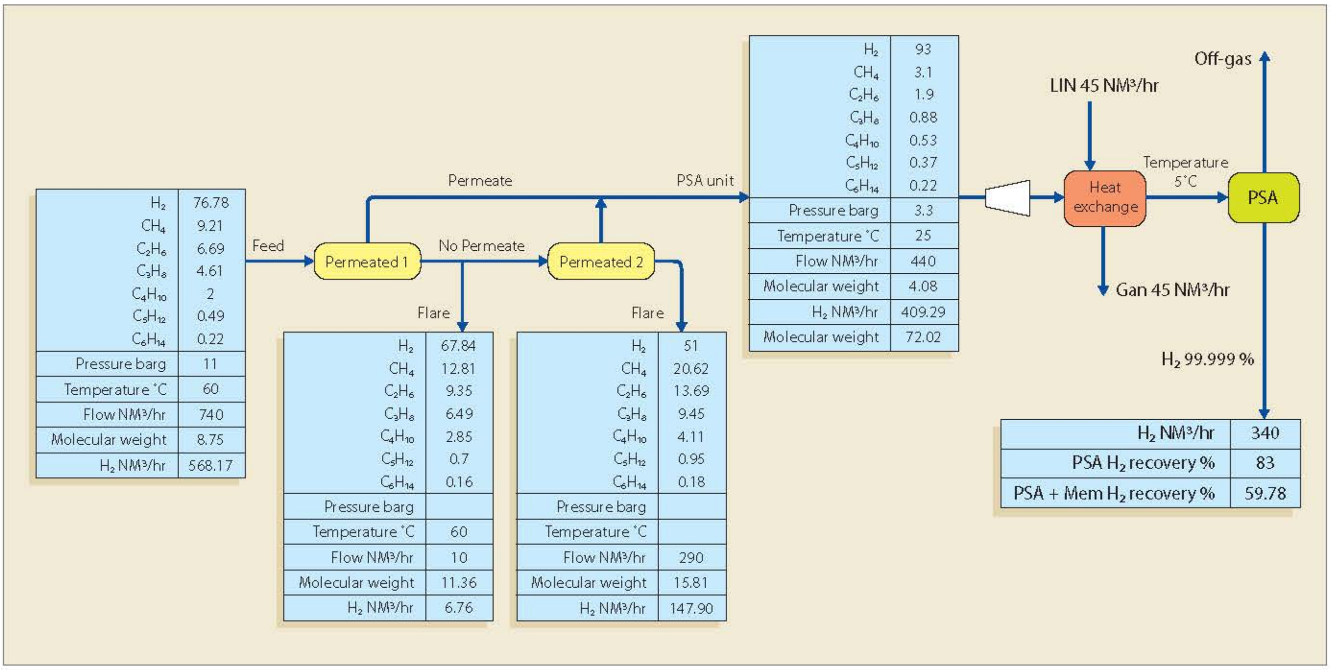
Membrane technology

Hydrogen is selectively separated from CH_4 and heavy hydrocarbons by permeation through a polymeric hollow fibre membrane. The driving force is the partial pressure difference across the membrane for hydrogen, hydrocarbons, and other impurities. H_2 is the 'fast' gas, whereas CH_4 and heavier hydrocarbons are the 'slow' gases. The pressurised feed gas enters the bundle from the shell side; the hydrocarbons stay under pressure while hydrogen is collected at a lower pressure from the fibre bore.

Benefits and drawbacks

Membrane gas separation does not require moving parts; it has a small footprint and it is a compact system; it provides operating flexibility to feed fluctuations; it demands comparatively lower energy requirements, leading to lower operating costs; it does not involve chemicals, make-up, and solvents; it is easy to start up and shut down; it requires minimal maintenance and operator attention; it allows a modular design; it requires minimal utilities; and it is easy to control.

The main drawbacks include no



H_2	76.78
CH_4	9.21
C_2H_6	6.69
C_3H_8	4.61
C_4H_{10}	2
C_5H_{12}	0.49
C_6H_{14}	0.22
Pressure barg	11
Temperature °C	60
Flow NM^3/hr	740
Molecular weight	8.75
H_2 NM^3/hr	568.17

H_2	67.84
CH_4	12.81
C_2H_6	9.35
C_3H_8	6.49
C_4H_{10}	2.85
C_5H_{12}	0.7
C_6H_{14}	0.16
Pressure barg	
Temperature °C	60
Flow NM^3/hr	10
Molecular weight	11.36
H_2 NM^3/hr	6.76

H_2	51
CH_4	20.62
C_2H_6	13.69
C_3H_8	9.45
C_4H_{10}	4.11
C_5H_{12}	0.95
C_6H_{14}	0.18
Pressure barg	
Temperature °C	
Flow NM^3/hr	290
Molecular weight	15.81
H_2 NM^3/hr	147.90

H_2	93
CH_4	3.1
C_2H_6	1.9
C_3H_8	0.88
C_4H_{10}	0.53
C_5H_{12}	0.37
C_6H_{14}	0.22
Pressure barg	3.3
Temperature °C	25
Flow NM^3/hr	440
Molecular weight	4.08
H_2 NM^3/hr	409.29
Molecular weight	72.02

H_2 NM^3/hr	340
PSA H_2 recovery %	83
PSA + Mem H_2 recovery %	59.78

Figure 6 PSA + membrane recovery when cooling the feed

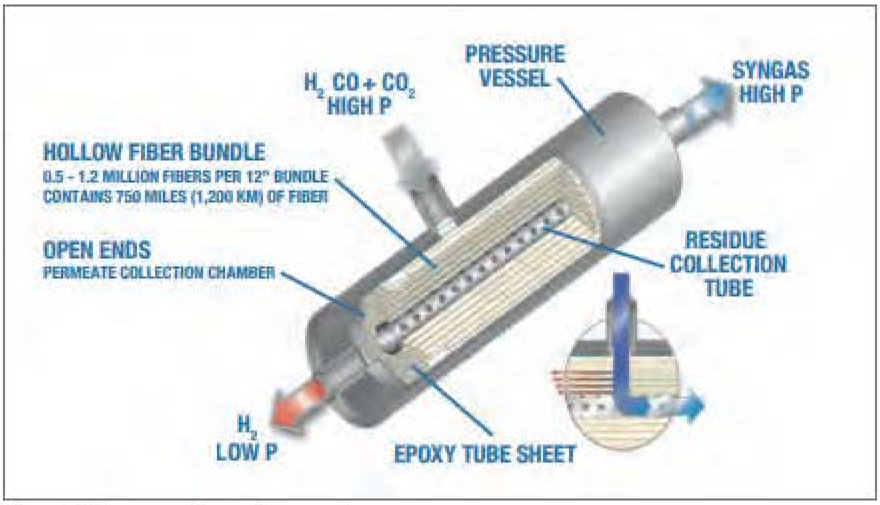


Figure 7 Diagram of a typical membrane

Hydrogen and LPG recovery

Unit	Pressure, barg	Temp, °C	Flow, Nm³/h	Destination	Composition, mol% H_2	C_1	C_2	C_3	C_4	SH_2
1- Pre-processing	0.6	40	50	FL	5	91				
2- Pre-processing	0.4	23	50	FL	3	93				
3- Hydrobon	6.0	40	100	FG	78.1	0	5	2		
4- Hydrobon	1.8	40	100	FL	10	18	32	25	15	
5- Pacol	2.2	40	480	FL	95	3	2			
6- Pacol	1.1	55	20	FL	70	10	10	5	5	
7- Platforming	0.84	0	200	FL	19	19	20	20	20	
8- H.T.N.C.	4.5	45	2000	FG	21	43	22	6	5	0,6
9- H.T.N.C.	38.0	60	200	FG	79	18	2	0.6	0.4	0.1
10- H.T.G	35.0	60	1502	FG	78	18	3	3	0.5	0.02
11- H.T.A	40.0	60	1300	FG	82	10	3	3	2	0.25

FL = Flare
FG = Flue Gas

Table 3

economy of scale due to the modular design; pretreatment of streams with particulates, organic compounds, or moisture can be difficult and/or expensive; sensitivity to chemicals can be problematic in some cases; and there is a need for electrical power for compression.

A representative diagram of a membrane is shown in **Figure 7**.

We previously discussed the basics of PSA and membrane technology. A point to consider arising from practical experience is that PSA technology offers the advantage of obtaining the required hydrogen at almost the pressure of the feed. An unfavourable point is its numerous moving parts which, if not properly maintained, begin to show faults that are detrimental to their reliability. In practice, today's PSAs are offered with one or two more adsorbers than is necessary to effect the desired recovery. The reasoning here is to have an adsorber under maintenance without disturbing normal operation. Modern technologies allow an adsorber to automatically exit or enter the system in the event of a failure in some of its components.

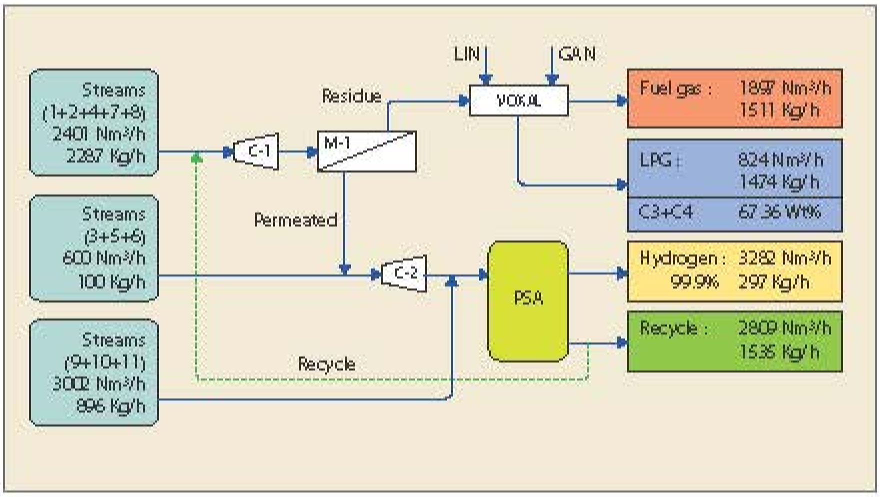


Figure 8 Cryogenic condensation + membrane + PSA (maximum recovery)

On the other hand, membranes offer the advantages of a lack of moving parts and very easy operation while, at the same time, they are easily expandable. But they offer hydrogen at low pressure, and they are sensitive to some contaminants or condensation of some species.

Recovery of hydrogen and LPG

Cryogenic condensation is a process that allows recovery of volatile organic compounds (VOC) for reuse. The condensation process requires very low temperatures so that VOCs can be condensed. Traditionally, chlorofluorocarbon (CFC) refrigerants like CFC-12 have been used to condense VOCs but, with the phasing out of these ozone-depleting substances, LIN has emerged as a viable substitute for use in the extremely low temperature process (less than -160°C).

Cryogenic condensation is a versatile process which is not VOC specific. Typically, condensation takes place with LIN as the refrigerant in a straightforward heat exchange process. Non-toxic, non-corrosive, and non-flammable, LIN is a versatile coolant with a normal boiling point of -196°C and which does not deplete ozone.

As the organic-laden vapour stream is cooled, VOCs will condense when the dew point is reached. Fluctuations in VOC stream velocity or content are easily handled by quick response controls on LIN injection. Typically, the only constraint on the VOC itself is that its freezing point should be below about -30°C; otherwise, freezing is likely to occur.[4]

Cryogenic condensation systems generally consist of one or a series of plate-fin or shell-and-tube heat exchangers. The VOC stream and the LIN stream flow through the heat exchanger counter-currently, maximising heat transfer. The VOC condenses on the shell side of the exchanger then drains into a collection tank, from which it can be recycled, reclaimed, recovered for reuse, or, at worst, accumulated for disposal.

Table 3 shows different ROG currents emanating from different processes in a refinery. In this case, the intention was to recover as much hydrogen and LPG as possible. This could not have been done with just one of the procedures described so far. For this reason, after studying several possible combinations, the best option (see **Figure 8**) was obtained. The processes mentioned above are interleaved to obtain an economically attractive result which is consistent with care of the environment since the waste is derived from the fuel gas system and the gaseous nitrogen obtained is sent to the appropriate network in the refinery.[3,5]

Conclusion

We have reviewed the three most important techniques to recover hydrogen and hydrocarbons from different ROG streams. Acquisition of these technologies makes it possible to optimise hydrogen networks and forces the refinery to evaluate its hydrogen supply system and send the appropriate hydrogen to the appropriate consumers.

The separation techniques mentioned here are generally the best, most cost-effective investments. The main key to studying the feasibility of using or optimising these techniques is to start with the assumption that not all processes need the same hydrogen purity.

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IIoT in energy optimisation

Leveraging IIoT concepts leads to a reduction in energy consumption and improved refining margin

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To some, the Industrial Internet of Things (IIoT) is just a new buzzword – but to the process industries IIoT is becoming a necessity to maintain competitiveness. Refineries are trying to cope with various market forces, many of which require improved plant performance. Over the years, refinery operation has undergone tremendous change. Due to stiff competition, there is a need to operate at higher gross refinery margin (GRM). Moreover, environmental regulations have become more stringent. Both these requirements have pushed refineries to look for available methods to reduce energy consumption. Therefore, in the past few years, the need for effective cost reduction in addition to ever more carbon-conscious operation has driven refiners to look for ways to improve the energy efficiency of their units, in particular the crude and vacuum distillation unit, as one of the few available avenues for sustainability. This has led designers as well as operators to undertake optimisation studies which increase energy efficiency.

A multiplicity of variables and parameters for this optimisation, as well as time being an important factor in implementation, makes it imperative to use IIoT to keep pace with the technological advances the world is seeing today.

The discussion in this article pertains to the benefits of using IIoT applications in energy optimisation during refinery operation. Crude and vacuum distillation unit operation is used for this discussion. The basic methodology involves a digital twin updated for crude processing using a knowledge base with the help of an optimisation tool to prepare a set of optimum operating conditions for the refinery operations team. The difference between key plant operating parameters and optimum performance is highlighted with suggestions for changes. Energy consumption is mapped with optimum values to highlight achievable benefits in terms of net refinery operating margins expressed as dollars per barrel.

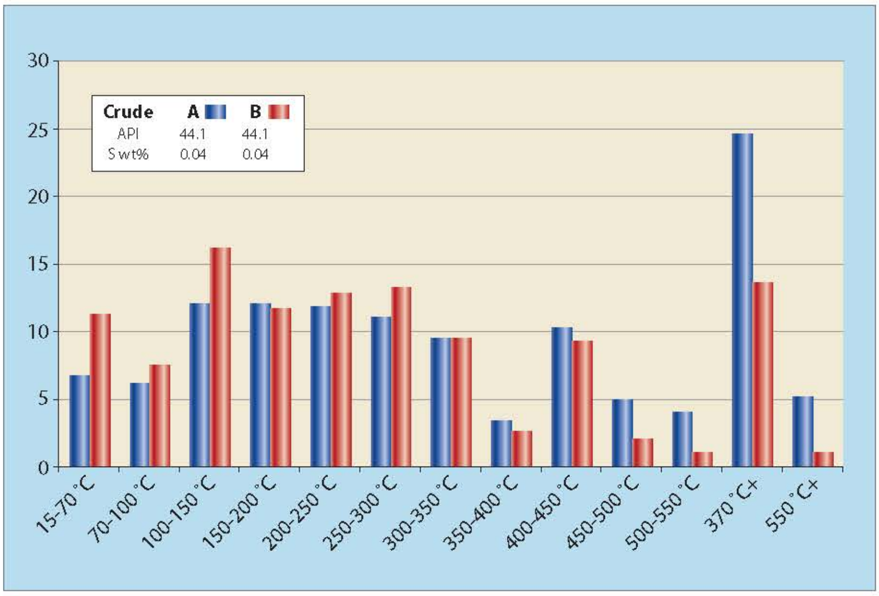


Figure 1 Differences between yields of various cuts from two crude types

Background

Refineries typically run on tight profit margins. Because of changing market scenarios and global competition, refineries are faced with the task of minimising costs and ensuring high profitability. Any opportunity to reduce operating costs is of interest to the refiner. As refineries have little control over crude and product prices, they need to rely on operational efficiency for their competitive edge. This is achieved by increasing yields and reducing energy consumption, thereby reducing operating costs and improving gross refinery margin.

Refinery processes require high energy consumption during operation in the form of fuel, steam, power, and cooling water. Therefore, minimising consumption of utilities is a primary goal. Apart from the cost of feed, energy consumption represents the major share of the operating costs.

There are many factors influencing refinery operations, including changes in the crude oil processed, economic factors related to market demand, and the processing feasibility of each unit. Even a single factor such as a change in crude oil composition can have a significant impact on product yields. As **Figure 1** shows, although both Crude A and Crude B have the same API of 44.1 and sulphur content of 0.04 wt%, there are major differences between the yields of various cuts. The yield for the 15-70°C cut is 65% higher for Crude B, whereas 370°C+ yields are 80% higher for Crude A. Therefore, optimised operation with Crude A processing

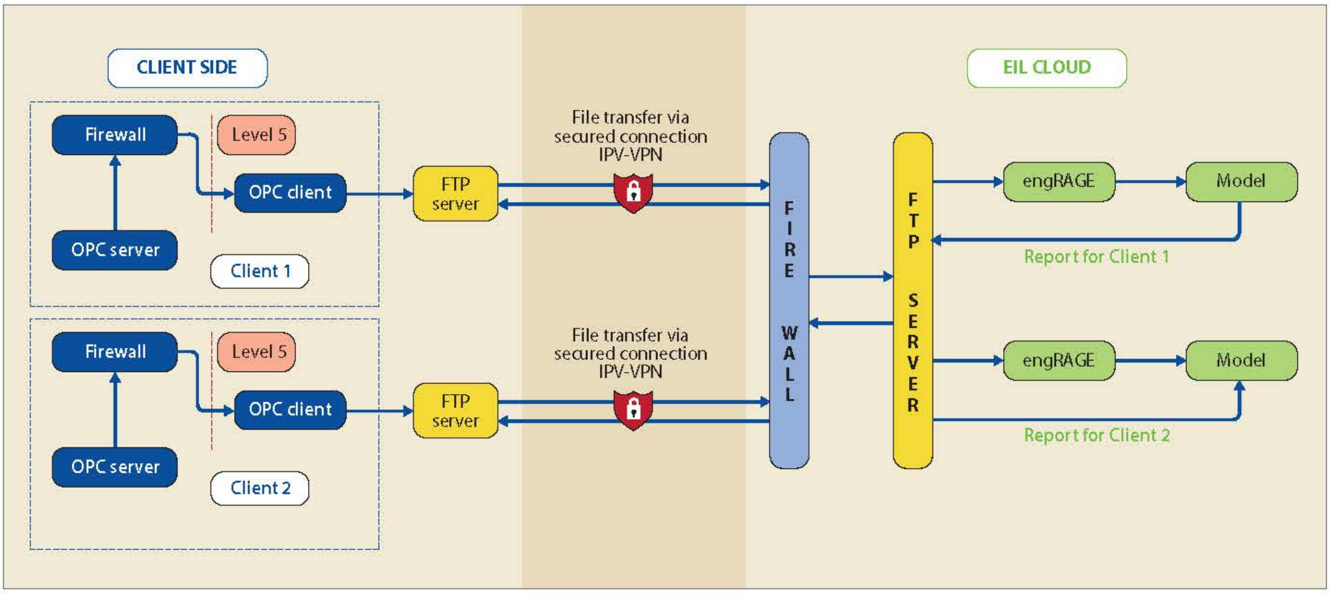


Figure 2 Architecture of an IIoT model representing a plant

would be different from optimised operation with Crude B.

Furthermore, there are many variables which can be used to optimise energy consumption, namely operating pressure, operating temperature, flow rate of streams, and so on. Because there are multiple factors influencing refinery (unit) operation, and multiple optimisation variables, IIoT can be leveraged to optimise unit and refinery operation.

The crude and vacuum distillation unit (CDU/VDU) has the highest processing capacity in a refinery. It is a highly energy intensive process representing around 20% of a refinery's total energy consumption. In terms of fuel oil equivalent, it consumes around 2% of the total crude processed to meet its energy requirement. In the present market scenario, where refinery margins are shrinking due to crude price volatility, it becomes imperative to target the crude and vacuum distillation unit for energy optimisation because its energy footprint is among the largest in the refinery.

Energy in the CDU/VDU is consumed in the following ways:

- As direct fuel in process heaters
- As steam for stripping or motive fluid
- As power for drivers

Application of IIoT helps to build an analysis solution for plant processes which uses operational data coupled with design and engineering models to suggest improvements for enhancing yield, based on a crude assay to match the refinery's configuration and market demand, and achieving energy optimisation in the CDU/VDU.

Industrial Internet of Things

IIoT is based on gathering information and automating physical processes to provide remote monitoring and operational support for plant or equipment.

IIOT targets optimisation at three levels: asset, process, and business. The asset level pertains to individual equipment such as heat exchangers, pumps, columns, and heaters. The process level is the unit level, including CDU/VDU, FCC, DCU, and so on. The business level involves optimisation at the refinery complex level. The benefits of implementing an IIoT model include:

- Improved operational support
- Improved operating efficiency
- Optimum utilisation of assets
- Reduced unplanned downtime
- Improved operational safety
- Reduced maintenance costs

Core IIoT technologies comprise smart sensors and actuators, connectivity via the internet, and a computer system or cloud with an IIoT model which includes a digital twin combined with a data historian, database, optimisation tool, and knowledge base. The digital twin is a virtual replica of a plant and its equipment.

The major constituent of a digital twin is the simulation model, which refers to using a computer program to quantitatively model the characteristic equations of a chemical process using equilibrium relationships, and mass and energy balance to predict stream flow rate, composition and properties, and the operating condition of equipment.

The knowledge base coupled with an optimisation tool can use the digital twin to gain an accurate representation of the plant over its full range of operation.

The architecture of the model is shown in **Figure 2**. The historian data and lab analysis flows from the refinery via a secure line and is captured. Data plays a key role in any plant and is a critical part of preparing an IIoT model. Accuracy of measurement and reliable instrumentation are key to process flexibility and improved process control. Confidence in the quality and the accuracy of sensor data are paramount to the success of the model. Therefore data cleaning or validation must be carried out. After reconciliation, the data is fed to a model consisting of a simulation model, equipment sizing tools, optimisation tools, and a knowledge base. Based on its analysis, a report to optimise plant operation is then sent via a secure line to the refinery.

Crude and vacuum distillation unit

Figure 3 shows a typical process flow for a conventional crude and vacuum distillation unit. Crude is first heated in a heat exchanger network using hot products and pumparound streams before entering the desalter at the desired temperature. Water is mixed with crude as it enters the desalter to remove water soluble salts from the crude. The desalted crude enters another heat exchanger network and receives heat from hot streams. The preheated crude is flashed in the preflash drum. The function of a preflash device (either drum or tower) is simply to remove lighter components of the crude before it enters the crude heater. The preflashed crude enters another heat exchanger network before entering the crude heater.

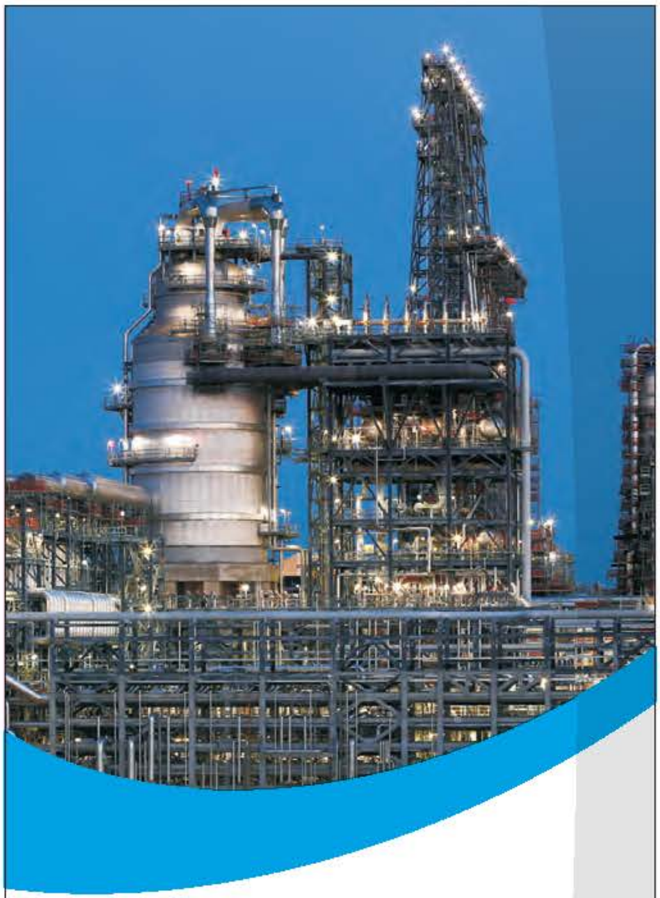
Partially vaporised crude from the heater is fed to the flash zone of the atmospheric column. The vapour from the flash zone travels upwards in the column, whereas liquid falls to the bottom of the column. The vapour is then fractionated into distillate products such as naphtha, kerosene, and diesel in the upper section of the column. To recover heat at different temperature levels, the heavy naphtha, kerosene, and diesel pumparound circuits are used along with the overhead condenser.

The distillate products withdrawn from different trays of the column are then stripped by steam in their respective side strippers to remove lighter components and meet (ASTM D-86) distillation specifications. Liquid falling from the flash zone is stripped out using steam at the bottom of the column to remove lighter, diesel-range material from the residue.

The residue from the atmospheric distillation column is fed to the vacuum heater along with the coil steam. Partially vaporised crude from the heater enters the flash zone of the vacuum column. The vapour from the flash zone is then fractionated into distillate products such as vacuum diesel, light vacuum gasoil, and heavy vacuum gasoil. The liquid from the flash zone is stripped using steam at the bottom.

Heat from the vacuum column at different temperature levels is recovered using the vacuum diesel, light vacuum gasoil, and heavy vacuum gasoil pumparound circuits. The combined flow of pumparound and product is taken from the specific column chimney tray and cooled to the desired pumparound return temperature. The combined stream is then divided into product and pumparound streams. The pumparound stream is returned to the upper section of the column. The product stream further exchanges heat with the cold streams and is finally cooled by exchanging heat with cooling water in an exchanger to attain the desired rundown temperature.

As **Figure 3** shows, energy in the form of fuel is used in the crude and vacuum heaters, stripping steam in the columns, coil steam in the vacuum heater, motive steam in the ejectors, and power



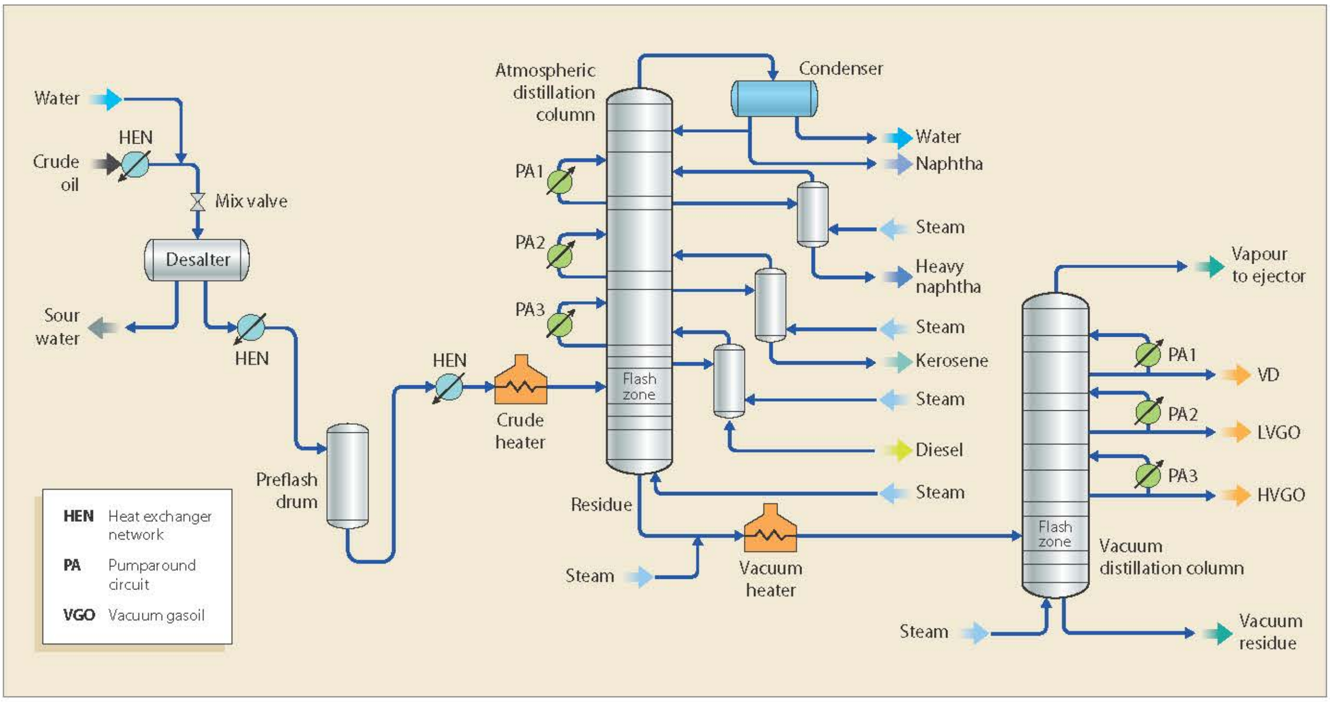


Figure 3 Schematic of a conventional crude and vacuum distillation unit

in the pump drives. The objective of the IIoT model is to minimise energy consumption while meeting product yields and their specification requirements.

Energy optimisation case study

In the CDU/VDU, energy is consumed in the form of fuel, steam and power. Optimisation is be carried out for each of these utilities. Fuel consumption in the furnace is a significant component of the overall energy requirement. Therefore, even marginal optimisation in fuel consumption has an impact on GRM.

Optimising fuel consumption in the furnace can be achieved by many means. These include:

- Recovering more heat from the column by optimising pumparound duties; related to design
- Reducing fouling in the preheat exchangers; related to predictive maintenance
- Optimising excess air level; related to heater operation

Optimisation of pumparound duties

Pumparound duty affects the preheat temperature, that is the inlet temperature of the furnaces. Hence it is a key parameter for fuel consumption in the furnace. Increasing the preheat temperature by 1°C may lead to a yearly saving of about 450 tonnes of fuel oil in a 9 million t/y crude furnace. However, increasing the crude preheat temperature to reduce the fired heater duty and save energy depends on more than just increasing pumparound duty. Other factors influencing the crude preheat temperature include exchanger network configuration, distillation system design, crude hydraulics, exchanger fouling, fired heater operation, and so on.

There is a need to establish that the existing preheat network is able to accept higher duty. Increasing pumparound duty leads to higher pumparound flows. This results in a higher pressure drop in the pumparound exchanger circuit. The pumparound pump needs to be adequate to handle higher flow and head requirements. Exchanger fouling, existing equipment mechanical limits, and other peculiarities of an existing crude unit also must be checked. Crude type affects the crude preheat temperature and the exchanger network solution. Heavy crudes have higher viscosity, reducing preheat temperature. Some crudes may be more difficult to distil than lighter crude oil blends.

Therefore, the pumparound duty which constitutes the flow rate and temperatures of the pumparound is crucial and should be optimised according to crude type, unit throughput, and separation requirements from the unit, network design, fouling condition and pump hydraulics.

The complexity of these interlinked variables and parameters, for optimisation in the shortest possible time, makes it imperative to use an IIoT model.

Reducing fouling in the preheat exchanger

The preheat train, a network of heat exchangers, is targeted to recover about 60% of the energy required to heat crude oil to the furnace outlet temperature by utilising heat available from hot streams from the CDU/VDU column.

These heat exchangers become fouled during service, reducing their heat transfer capacity. This results in higher furnace duty. Fouling also increases hydraulic resistance, thereby impacting power requirements.

There are typically around 40 exchangers in a preheat train. Fouling in any one or a few of them would result in a reduction in inlet temperature to the heater, resulting in higher fuel consumption.

Proper analysis is required to find the exchanger(s) with increased fouling. Normally, temperature measurement is available across each exchanger in the DCS and this is available for analysis. Based on crude assay information and operational data, the process fluid flow rate to each exchanger, along with its operating properties, is available. Using this information with the geometry of an exchanger, fouling can be estimated and compared with a normal or design value of fouling. This analysis can be carried out for all exchangers in the preheat train. Therefore, captured plant data and exchanger analysis as part of an IIoT model can be utilised to predict and schedule the cleaning of fouled exchangers.

An important aspect connected to the preheat train is to ensure the proper desalting temperature. The desalter is critical equipment for controlling corrosion in the crude unit. The performance of the desalter depends on crude oil properties, wash water flow rate, and desalter temperature. The desalter analyser within an IIoT model can assist the refiner in desalter operation along with other factors. Improper operation of the desalter can also lead to increased fouling in the preheat exchangers.

In certain designs of crude unit, the crude column overhead condenser is part of the preheat train. Crude entering these exchangers to exchange heat with crude column overhead vapours must be at optimum temperature. If the temperature is high then sufficient heat recovery will not happen. Too-low temperatures result in a reduction of the tube wall temperature below the water dewpoint of the overhead vapours. This could result in corrosion due to acid formation. A preheat analysis can predict this condition and guide the refiner in resetting the operation.

Optimising excess air level

Furnaces in crude and vacuum distillation units are normally designed for an efficiency greater than 90%. Based on fuel composition specified during the design stage, the design air flow can be fixed. However, actual fuel composition during operation may change depending on various operating scenarios in the refinery. Based on actual fuel composition and other process parameters, excess air levels can be optimised. This helps to reduce the gap between design efficiency and operating efficiency.

Conclusion

A refinery operating with the crude slate for which it was designed is an ideal scenario. In today's volatile environment, refiners must shift operations to adapt to ever-changing demand, and to do so with an increasingly remote workforce.

Refinery operations have never taken full advantage of the data they capture. This data, along with knowledge of equipment and optimisation methodology, can be the basis of a powerful tool.

IIoT is a synergy between measurement, digital twin (simulation), and knowledge base. Application of IIoT in a refinery helps to increase operational efficiency and can be applied at various levels: asset, process, and business.

Taking the crude and vacuum distillation unit as a case study, it can be seen that there are three main utilities which constitute energy consumption. Each of these is affected by various parameters which in turn depend on many factors. Optimisation of plant operation is achieved through analysis of each parameter along with all of its factors. This can be accomplished effectively by an IIoT model. Since each plant is unique, the IIoT model must be tailor made.

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SAE
30%
Aromatic Technology
ACN
S-ACT
Organic Materials
PX
SSBR
ART
ODB
LHTA
LECT
OCC
S Zorb
SERT
MTO
CCR
COAT
SINOPEC TECH
FOCUSING ON
UPGRADING AND OPTIMIZATION

SMR for fuel cell grade hydrogen

Affordable and sustainable production of blue hydrogen is key to the successful use of fuel cells in transportation

KALPANA GUPTA, ISHITA AGGARWAL and MARUTHI ETHAKOTA
Technip India

Worldwide, the transport sector is one of the significant contributors to greenhouse gas emissions. In 2018, global CO_2 emissions increased by 2% worldwide and this has focused attention on decreasing these emissions by the transport sector.

Still, there is a negligible contribution of renewable sources to fuel the transport sector. Among alternative fuels, hydrogen is emerging as a promising solution to decarbonise transport, while in the power sector renewable energy has already taken a good share, but hydrogen's share is negligible.

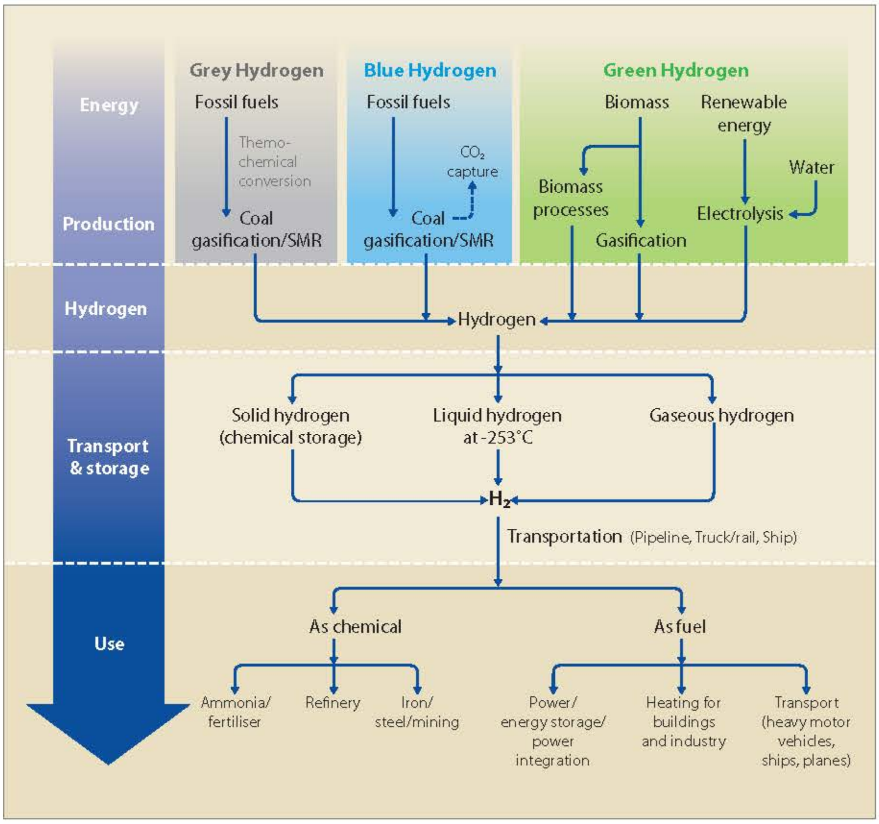

Figure 1 Complete life cycle of hydrogen

Complete cycle of hydrogen

The complete chain of hydrogen production, transport, storage, and use is shown in **Figure 1**. Hydrogen is produced mainly via three platforms: thermal processes, electrolysis, and biological processes. Traditionally, hydrogen is produced from fossil fuel by coal gasification and steam reforming. Globally, 48% of hydrogen is produced by natural gas steam reforming and 30% by oil reforming. Of the remainder, 18% is generated by coal gasification, and only 1% of hydrogen is produced by green processes.

Produced hydrogen is stored in gaseous/liquid or metal hydride form. Hydrogen need not be stored and transported in the case of on-site generation and consumption, as in a refinery or fertiliser plant. At the same time, storage and transportation is an integral part of the use of hydrogen as fuel. Currently, hydrogen is utilised mostly as a chemical in various industries and refineries. Today, 70 million t/y of produced hydrogen is mainly used as a chemical in the fertiliser (30%), refinery (50%), metal processing and food, electrical and aerospace industries. The next highest is the mobility sector. Predicted demand for hydrogen as a fuel is 4 million t/y by 2030.

Serious attention is given to producing low-carbon hydrogen. Indeed, green hydrogen with a zero carbon footprint is the future. With technologies available for CO_2 capture and storage, well-developed methods of hydrogen production such as steam methane reforming (SMR) can be relied on for near-term developments. The reforming process, combined with CO_2 capture and storage, has emerged as a sustainable solution and is described in detail in this article.

Hydrogen production by SMR

The most reliable and efficient process for hydrogen production is steam reforming of fossil fuels. SMR can be generally divided into the following steps: feed pretreatment, steam reforming, shift process, synthesis gas cooling, and purification (see **Figure 2**). The primary reaction of reforming is strongly endothermic. The heat needed to drive the reaction forward is usually supplied by burning natural gas and thus producing CO_2. Carbon monoxide (CO) in the output stream from the primary reaction is usually converted to CO_2 via the water gas shift reaction to increase hydrogen production:

$$CH_4 + H_2O + \text{heat} \rightleftharpoons CO + 3H_2 \qquad [1]$$

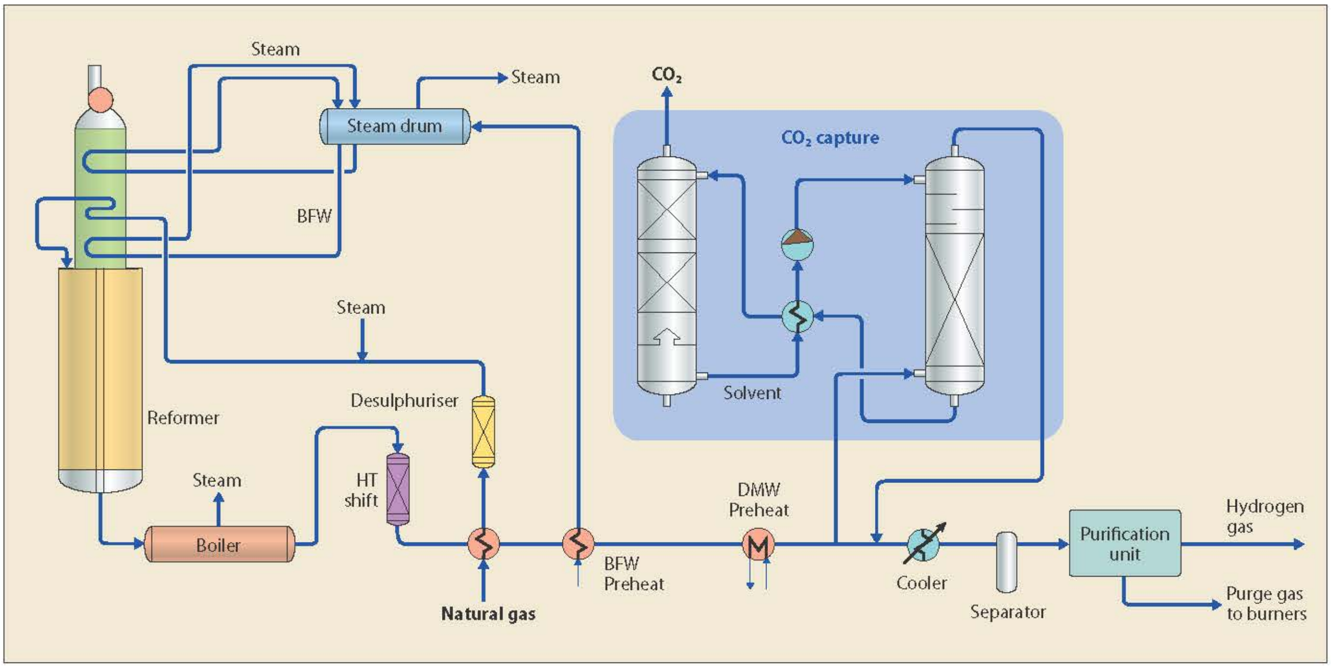

Figure 2 SMR process with CO_2 capture flow scheme

$$CO + H_2O \rightleftharpoons CO_2 + H_2 + \text{heat} \quad [2]$$

The reformed gas is cooled and routed to a shift reactor to maximise the hydrogen content. The produced syngas is further cooled and process condensate is separated out. The reformed gas has an approximate composition of H_2 74 mol%, CH_4 7 mol%, CO 1 mol%, and CO_2 18 mol%, the exact proportions depending on feed composition, operating conditions, and the selected process scheme. The gases are purified in the PSA section to remove CO, CO_2, and CH_4 impurities and produce grey hydrogen.

To produce low-carbon 'blue hydrogen', a carbon capture process is integrated into the base scheme. A solvent based CO_2 capture process is illustrated in **Figure 2**. The captured CO_2 can be used in a variety of industries.

SMR is an efficient, widely used, and economical process. The efficiency of SMR and its specific energy consumption are best among current commercially available hydrogen production methods. SMR is the most reliable technology and has the highest availability among all hydrogen production methods. The process can be easily integrated with CO_2 capture options, has very low NOx emissions, and there is no liquid discharge from the processing unit. SMR also has a small footprint per tonne of hydrogen produced.

Classification of hydrogen

Depending on the production method and feed source, hydrogen is classified as blue, grey, or green hydrogen. Hydrogen from coal, oil, and natural gas is grey hydrogen. All of these non-renewable sources and production methods, when integrated with a CO_2 capture unit, then produce blue hydrogen. Hydrogen produced from biomass, wind, solar, and hydro-powered electrolysis is green hydrogen. Green hydrogen is typically produced via electrolysis of water in which water is split into hydrogen and oxygen. Dedicated 'green' hydrogen production electrolysis remains a niche component of global hydrogen production. But with renewable energy sourced electricity costs on a downwards trajectory (from solar photovoltaics, onshore, and offshore wind), focus and interest are growing. There are three distinct types of electrolyser: alkaline electrolysis, proton exchange membrane electrolysis (PEM), and solid oxide electrolysis cells (SOECs).

> **SMR is the most reliable technology and has the highest availability among all hydrogen production methods**

Blue and green hydrogen

Blue and green hydrogen are the solution to decarbonised hydrogen fuel production. According to DNV-GL[1], "We will ultimately move to a green hydrogen economy. But we are convinced that you can make the step towards green hydrogen via blue hydrogen first." Hence blue hydrogen can be a supply step between grey hydrogen and green hydrogen. Production of blue hydrogen offers several advantages in the near to medium term as it utilises conventional, large-scale commercial hydrogen production pathways and infrastructure, with 75% of global hydrogen production relying on natural gas.

Hydrogen as fuel is used in the transportation sector in two ways: as an internal combustion engine (ICE), or as a fuel cell electric vehicle (FCEV). The ICE has a disadvantage in terms of nitrogen oxides or NOx formation, inefficiency, higher maintenance, and unsafe operation.

Fuel cells

A fuel cell is a device that generates

electricity through an electrochemical reaction, not combustion. In a fuel cell, hydrogen and oxygen are combined to create electricity, heat, and water. The fuel cell can produce direct current (DC) power to run an electric vehicle. There are many types of fuel cell, including the proton exchange membrane fuel cell (PEM), solid oxide fuel cell (SOFC), alkaline cell, and so on. The PEM device is the only fuel cell found to be suitable for automobiles. It has an overall efficiency of 40-60% and, when running on pure hydrogen, the only emission is water vapour (see **Figure 3**).

Figure 4 shows applications of fuel cells in stationary plant, transportation, and materials handling. Their application to road transportation is discussed in this article. The fuel cell has several benefits including low to zero emissions, high efficiency, reliability, fuel flammability, energy security, durability, scalability, and quiet operation.

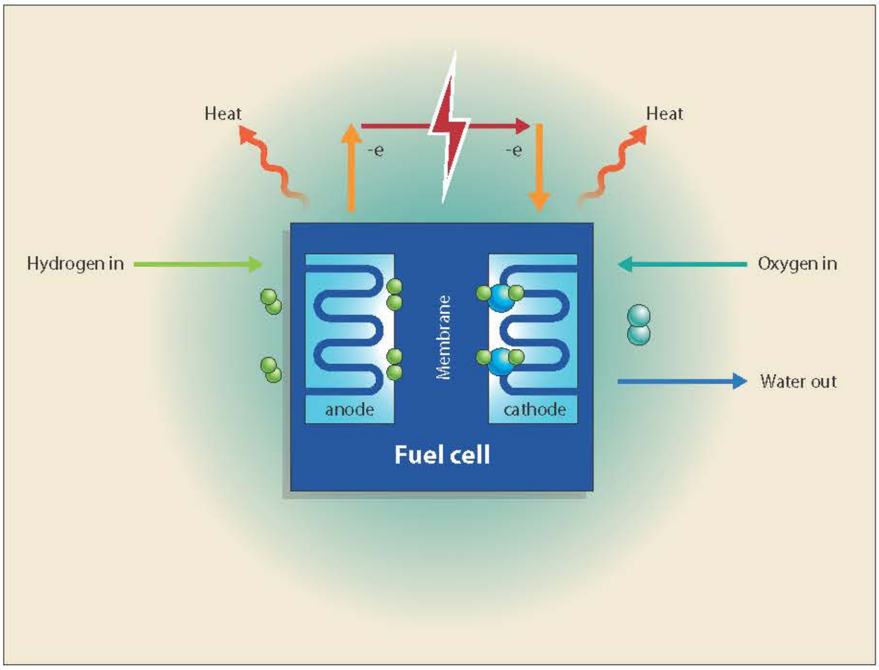

Figure 3 Operation of a fuel cell

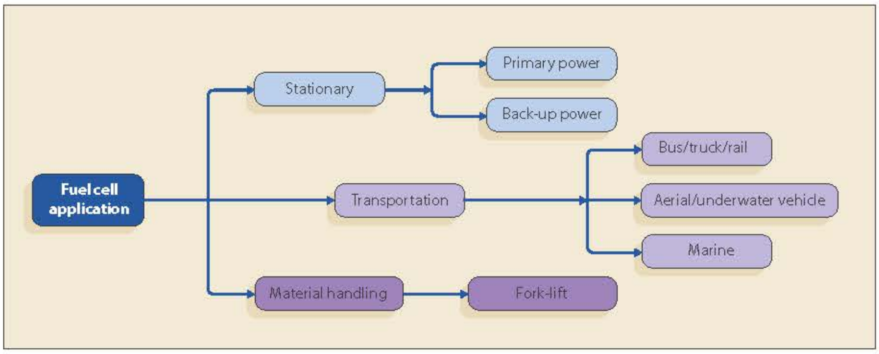

Figure 4 Major fuel cell applications

Quality of hydrogen

The quality of hydrogen required for a fuel cell is different to that of hydrogen used in a typical refinery (see **Table 1**).[2] SOFCs can accept refinery quality hydrogen, but most PEM fuel cells need higher purity, according to ISO-14687-2.

Quality of hydrogen for a refinery and a fuel cell

Components	Refinery	Fuel cell
Hydrogen (H_2), vol%	99.9	99.97
Methane (CH_4), ppmv	Balance	<2
Nitrogen (N_2), ppmv	50	100
Carbon monoxide (CO), ppmv	20	<0.2
Carbon dioxide (CO_2), ppmv	20	<2
Water (H_2O), ppmv	50	5
Chlorides & chlorines, ppmv	1	<0.05
Sulphur, ppmv	Negligible	<0.004

Table 1

The small number of impurities present in hydrogen fuel affects the performance of the PEM cell. To meet the required quality of hydrogen, various schemes have been explored, for instance pressure swing adsorption (PSA), membrane separation, catalytic conversion, either alone or in combination. The PSA system is designed to remove many contaminants to even lower levels, with a compromise in hydrogen recovery.

Inert compounds included in the ISO and SAE standard specifications are helium (He), nitrogen (N_2), argon (Ar), methane (CH_4) and other saturated hydrocarbons (paraffins), and carbon dioxide (CO_2). These compounds are considered inert because they do not affect the electrochemical reactivity of the PEM fuel cell but are included in the specification because they can dilute the hydrogen fuel stream and affect system operation. It is important to note that the ISO and SAE standards limit total non-hydrogen gases in the fuel to 300 ppm. However, the oxygen content required is less than 5 ppm.

The presence of particulate matter (PM) in the hydrogen fuel stream should not directly affect a PEM fuel cell's performance and durability. Still, PM can affect the integrity of components such as seals, gaskets, and valve seats and cause fuel leaks and other problems.

CO_2 and water can be removed easily, while CO and N_2 are the most challenging contaminants to remove. In SMR, sulphur is mostly removed in the feed (natural gas) pretreatment section as it is poisonous to the reformer catalyst. The extra purity required for fuel slightly increases the cost of hydro-

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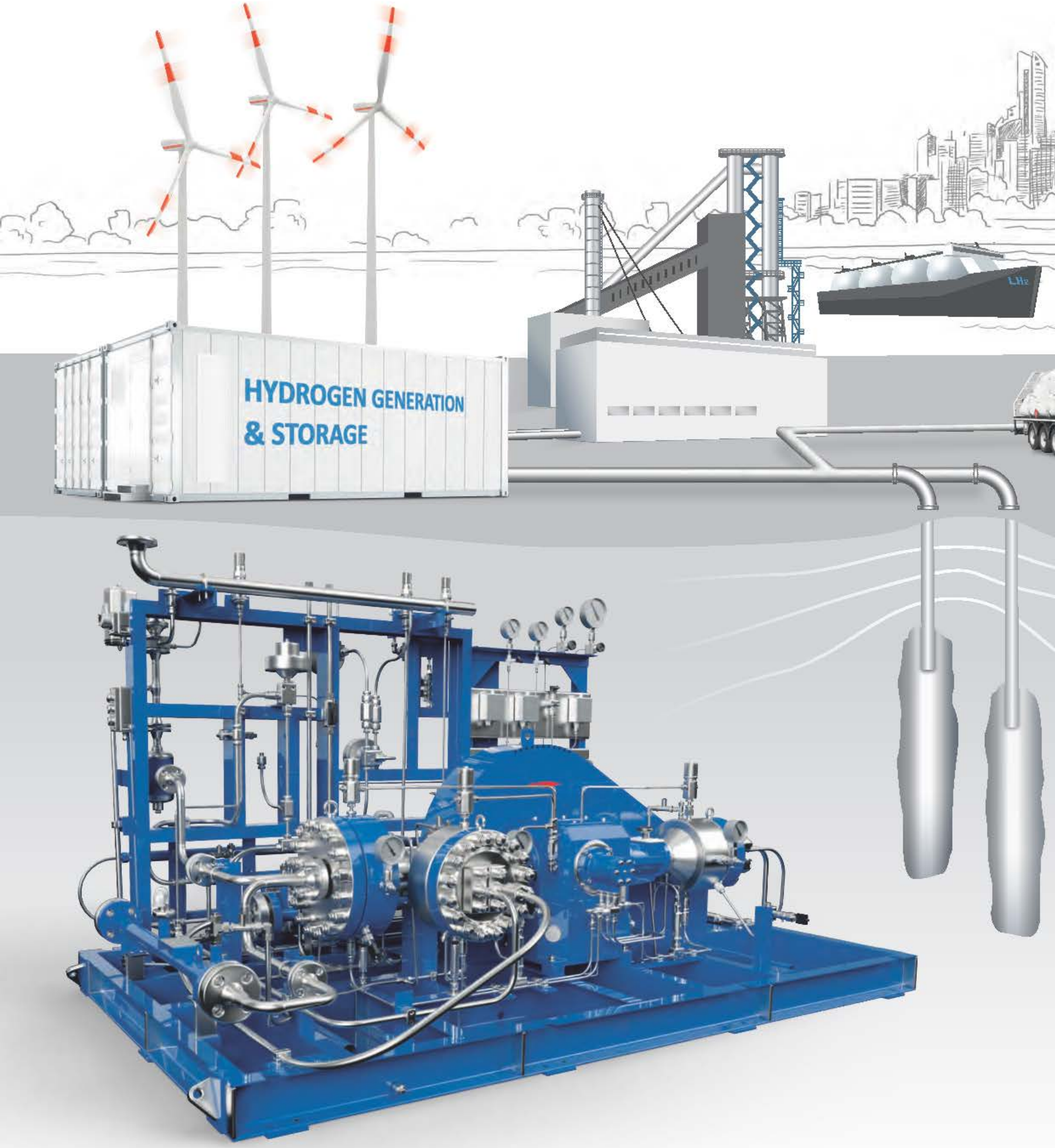

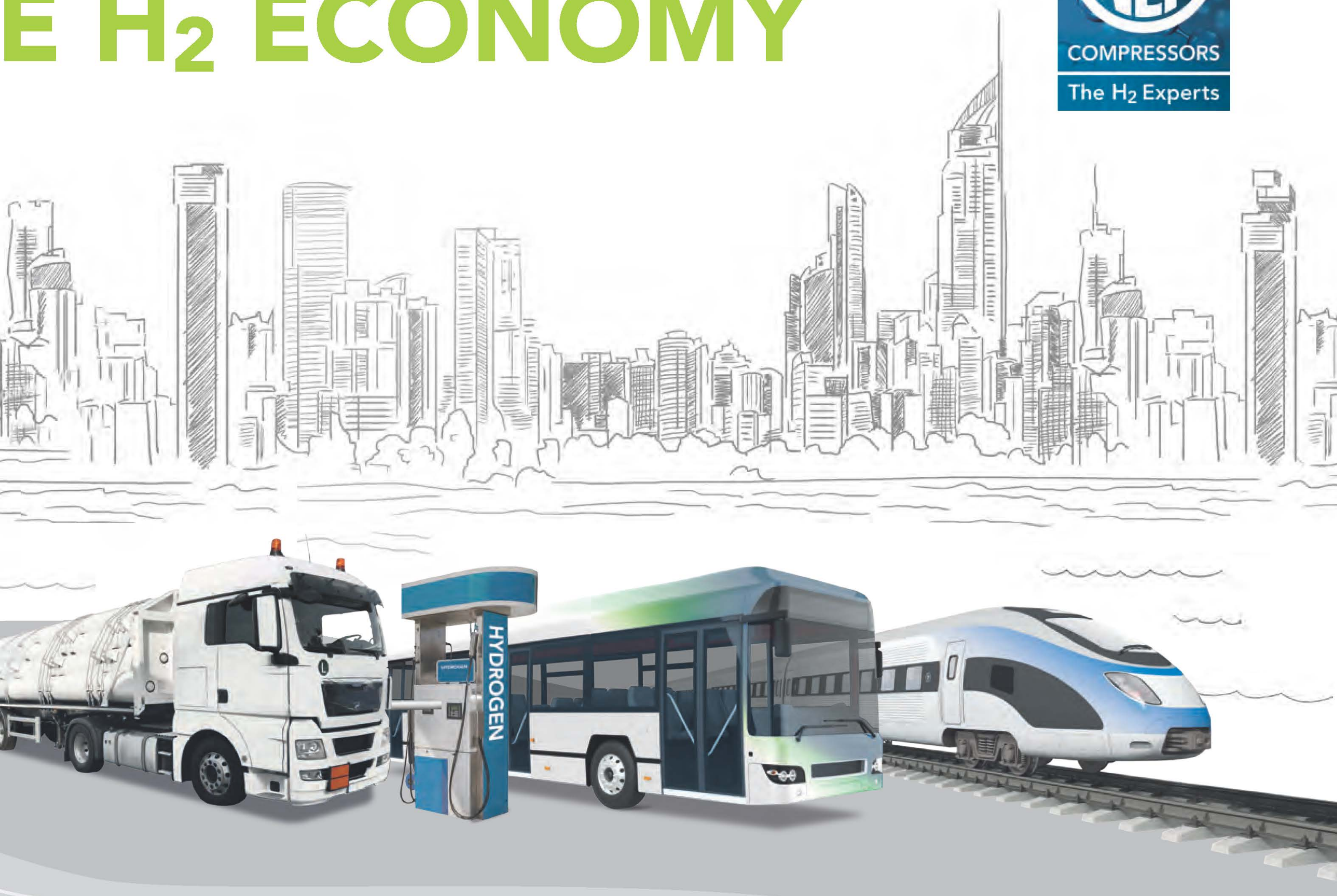
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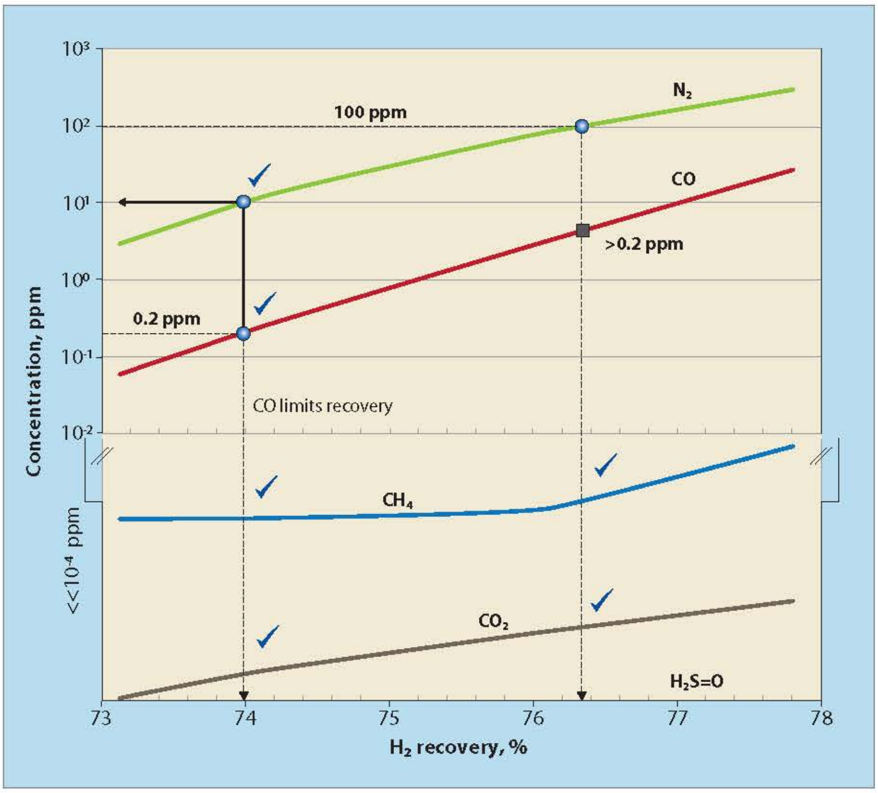

Figure 5 Typical PSA recovery and concentration of impurities[7]

Comparison of grey and blue hydrogen

Parameter	Grey hydrogen	Blue hydrogen
Capital cost, M$/TPA H_2	0.009-0 .013	0.01-0.016
Cost of production, $/kg	2.8	2.94
System efficiency, %	62-65	58-60
Specific energy, Gcal/1000 Nm³ H_2	4.1	4.2
CO_2 emission, kg CO_2/kg H_2	8-12	0.2-4

*The value presented in the table is typical and depends on various factors like geographical location, size of the unit, feedstock, and utility price.

Table 2

gen, but this is negligible for the overall cost model.

CO_2 capture

The second biggest challenge on the path to a hydrogen economy is CO_2 capture and storage. All fossil fuel routes produce CO_2 as a byproduct. Biomass gasification, a non-fossil route, also generates CO_2. The electrolysis route also produces CO_2 if the electricity consumed is produced from a non-renewable source. Thus, for an actual hydrogen economy, effective CO_2 capture and disposal is required.

A fossil fuel based hydrogen unit typically produces 8-12 kg CO_2/kg H_2. The integration of a CO_2 recovery option with the basic scheme can reduce emissions by 0.2-4 kg CO_2/kg H_2. There can be two locations to recover CO_2 from the hydrogen producing unit: pre-combustion CO_2 removal, which is CO_2 recovery from synthesis gas; and post-combustion CO_2 removal, which is CO_2 recovery from flue gas. The first option is cost-effective and removes up to 0.2-4 kg CO_2/ kg H_2. The second method is cost-intensive but can reduce CO_2 emissions by only 0.1-1 CO_2/kg H_2.

The method of CO_2 removal can be solvent based or adsorption based, though the former method is mostly used in the SMR process.

Of the other emerging technologies, biomass gasification process produces 17-19 kg CO_2/kg H_2. Though biomass is carbon neutral feed thus overall carbon dioxide emissions for the process is not considered. Electrolysis emits 50 kg CO_2/kg H_2 if the power source is non-renewable, but can be as low as 0.3 kg CO_2/kg H_2 if the power source is renewable.

Case study

SMR is extensively used for hydrogen production around the world. The key parameters for small capacity production of grey and blue fuel cell grade hydrogen are summarised in **Table 2**. The cost of natural gas used for this case study is $9-10/MMBtu, and hydrogen delivery pressure is 350 barg. The key parameters vary as per size of the unit, quality of hydrogen, hydrogen delivery pressure, and geographical location.

Blue hydrogen's capital cost is 15- 20% higher than that of grey hydrogen. The cost of production is slightly more for blue hydrogen. At the same time, there is a significant reduction in CO_2 emissions with blue hydrogen.

Capital cost

The capital cost of a hydrogen unit includes contributions from equipment, bulk materials, erection, engineering, and taxes. Among the equipment, the reformer package contributes around 35-40% and the compressor 15-20%.

Operating cost

The main contributor to the operating cost of a hydrogen plant is the natural gas feed (55-75%), while the balance is due to utilities and other plant overhead, hence the operating cost of hydrogen depends greatly on natural gas prices (see **Figure 6**). Hydrogen production costs therefore depend on geographical location and availability of natural gas. Another associated cost is that of hydrogen compression from 20-30 barg to 350-700 barg, which leads to an increase in the price by $0.27-$0.54/kg.

Disposal of CO_2

SMR, along with CO_2 capture, can be used to produce cost-effective hydrogen for fuel cells, but it is crucial to dispose of the captured CO_2 to close the loop. There are various methods for CO_2 disposal. CO_2 based enhanced oil recovery (EOR) is a significant application of recovered CO_2. CO_2 based EOR involves pumping compressed CO_2 through injection wells to an oil-bearing formation. This restores pressure in the formation and forces the remaining oil toward production wells. It also mixes with the oil, expanding its volume and reducing its viscosity. This enables it to flow more quickly through the porous rock of the oil reservoir. Injection of CO_2 into mature oil fields is increasingly considered the most effective method available to revive output.

Algae based carbon dioxide (CO_2) sequestration has gained more interest due to its ability to utilise produced CO_2 as a carbon source, its high capacity for CO_2 fixation, and a faster growth rate than conventional crop plants. The biomass produced can be used as a feedstock for other value-added products such as biofuels and chemicals.

A hydrogen unit integrated with a fertiliser unit using recovered CO_2

Figure 6 Hydrogen price compared with natural gas price

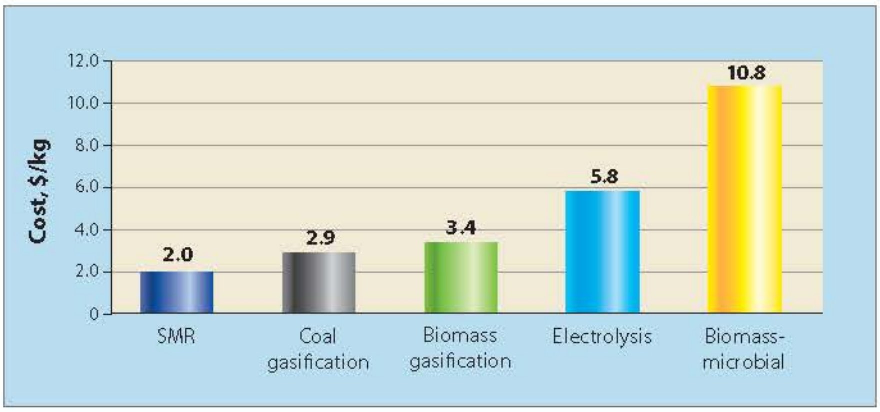

Figure 7 Cost comparison for hydrogen production technologies

Comparison of a city bus, car and truck

	City bus	Car	Truck
Hydrogen, Km/MJ	0.08	0.84	0.09
CNG/gasoline/diesel, Km/MJ	0.06	0.58	0.14
Travel/day, Km/day	250	500	800
FCEV op. cost, \$/km	0.26	0.03	0.23
CNG/gasoline/diesel op. cost, \$/km	0.2	0.05	0.21
CO_2 emissions-grey hydrogen-WTW, kg CO_2/km	1.26	0.13	1.12
CO_2 emissions-blue hydrogen- WTW, kg CO_2/km	0 .2	0.02	0.18
CO_2 emissions-CNG/gasoline/diesel, kg CO_2/km	1.1	0.11	0.68

Table 3 * typical data collected from open literature and estimated for Indian sub-continental

FCEV vs BEV

	FCEV	BEV
Vehicle cost, 1000\$	40-50	18-25
Weight*, kg	1280	2270
Storage vol*, lt	100-310	560
Refuelling time*, min	3-5	60-240
Pickup time (0-100), sec	10	5.5
Operating cost, \$/km	0.15	0.03-0.06
CO_2 emissions, kg CO_2/km	0.15	0.4-0.6
Overall efficiency, %	40-60	70-80

*Values given for vehicles with a 300-mile range

Table 4 * typical data collected from open literature and estimated for Indian sub-continental

for urea production is another possible solution, while conversion to valuable chemicals is an emerging solution for disposal.

Decentralised production of hydrogen

The normal capacity of a hydrogen plant in a refinery is 10 000-350 000 Nm^3/h. In the case of fuel hydrogen, a small capacity plant can be looked upon to fulfill local requirements. A small, modular hydrogen unit with a capacity range of 100-1000 Nm^3/h avoids challenges related to hydrogen transport and distribution.

SMR compared with other emerging technologies

Hydrogen from biomass gasification or biogas reforming are promising as applications of carbon-neutral feedstock, but not proven at the commercial scale yet. On the other hand, hydrogen from electrolysis is only promising if the electricity is generated from a renewable source and excess electricity is available. Electrolysis is an inefficient process at 55-60 kWh/kg H_2; the hydrogen price depends on the electricity price. Power consumption for the electrolysis process is expected to come down in the future through extensive research. In a nutshell, SMR with carbon capture (blue hydrogen) is the most suitable option in the near term while biomass gasification and electrolysis are mid-term solutions. Other pathways like dark fermentation and solar-hydrolysis are projected as long term solutions.

Fuel cell grade hydrogen

The hydrogen produced by steam reforming fossil fuels requires further purification to achieve fuel cell grade. The primary process is followed by compression (to 350 barg/750 barg) to fill cylinders for storage, followed by transportation to fuel cell-powered vehicles.

A comparison of a hydrogen-powered fuel cell vehicle and a convention internal combustion engine is summarised in **Table 3**. A typical hydrogen filling station of 1200-1500 kg/day can serve 50 city buses or 250 passenger cars or 18 trucks. Heavy-duty vehicles represent a lower percentage of the total vehicle fleet but contribute more in the total percentage of emissions from all vehicles, which makes them an area of focus for fuel cell applications. Fuel cell buses can replace conventional buses in range, power, and passenger capacity. The fuel cell operating cost is at par with a fossil fuelled vehicle. CO_2 emissions are 60-80% lower when using blue hydrogen, compared to fossil fuelled vehicles. Other emissions like NOx, unburned hydrocarbons and particulate matter are significantly lower in the case of a fuel cell vehicle.

Although FCEVs are currently more expensive to operate than battery electric and internal combustion commercial vehicles, they are set to become much lower in cost as manufacturing technology matures, economies of scale improve, hydrogen fuel costs decline, and infrastructure develops.

FCEV & battery electric vehicle (BEV)

BEVs and FCEVs both have zero exhaust emissions and the ability to be fuelled using renewable and sustainable energy sources through the use of electric motors.

In the case of FCEVs, the major concerns are hydrogen production, delivery and storage to the vehicle hydrogen tank and consumption of hydrogen by the fuel cell vehicle during operation. In the case of battery electric vehicles, the main concerns are electricity generation, transmission in the grid, charging the battery, and use during vehicle operation.

BEVs have the advantage in vehicle cost and operating cost (see **Table 4**). The major drawback of BEVs is that they usually have a limited range due to the size and the cost of batteries needed for vehicle power. The refuelling of battery systems requires several hours, rather than a few minutes with an FCEV, and CO_2 emissions are much lower in the case of FCEVs.

Conclusion

Hydrogen is a decarbonising fuel with high potential for transportation and power generation. But it has to overcome many challenges before establishing itself as the cleanest available fuel. Production of low-carbon, cost-effective hydrogen is the foremost challenge.

SMR, typically producing refinery grade hydrogen, is on hand to produce fuel cell grade hydrogen for transportation and power generation at an affordable cost and in a sustainable way. The SMR process used in refineries and other applications requires modification in its purification section to produce fuel cell grade hydrogen. The purification step has a solution based on PSA with or without a catalytic process for producing fuel cell grade hydrogen. A small, modular SMR base hydrogen unit can produce fuel cell grade hydrogen at 350 barg pressure at a cost of <\$2.8/kg with an investment of \$ 9000-15 000/t/y H_2.

At the next stage, SMR integrated with a CO_2 recovery option is available with a slight increase in investment to reduce CO_2 generation substantially.

Emerging technologies like biomass gasification producing green hydrogen are promising, but the technology is at the development stage. The oldest technology, widely studied, is water electrolysis. However, the efficiency of the process from electricity to hydrogen is low and the process is the most environmentally friendly only if the source of power is renewable.

A small hydrogen unit of 100-500 Nm^3/h can fuel 10-50 city buses or 50-250 passenger cars. A fuel cell powered bus has an operating cost of \$0.2-0.3/km and reduces CO_2 emissions compared with fossil fuelling by 60-80%. Blue hydrogen should help to create the infrastructure required for the use of fuel cells in the transportation sector.

Acknowledgment

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Column revamp boosts diesel production

Revamping the internals of a main fractionator column enabled a refinery to increase its diesel throughput

LEE SIANG HUA and MARK PILLING *Sulzer*
KRITSADA SATTAYAVINIJ and ANUSARA BUACHAROEN *IRPC*

Tight oil availability in the opportunity crude market provides refiners more profitable options in crude blending. However, blended crudes may greatly impact unit operation. When IRPC Public Company Limited's refinery needed to modify its hydrotreating reactor to support increased variability in the feedstock, it contacted Sulzer. Sulzer provided a solution that debottlenecked the main fractionator, enabling the refinery to nearly triple its treated diesel to feed ratio without replacing the existing column. As a result, the company could maximise its throughput and benefit from a quick payback on its investment.

IRPC Public Company Limited is a Thai oil refiner and petrochemical producer. Its integrated refinery and petrochemical complex in Rayong, Thailand operates two crude atmospheric distillation units (ADU). These have a combined capacity of 215 000 b/d and were designed to handle various types of sweet and sour crudes, with API values ranging from 30 to 45. The long residual from the bottoms of these ADUs is further distilled in a vacuum distillation unit (VDU) to produce vacuum gasoil (VGO).

The VGO is combined with the atmospheric gasoil (AGO) from the ADUs and then fed to a fixed bed gasoil hydrotreating unit. The reactor effluent, after the off-gas and hydrogen sulphide are removed, is processed in the main fractionator to produce diesel with less than 50 ppm sulphur to comply with current emission standards.

The main fractionator was originally equipped with 34 conventional valve trays, numbered from top to bottom (see **Figure 1a**). Feed from the furnace is directed onto tray 30, while the diesel draw-off is located at tray 10. There is a pumparound recirculation from tray 16 to tray 12 and the stripping steam is fed below tray 34. The column was designed to accommodate a feed capacity of 16 600 b/d, with a VGO to AGO ratio of 4.23 and a diesel yield around 14.3 wt%.

In order to maximise profitabil-

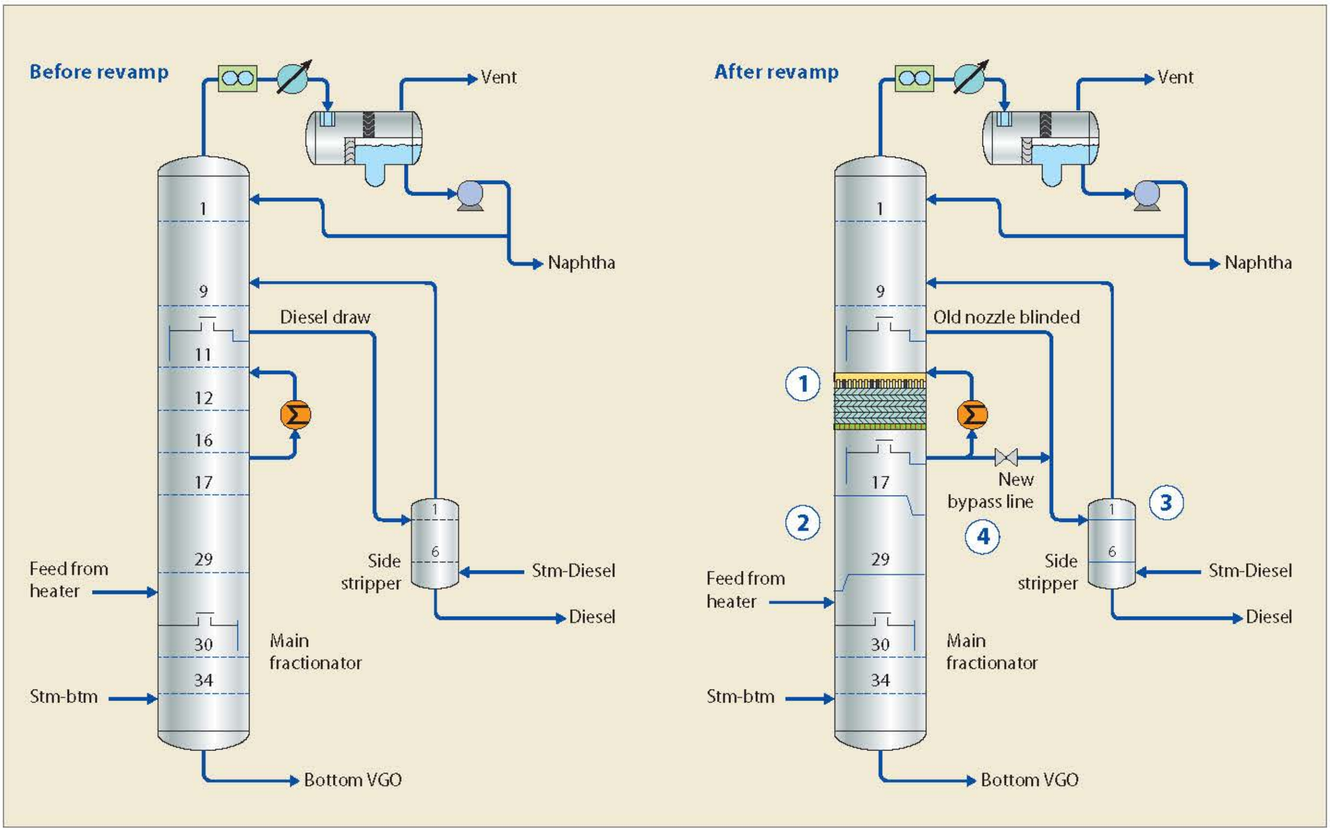

Figure 1 Main fractionator column configuration before and after revamp: **1a** before revamp; **1b** after revamp

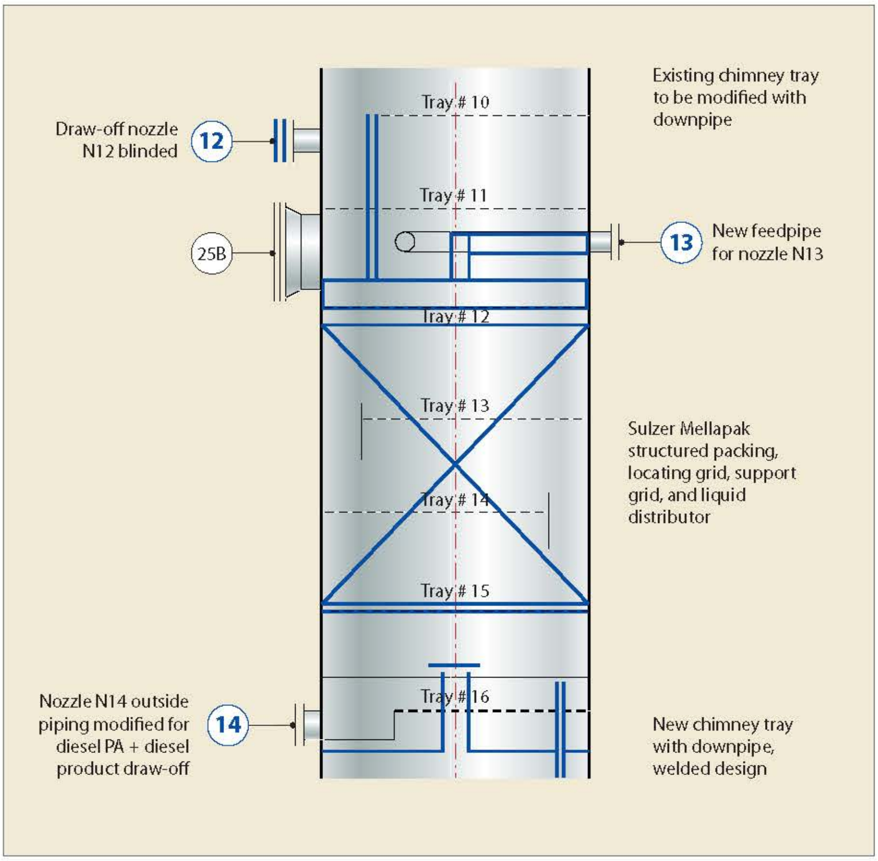

Figure 2 Modification of diesel pumparound section from tray to packing (scope 1)

ity, IRPC wanted to increase the hydrotreating unit capacity by 19% and diesel production from 30 wt% to 40 wt%. After the revamp, the column was able to support an 18 600 b/d feed rate, with a VGO to AGO ratio of 1.48. The treated diesel yield reached 40 wt% of the total feed rate.

Due to production planning changes in the plant, feed to the hydrotreating unit was subsequently changed to accommodate more AGO. It was observed that the column was able to maintain good separation between treated diesel and treated VGO when the latter was approximately 1.5 times the content of AGO in the feed. However, when the ratio dropped to 1.3, the treated diesel yield was approaching 42 wt% of the total feed rate, and separation between treated diesel and treated VGO was compromised.

In particular, when the feed temperature was reduced, the boiling temperature overlap between treated diesel and treated VGO could be improved, but this would reduce the yield of treated diesel. Also, despite the enlargement of a control valve for treated diesel draw-off, when plant operators tried to draw more diesel from the side stripper the liquid level in this section dropped quickly.

Room for improvement

The refinery then asked Sulzer to evaluate a potential revamp of the hydrotreater's main fractionator to improve the separation overlap between the treated diesel and treated VGO products, while maintaining a high diesel yield. Sulzer set up a process simulation model of the hydrotreating unit, matching different sets of test run data. The simulated vapour and liquid flow rates and physical properties were then input into Sulzer's column mass transfer internals rating program Sulcol to evaluate column performance.

The simulation was also used to model the unit's conditions after revamp. The fractionator feed throughput was expected to increase by 7%, while the treated diesel yield was modelled to increase by 3-5% on feed basis, due to higher AGO in the feedstock.

Based on the model created, Sulzer's engineers noticed that in the existing configuration, the treated diesel draw-off nozzle was above the diesel pumparound section. Since the diesel product was expected to increase, the diesel pumparound duty needed to be reduced to allow vapour to reach the top section of the column, condense at the top, return to tray 1 and be collected in chimney tray 10 as diesel product. This arrangement is less favourable for energy saving, as energy lost into the air and cooling water cannot be recovered.

The engineers therefore proposed an optimised design to IRPC that would allow the plant to maximise heat recovery in the steam generator via a diesel pumparound exchanger. To do that, the diesel product draw-off nozzle needed to be relocated to the pumparound section. **Figure 1b** shows the modified scheme.

The proposed design was also key to identifying various bottlenecks in the existing system. Firstly, increasing heat recovery in the diesel pumparound implied that the diesel pumparound circulation flow rate needed to be increased. However, the exit nozzle, pipelines, pumps, and trays in the diesel pumparound section could have limits in hydraulic capacity. Secondly, due to increased diesel product, the trays in the side stripper were experiencing downcomer flooding, causing fluctuations in the side stripper level controller. Thirdly, a minimum wash rate should be maintained in trays 17 to 29 to maintain a proper separation gap between treated diesel and treated VGO product. Lastly, an additional pump could possibly be needed for a new diesel draw-off location to the side stripper.

Column internals upgrades

Sulzer recommended using Mellapak high efficiency structured packing to replace trays 11 to 16, which were hydraulically limited. While these internals were removed, the existing support ring at tray 15 was strengthened and reused for the new structured

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This will in turn avoid production losses and budget will be beaten...with no effort and stress...typical of any turnaround planning and execution.

Regular application of ITW Online Cleaning will target an increased run length under *clean* conditions with related value.

For turnaround applications, ITW Online Cleaning can eliminate/dramatically reduce the need for mechanical cleaning, thereby reducing downtime and improving operational HS&E.
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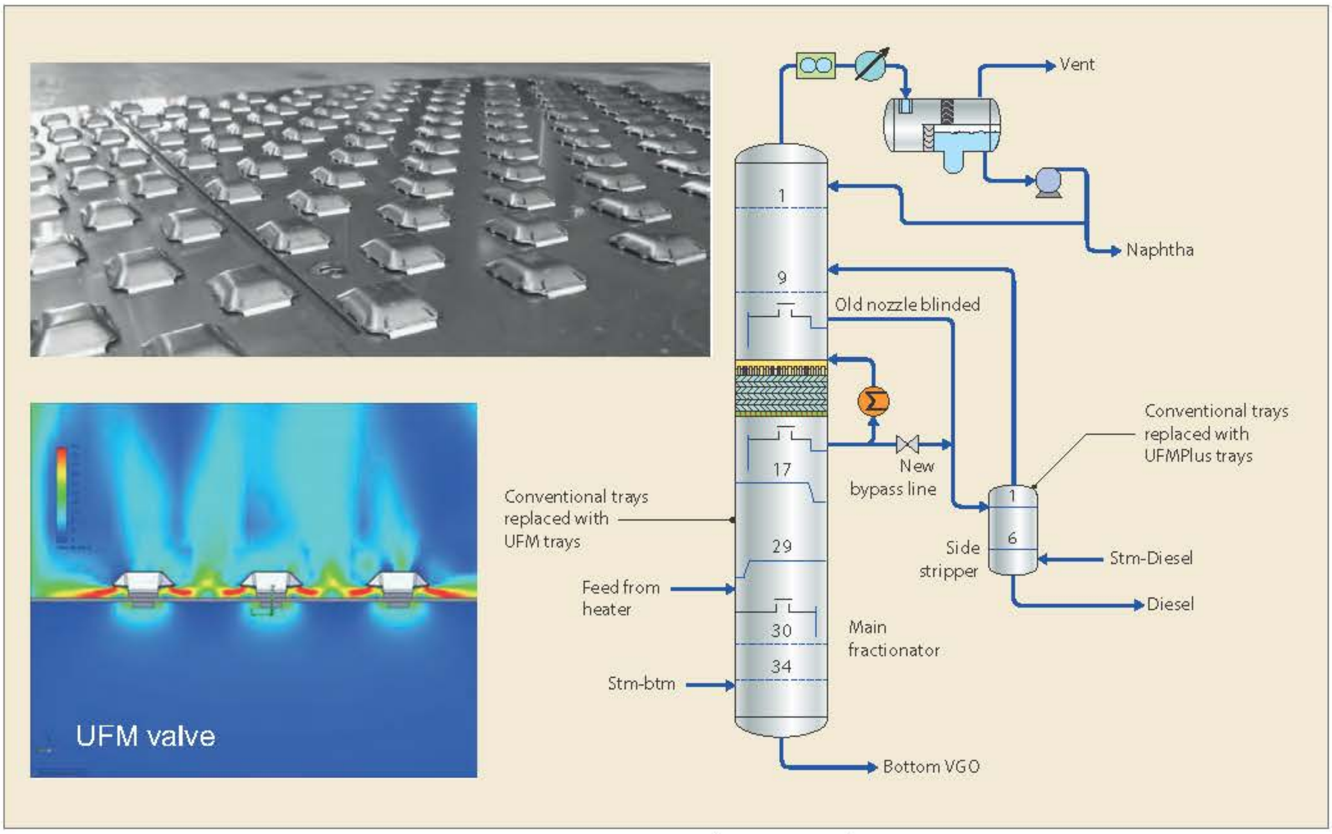

Figure 3 High capacity trays applied on overflash section and side stripper (scope 2 and 3)

packing beds. Also, a new collector tray was installed at the same elevation as the existing draw-off gutter for the diesel pumparound. The draw-off nozzle size was checked and found adequate for both pumparound and product flow rate, hence no modification was needed. The existing diesel draw-off nozzle was blinded at the column. Existing collector tray 10 was modified to add a liquid downflow pipe. A new feed pipe was added from the first flange of the existing pumparound return nozzle (see **Figure 2**).

To address potential liquid entrainment, trays 17 to 29 were replaced with Sulzer UFM high performance trays. **Figure 3** shows typical UFM valves and a computerised fluid dynamic simulation of the downwards vapour flow direction exiting the UFM valves. The downward vapour flow direction increases mass transfer efficiency and reduces liquid entrainment. The UFM valves enable higher vapour loading and minimum wash oil flow rate in the overflash section while maintaining good separation efficiency. The same UFM valves were used in the side stripper along with enhanced downcomers to handle high liquid loads in the side stripper.

Piping modifications

IRPC and Sulzer surveyed the column and existing piping layout. Particular attention was placed on the analysis of the hydrostatic head for three tie-in points to find the best location to connect from the pumparound draw-off line to the diesel side stripper without a pump. Approximately 10 m below the draw-off nozzle was found to be the ideal option. There was a readily available platform for personnel access, and the piping pressure drop was minimal.

The results from pipe stresses and nozzle loads analysis were found to be within ASME B31.3 process piping code allowable limits. The bypass line was installed and tested.

All the modification work was safely completed by Sulzer's team in record time: within 14 days for

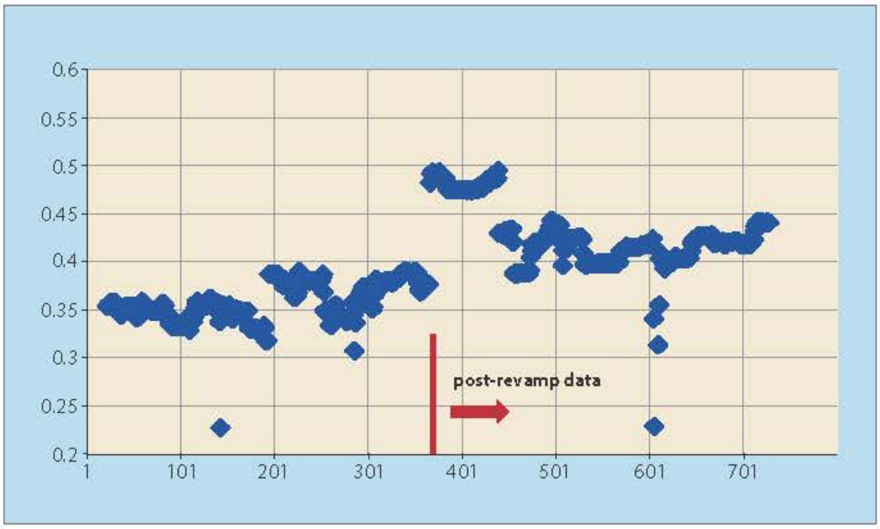

Figure 4 Plant data showing increase in diesel yield after revamp

the main fractionator, 11 days for piping, and a week for the side strippers.

Results after revamp

After start-up, Sulzer performed high load tests, together with IRPC's process team. The column was operated continuously for 72 hours and operating data and product samples were collected for analysis.

The VGO was fed at 1.2 times the AGO flow rate during the test run. The total combined feed flow rate was estimated to have reached approximately 8% higher than the original set-up. In addition, the treated diesel to feed ratio was approximately 4-11% higher than before (see **Figure 4**). Finally, after removing the bottlenecks in the fractionator column, the plant has more flexibility in feedstock selection.

Another significant improvement was in the column pressure drop, which was nearly halved (see **Figure 5**). The major contribution of pressure drop reduction resulted from the high performance structured packing in the diesel pumparound section, which allowed the unit to deliver higher throughput. Also, its high surface area per volume allowed more contact between vapour and liquid, promoting heat exchange between the phases.

After the revamp, Sulzer elevated the treated diesel cut point to deliver additional benefits. This increased the diesel product stream temperature, which was used to heat up the feed stream before it entered the fired heater. A higher coil inlet temperature resulted in less fuel gas to the fired heater, thus generating substantial energy savings.

All of these modifications quickly paid for themselves, as the plant was able to reach payback in less than three months. The overall achievements are summarised in **Table 1**.

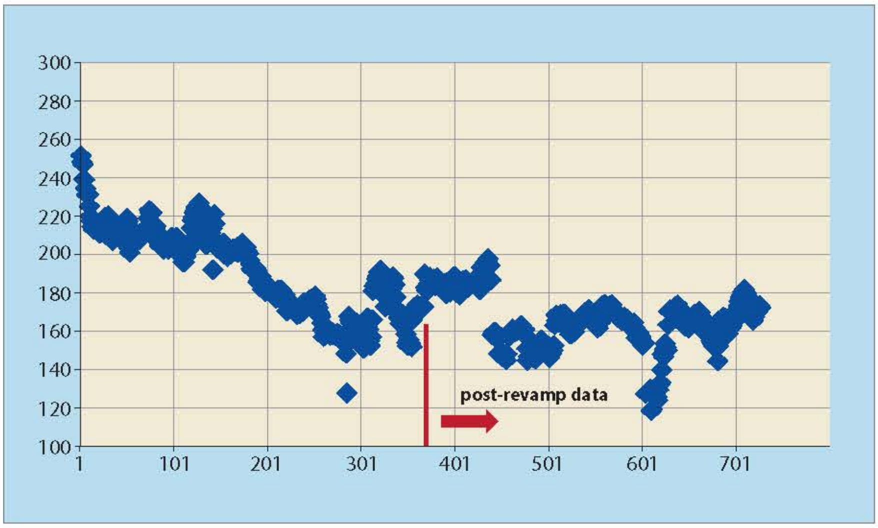

Figure 5 Plant data showing decrease in main fractionator pressure drop after revamp

Conclusion

It is crucial for refining units, such as this hydrotreater, to run at peak performance while processing different feedstocks. The revamp of IRPC's fractionator in Rayong's facility shows the potential benefits of using state-of-the-art separation technologies, coupled with know-how from mass transfer specialists, to upgrade existing units. As a full service provider of high quality mass transfer products and services, Sulzer was able to support the refinery and increase its competitiveness within a short time frame. Crucial to the completion of this project was Sulzer's consideration of all aspects of the operations and equipment. Accurate plant data collection, data analysis and simulation allowed the design team to identify any bottlenecks and provide highly effective solutions. Finally, precise engineering and site execution allowed the plant to benefit as quickly as possible from a successful implementation and start-up.

Precise engineering and site execution allowed the plant to benefit as quickly as possible from a successful implementation and start-up

Lee Siang Hua is a Lead Process Engineer with Sulzer Singapore. She has more than 22 years of process experience in plant operations, optimisation, and mass transfer equipment design.

Mark Pilling is Manager of Technology with Sulzer Chemtech USA where he oversees mass transfer equipment technology and specialises in engineered applications for various process technologies.

Kritsada Sattayavinij is a Senior Process Engineer with IRPC Thailand. He has 16 years of refinery process experience in unit operation, process design basis, and process optimisation.

Anusara Buacharoen is a Senior Process Engineer with IRPC Thailand. She has 10 years of refinery process experience in process design calculation, and basic design package and FEED.

Summary of revamp achievements

Goal	Achievements
Increase yield	Yield increased more than 2.65 wt% of feed basis
Save energy	Minimised top duty Maximised pumparound steam generation
Operational flexibility	Allowed higher AGO/VGO feed ratio to increase the diesel yield
Minimised investment	Less than three months' payback

Table 1

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Internals **Random Packing** **Process Design**

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Raising diesel yield by chemical treatment

A chemical treatment programme combined with process monitoring enables increased production of middle distillates

BERTHOLD OTZISK and MICHAEL URSCHEY
Kurita Europe

Since the summer, worldwide oil prices have been low or moderate and margins are already running at low levels. The Covid-19 pandemic influences our lives and has far-reaching implications for industry and its processes. The increasingly noticeable climate changes affect the world with challenges that go beyond environmental issues. Electric vehicles, hydrogen, and biofuels will play an increasingly important role in achieving a 'climate neutral' industry by 2050. It is foreseeable that the market for cars powered by fossil fuels will change in the coming years.

Most refineries in Europe were built or upgraded in the 1960s and 1970s to make a gasoline dominated product. In the meantime, more and more diesel is produced and demand is satisfied by imports from the Middle and Far East, US, and Russia.

In recent years, the main importer of EU gasoline has been the US. Industry analysts like Wood MacKenzie have been predicting a steady and rapid decline in US gasoline imports for some time. Demand for gasoline is mainly located in the passenger car segment and will decline in the long term. Gasoline-oriented FCC units will probably have lower maximum capacity utilisation in the future, which could lead to lower operating margins. Demand for diesel in the passenger car segment reflects only half of diesel demand in Europe. Large trucks and delivery vans, or industrial machinery, still require diesel. Worldwide, the medium-term prospects continue to favour middle distillates (diesel, heating oil, jet/kero). This offers a positive outlook for refineries that can focus on the production of middle distillates. Diesel-oriented refineries should be able to maintain maximum capacity utilisation.

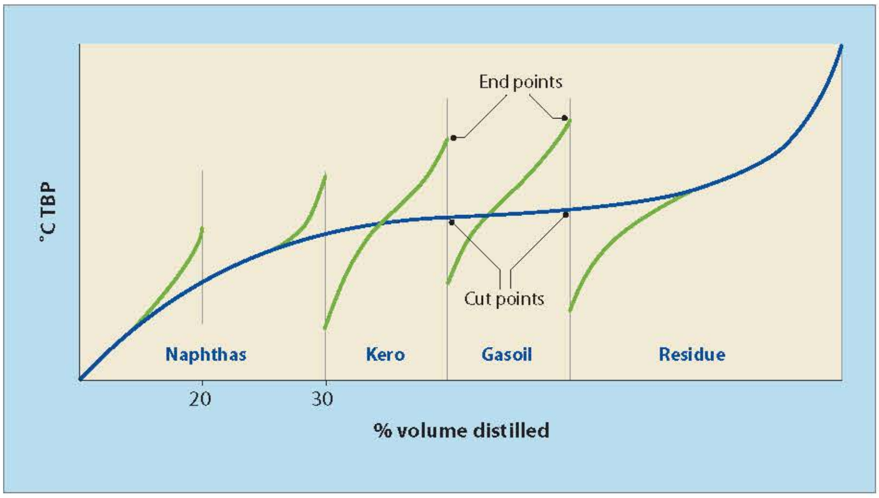


Figure 1 True boiling point curve with cut points

Cut point adjustment

How can middle distillates be increased now without major modifications? A higher yield can be achieved by optimising the feed qualities, but the operating window is very limited in order to change the feed qualities at all, or only slightly, over a longer period of time. This reduces flexibility and requires longer term planning of which feed mixtures and qualities can be used.

Another alternative, providing more flexibility, is a cut point adjustment by lowering the top temperature of FCC columns, where a higher yield can be achieved quickly. A higher jet fuel yield while staying within all product specifications requires a detailed optimisation study for each process unit. Depending on the market values for gasoline and kerosene, it can be economically very attractive to the refiner to optimise operational parameters in favour of an increased middle distillates rate in order to maximise the refinery's profit. **Figure 1** shows how a reduced top temperature will shift the heavy components of the naphtha cut into the kerosene product.

The crude oil feed is typically a blend of several different crude oils and can be characterised by its true boiling point (TBP) curve. The yield for each cut can be estimated by adding the cut points for the different products to the TBP curve. The separation between the different cuts is not perfect. There will always be overlaps between the different products. For example, the back end of the heavy naphtha cut TBP curve is higher than the crude oil TBP curve in this section. Some heavier components that should be in the kerosene cut stay in the naphtha cut. At the same time, the front end of the kerosene TBP curve is lower than the crude oil curve, because some of the lighter naphtha components stay in the kerosene cut. The imperfect separation between these

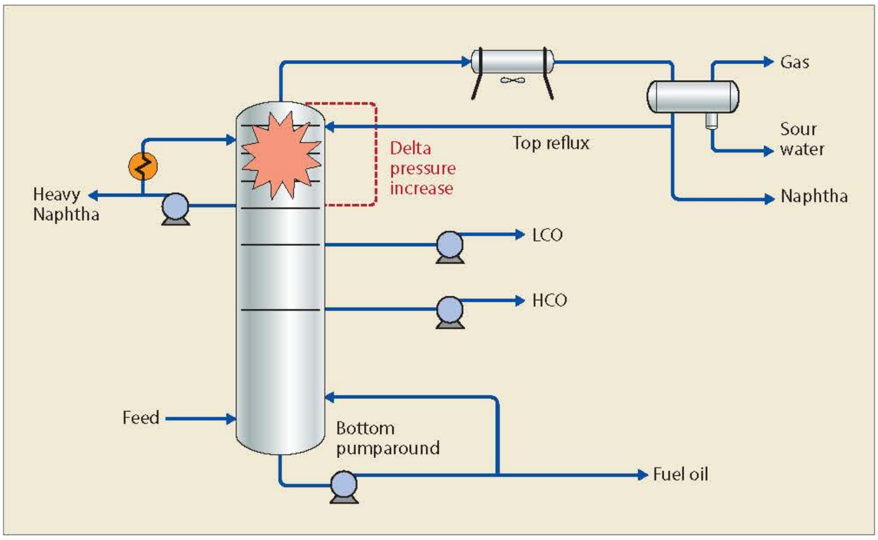


Figure 2 Potential fouling section of an FCC unit

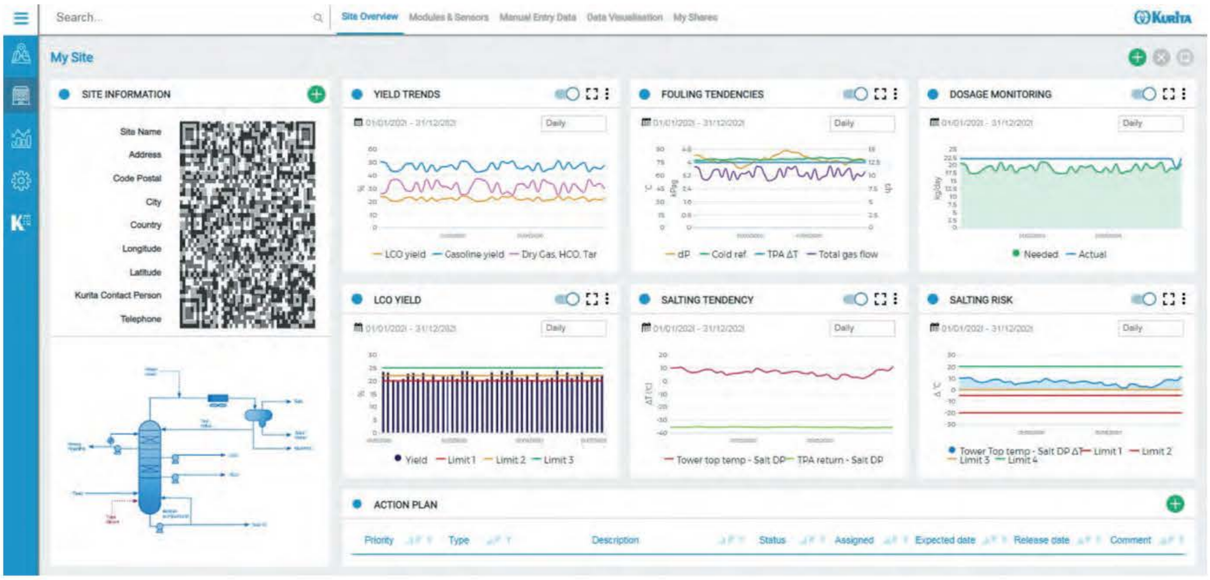
two products causes an overlap in distillation curves.

A residue fluid catalytic cracking (RFCC) unit is a device for upgrading heavy oil into gasoline base material, cracked gasoil, or light cycle oil (LCO) and derivatives. Among the middle distillates of FCC units, LCO serves as a base material for diesel production. Increasing the production of LCO without changing the feed volume to meet the high demand for light oil in winter is conducted as a common practice. In this case, it is necessary to lower the cut temperature of the gasoline base material in the main fractionator and increase the LCO extract volume. However, to lower the gasoline base cut temperature, refiners have to decrease the top temperature of the distillation column. Lowering the temperature of the distillation tower significantly increases the risk of deposition of ammonium salts including NH_4Cl, neutraliser salts, and so on in the column. Deposition of ammonium salts would block the trays and pumparounds in the column and increase the differential pressure. That could eventually bring the unit to a halt. Washing off the salts with water is a commonly conducted practice, however this accelerates severe corrosion in the column. **Figure 2** shows the potential fouling section of FCC columns when the temperature is lowered for a longer time. The heavy naphtha circulation system can also be affected by salt precipitation and corrosion.

Kurita DMax Technology

This technology is an extensive chemical treatment programme with different components. The term DMax stands both for maximising the diesel yield and for maximum visualisation and evaluation of the digital process data to identify early signals of potential risks. Direct communication with the user takes place via a secure platform – My Kurita Portal (MKP). Controllers and sensors, connected to systems on the customer site, measure or detect the physical properties and record, indicate, or otherwise respond to alarm settings, if needed. All the collected, massive amount of data is processed by the digital platform to be able to perform actions to increase the operational efficiency (see **Figure 3**).

In addition to automatic data, manual data can be entered, KPIs can be defined, and dosing rates can be optimised based on process relevant data. Higher LCO or diesel yields, benefits, risks, and trend graphs are visualised on a customised dashboard, displayed on computers and mobile devices (iOS/Android), thus the service quality is improved and wasted time is avoided. Continuous, maximum communication with site data is possible anytime, anywhere to recognise the needs to react on-time with reliable data to plan ahead, reducing the risks. Moreover, as a part of Kurita DMax Technology, Kurita



Priority	Type	Description	Status	Assigned	Expected date	Release date	Comment

Figure 3 Digital platform, visualising analytical and operational data

provides end-to-end solutions by using digital and remote monitoring and management technologies.

Kurita DMax products are based on organic hydroxide chemistry, formulated into specific products tailored to different conditions in the treated systems. Organic hydroxides provide the full base strength of the hydroxide ion (which is by a factor of 10-100 stronger than typical organic amines) against acidic salts such as ammonium chloride, ammonium hydrogen sulphide, and neutraliser salts while completely avoiding the negative consequences of inorganic cations like sodium and potassium that would be introduced with inorganic caustic solutions. Unlike alternative chemistries, DMax products are able to fully dissolve ammonium salt based deposits into the process stream, removing deposits in curative treatments and preventing them from forming again later. This chemistry can even be applied at high temperatures.

If the top temperature is lowered by a few degrees, in order to shift the cut points and produce more middle distillates, this will inevitably lead to a rapid increase in differential pressure due to increased salt content and rising corrosion rates. Kurita DMax products counteract these negative effects with continuous dosing and ensure stable process conditions without significant pressure increase or rising corrosion rates.

A significant temperature reduction of up to 10°C can be realised without an increase in the differential pressure and operational problems. Severe fouling or corrosion in the main fractionator column, which would inevitably be observed in this situation without chemical treatment, can be avoided. Depending on the process conditions, it is possible to increase the LCO yield by 10-20% or even more and thus to significantly increase the diesel production. As a result, the refinery will experience far higher profits and better utilisation of the FCC plant.

If the chemical treatment is carried out with a sufficiently high dosage, salt deposits already formed are dissolved and mobilised. The reaction products leave the distillation column and are transported towards the overhead system where the formed liquid salts are removed with the sour water. There are now several refineries where Kurita DMax technology is used to significantly increase the production of middle distillates with stable operation. It is thus a proven technology that makes a significant contribution to increasing economic efficiency and profitability.

Case study

A refinery was considering maximising its production of LCO from an FCC unit in response to market trends.

However, to respond to fast changes in the market, the refiner was looking for a simple method that did not require time consuming approaches such as adjustments of reactor operations or feed adjustments. The simplest approach was to lower the cut temperature of the gasoline base material in the main fractionator and increase the LCO extract volume. But to accomplish this, the tower top temperature had to be lowered, which inevitably led to pressure build-up inside the tray from deposition of ammonium chloride in the tower.

DMax technology was applied to significantly increase LCO production by lowering the tower top temperature. As a result, a positive increase in LCO yield was accomplished without disturbing the tower operation. As part of the DMax technology, a detailed diagnosis of the plant was carried out on the process conditions, and analysis results were monitored, revealing the trends of salting risks in time, to be able to counteract them immediately. The process and analytical results obtained were fed back into the DMax program for optimisation and showed the successful treatment. For the refining customer, this performance means economic advantage and has become an important application.

Conclusion

The world's population continues to grow steadily and there is still high demand for energy which must be satisfied. Electric vehicles, hydrogen, and biofuels will play an increasingly important role in the future, but will not be able to completely displace fossil fuels.

It is to be expected that demand for gasoline and diesel will steadily decrease in the coming years. However, demand for diesel will probably remain high by comparison. Therefore it is still necessary to maximise diesel, especially for refineries that were designed for higher production of gasoline and now have to produce as much diesel as possible. There are several methods for increasing the yield of middle distillates. The DMax technology is a way to achieve significantly higher profits quickly and without extensive conversion work. The digital platform of DMax enables users to visualise not only harmful trends but also the archived benefit of increased diesel cuts.

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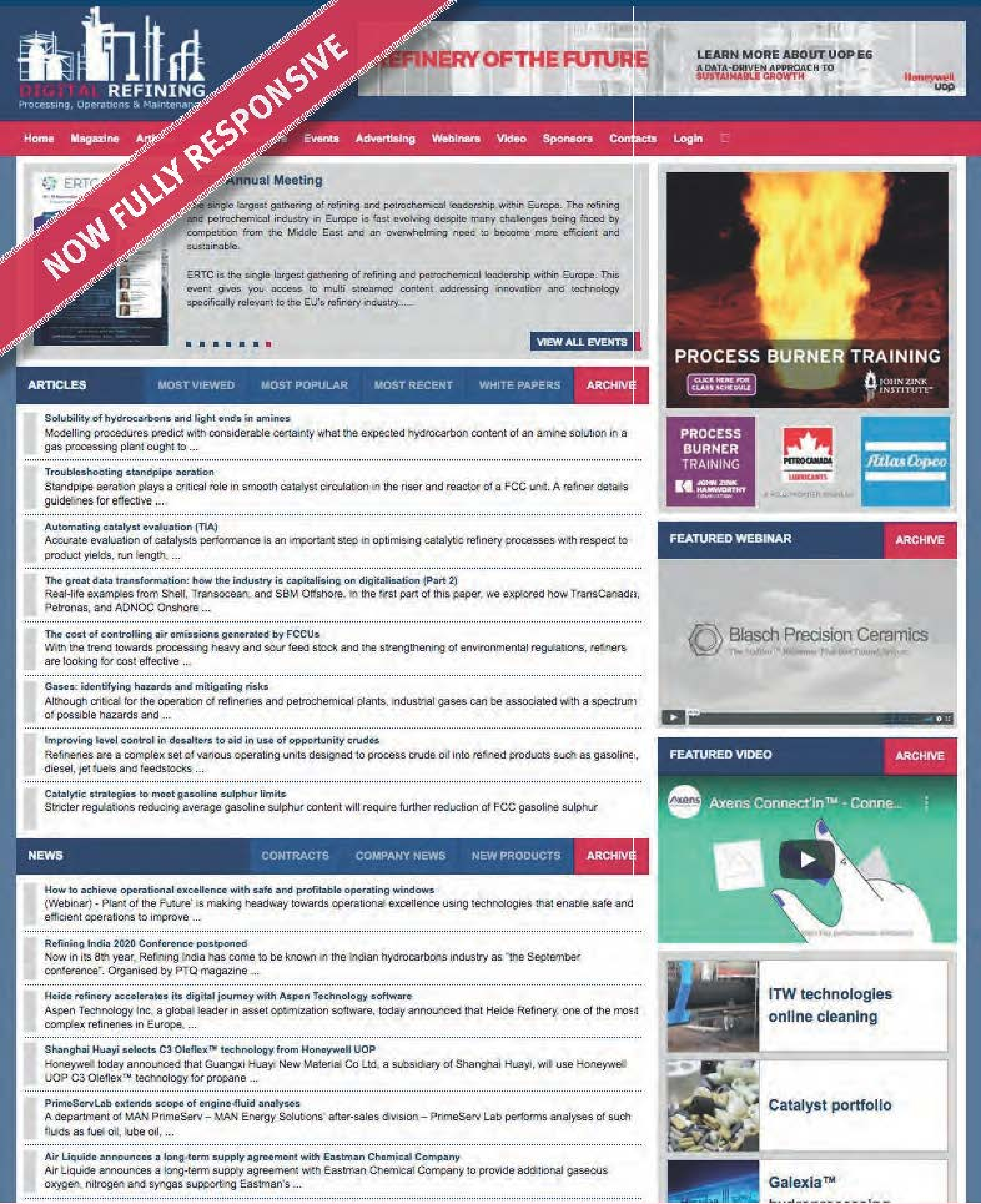

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Selecting turboexpanders for PDH

Expander compressors with active magnetic bearings increase reliability and simplify operations with lower maintenance costs in a propane dehydrogenation process

SHUKUI ZHAO and JAMES ZHAO *Enflex Group*
JOSEPH LILLARD *Atlas Copco Gas and Process*

First commercialised in 1990, the use of propane dehydrogenation (PDH) technology has grown exponentially in the last decade to address the global imbalance in the supply and demand of propylene, particularly in China. In purpose-built PDH plants ranging from 250 000 to 750 000 t/y of propylene production, turboexpanders are used in the cryogenic separation and recovery sections to efficiently produce the low temperature required while minimising the need for external refrigeration. These expanders have generally been configured as expander-gearbox-generators (EGIs). As this article shows, however, expander-compressors (ECs) are alternatives that bring with them several notable benefits, ranging from reliability to maintenance costs. In addition, expanders have been used in butane dehydrogenation (BDH) to produce isobutylene. Modern, high efficiency radial inflow expanders are engineered-to-order and can be designed and built by experienced suppliers in accordance with the oil and gas industry turbomachinery standard API 617, as well as other purchaser specifications.

Comparison of steam cracker yields for different feedstocks

(yield by weight)	Feedstock		
	Ethane	Propane	Naphtha
Ethylene	80%	45%	30%
Propylene	2%	15%	13%

Table 1

The cracker imbalance

Since 2011, the production of natural gas liquids (NGL) in the US has doubled, reaching 5 million b/d. The use of shale technologies — the combination of directional drilling and hydraulic fracturing — is responsible for the rise in both oil and natural gas production. Meanwhile, the midstream industry has responded to this increased production by building more than 200 new gas processing plants, which are responsible for the rise in extraction and recovery of NGLs.

NGLs consist of ethane, propane, butanes, and natural gasolines. Ethane is used exclusively as a petrochemical feedstock in steam crackers for ethylene production, and propane is used as a fuel but also as a feedstock by the petrochemical industry. Some ethylene producing plants can process either ethane or propane, or a combination of both, to ethylene, propylene, and other olefins. But as greater amounts of inexpensive ethane are produced through gas processing, the cracking economics favour the use of ethane feedstock rather than propane. As a result, the overall industry cracker yield of ethylene increases, while the yield of propylene decreases (see **Table 1**).

Nevertheless, the petrochemicals industry has a solution for this imbalance. Abundant propane produced by gas processing is converted to propylene directly in dedicated propane dehydrogenation (PDH) plants (**Equation 1**). In a similar way, isobutane is converted directly to isobutylene in dedicated butane dehydrogenation (BDH) plants (**Equation 2**):

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad [1]$$
$$C_4H_{10} \rightarrow C_4H_8 + H_2 \qquad [2]$$

In China, demand for propylene has been rising the fastest: this growth has been driven by the growing need for polypropylene, which is used for films, sheets, fibres, bottles and containers, automobile parts, and various other household and industrial goods. The domestic supply of propane in China, however, is not enough to fill total demand. Therefore, China must import propane from major exporters, such as the United Arab Emirates, Qatar, Kuwait, Saudi Arabia, Nigeria, and from the US (which has only recently become a significant exporter).

Dehydrogenation works by feeding a paraffinic feedstock (in this case, propane or isobutane) into fixed-bed reactors, where it undergoes hydrogen elimination at high temperatures, followed by separation and recovery of the desired olefin: propylene or isobutylene (see **Figure 1**). The three main commercialised processes are Oleflex (Honeywell UOP), CATOFIN (McDermott Technology), and STAR (ThyssenKrupp Industrial Solutions). In the separation and recovery section downstream from the reactors, isentropic expansion provided by turboexpanders is often used to produce the low temperatures needed while minimising the use of external refrigeration (see **Figure 2**). For many years, EGIs were favoured for this low temperature stage. New process design innovations, however, mean that

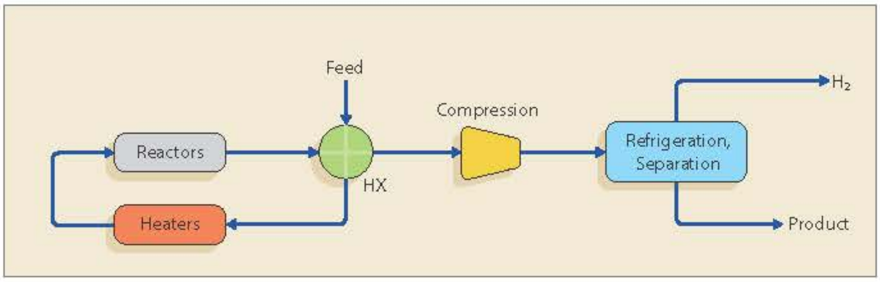

Figure 1 Simplified dehydrogenation process schematic

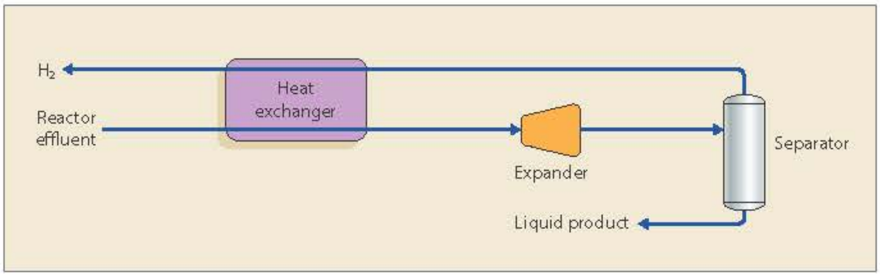

Figure 2 Simplified separation and recovery process schematic

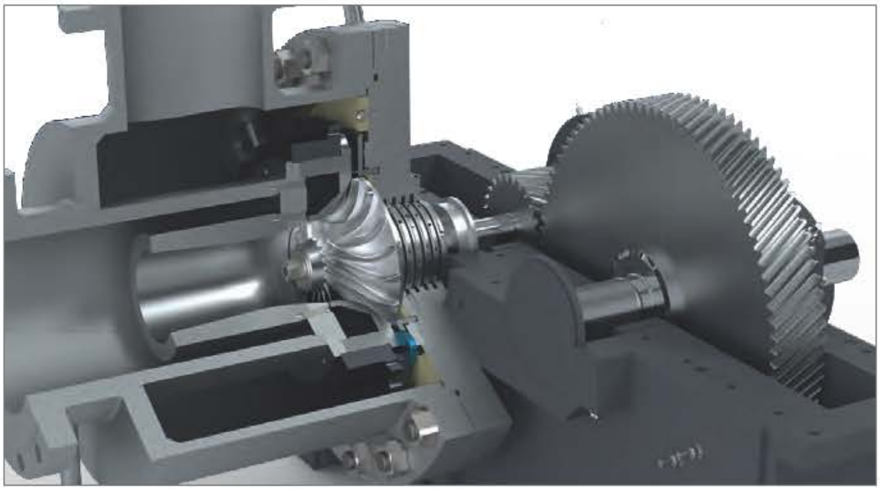

Figure 3 Integrally geared expander cross-section

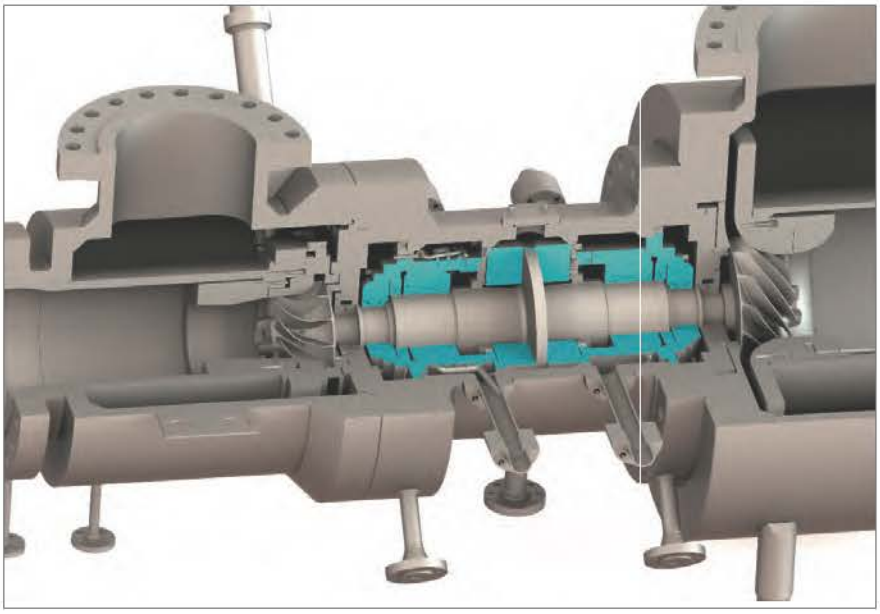

Figure 4 Single-shaft expander-compressor cross-section

nowadays ECs have become highly attractive alternatives.

Turboexpanders: refrigeration and power recovery

'Turboexpander' is used here to distinguish the turbines used for process refrigeration from other turbines used only as mechanical drives or electrical power generators, such as steam turbines or gas turbines. The radial inflow turboexpander, or 'expander', was developed in the late 1930s and 1940s in Germany, Russia, and the US, replacing less efficient and less reliable reciprocating expanders used in cryogenic air separation before that. By the 1950s, several manufacturers were producing air separation expanders. A decade later, their efficient refrigeration and power recovery meant expanders were being used in natural gas processing plants (NGL recovery), petrochemical plants (ethylene and ammonia production), and refineries (tail gas recovery). The oil and gas industry recognised the high reliability of radial inflow expander-compressors in 2002 with their inclusion in the seventh edition of API 617, an industry standard with design and construction guidelines to provide a minimum service life of 20 years and at least five years of uninterrupted service.

In an integrally geared configuration (EGI), the shaft power from an expander drives an electric generator (see **Figure 3**). In a single-shaft EC, the shaft directly drives a centrifugal compressor (see **Figure 4**). **Table 2** shows typical expander operating conditions for a typical PDH process. In most applications, two expander stages operating in series are required to efficiently expand the process gas over the available enthalpy drop, denoted HP (high pressure) and LP (low pressure).

High levels of efficiency characterise peak expander performance. **Figures 5** and **6** show that high efficiencies are achieved by running at high shaft speeds (above 30 000 rev/min) and at high tip speeds (1200-1400 ft/s, 365-427 m/s). This is determined by a combination of factors, such as outlet volume flow,

Sample expander process conditions for a large PDH plant

Inlet pressure, psia/bara	190/ 13	104 / 7.2
Inlet temperature, F/C	-134/-92	-173/-114
Outlet pressure, psia/bara	105/7.2	77/5.3
Outlet temperature, F/C	-173/-114	-193/-125
Gas molecular	3.05	2.85
Gas power, HP/kW	1833/1367	452/337
Pinion shaft speed, rpm	33 000	33 000

Table 2

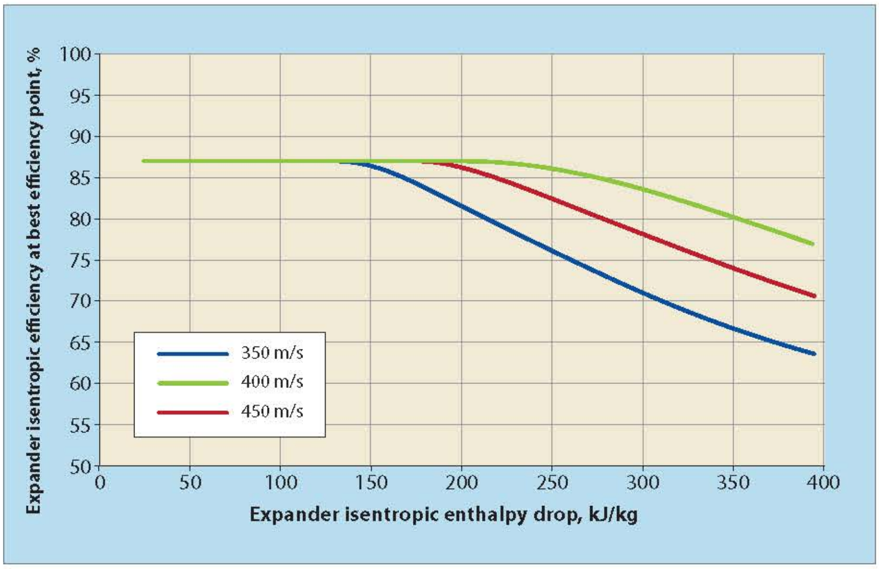

Figure 5 Expander enthalpy drop vs achievable performance

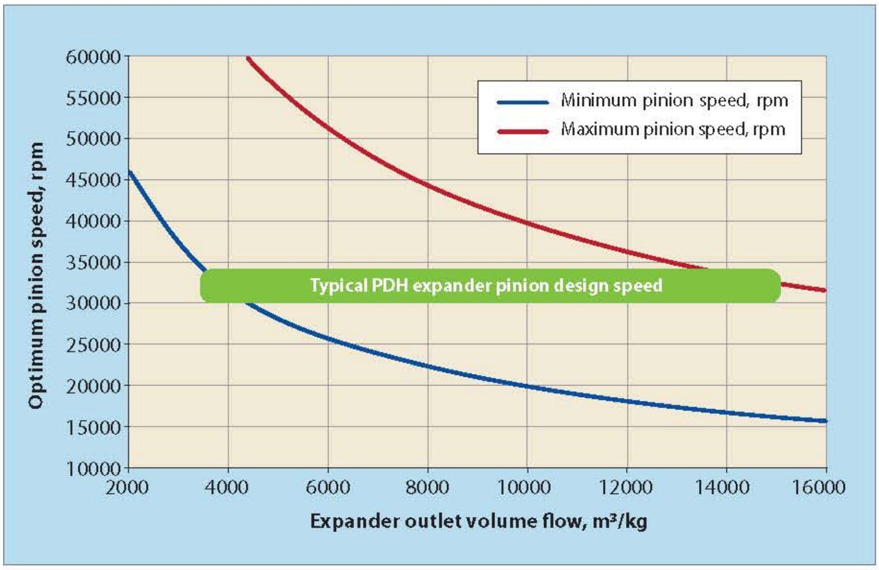

Figure 6 Expander shaft speed vs volume flow

isentropic enthalpy drop, and the use of high-strength aluminum or titanium-alloy impellers. It is important to note, however, that plant conditions can vary depending on feed composition and operating mode, so a broad and flat performance curve is desirable. The radial inflow expander with variable inlet guide vanes uniquely meets this requirement without inlet throttling (see **Figure 7**).

Bearings are central to the functioning of EC units and they can either be oil-fed or active magnetic. EC units featuring oil bearings are supplied with a hermetic lube oil system, seal gas system, and appropriate instrumentation and controls for monitoring and protection. The lube oil system uses a pressurised lube oil reservoir, which eliminates the need for mechanical shaft seals and enables recovery and return of seal gas to the process. In contrast, EC units featuring magnetic bearings have the advantage of eliminating lube oil altogether, though they still require filtered process gas as seal gas, which performs three important duties. Firstly, seal gas is a separation gas, keeping the cryogenic process gas separated from the bearings, which are not able to operate in cryogenic temperatures. Secondly, it is a cooling gas, carrying away the windage heat and eddy current heat from the bearing housing. Thirdly, it is a purging gas, keeping the bearing housing under positive pressure to eliminate any possible entrance of air/oxygen that would mix with the process gas, maintaining a non-flammable atmosphere in the bearing housing.

EGI units have an altogether different set-up. A specialised parallel-shaft helical gearbox is used to reduce the expander wheel/pinion speed down to 3600 rev/min (60 Hz) or 3000 rev/min (50 Hz) for coupling directly to a two-pole induction generator. The integral-geared design eliminates the need for an expander shaft, bearings, bearing housing, and high-speed coupling by mounting the expander wheel directly onto the gearbox pinion shaft. And in contrast to EC units, EGI units use dry gas mechanical seals to contain the process gas and use carbon ring seals with a buffer gas (typically nitrogen) to keep the lube oil away from the dry gas seal. In the past, both single seals and tandem seals have been used.

EGI units can be configured in several ways. A single gearbox driving a single generator can be used whereby both the HP expander wheel and LP expander wheel are mounted on individual pinions, each designed to run at the optimum speed. Alternatively, two separate gearboxes can be used, each driving a separate generator, each with a single pinion with a single expander wheel. The advan-

Figure 7 Expander variable inlet guide vane cross-section

tage of the first configuration is its lower cost; the advantage of the second is that production can continue (though at reduced efficiency and recovery) even if one of the two EGI units is down for maintenance or repair. The second configuration is often supplied with a three-skid package, in which each machinery train is mounted on its own rigid steel skid, and a single, common, duplex lube oil system provides lube oil to both gearboxes. Alternatively, a two-skid package can be supplied, where each machinery train has its own dedicated lube oil and seal gas system mounted on the machinery skid.

The method of connecting the induction generator to the local plant grid is another central consideration, and the method is similar to connecting an induction motor. The grid itself provides the generator excitation, voltage control, and speed control, and this means there is no need to include the switchgear that would be needed with a synchronous generator. For start-up, the expander variable inlet guide vanes are slowly opened to ramp the generator up to synchronous speed, then the generator breaker is closed to tie the generator to the local plant electrical grid.

In all expander installations, the machinery is monitored for overspeed, shaft vibration, and bearing temperatures, and likewise auxiliary systems are monitored for proper operation. Deviations are handled first by a warning ('alarm'), and then, as conditions worsen, by protection ('shutdown'). Since the expander produces its power from the incoming gas stream, the shutdown is accomplished by a quick-closing, air-to-open/spring-to-close trip valve located just upstream of the expander inlet flange. An EC compressor-loaded unit quickly comes to a stop in 5-10 seconds, but an EGI unit, with its high inertia, will take 2-3 minutes to coast to a full stop. If a plant problem results in a loss of the lube oil pump motors, then during the long EGI coastdown, lube oil is supplied by an overhead tank.

Radial inflow turboexpander technology provides both cryogenic refrigeration and power recovery in a variety of processing applications. In recent years, this technology has been widely applied in the separation systems of PDH and BDH petrochemical plants. The turboexpander equipment and auxiliaries are custom engineered for maximum efficiency and high reliability, and they are designed to conform with the specifications of each EPC, owner/operator, and process licensor. Ultimately, whether a plant uses an EC or EGI configuration depends on a range of factors, from questions of cost to reliability requirements.

Alternative process configurations

Both EC and EGI units have been designed or installed for dedicated PDH or BDH units using a recently patented cryogenic separation process designed by Enflex, a process licensor specialising in cryogenic process technologies. This separation process, PSHS, was specifically designed for Honeywell UOP's Oleflex technology to separate and recover propylene, isobutylene, and hydrogen from the reactor effluent streams. Cryogenic temperatures are achieved by expanding the high pressure effluent gas stream through two expanders arranged in series, providing cooling to the effluent gas stream to achieve the separation process. Both expanders can be configured either as EC units or as EGI units based on the specified requirements for the dehydrogenation unit.

Figures 8 and **9** illustrate the EC and EGI configurations designed for a 450 000 t/y PDH unit, similar to one that started operations in northwestern China in 2019. This innovative process refinement significantly improves start-up time, operational flexibility, and plant reliability. It achieves this by combining the expander system with a robust, integrated main heat exchanger that contains one or more custom-designed brazed aluminum heat exchangers (BAHX). Each

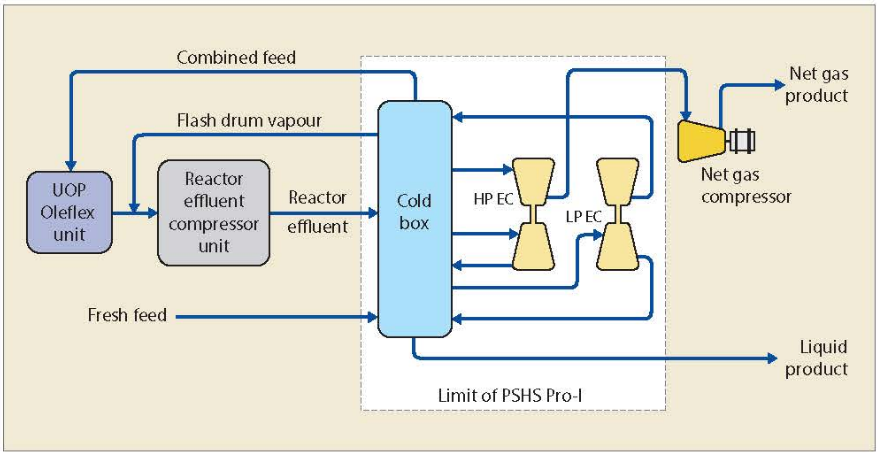

Figure 8 Configuration for a 450 000 t/y propane dehydrogenation unit using an EC

BAHX features proprietary liquid and vapour mixing, and distribution designs to achieve optimal thermal performance.

Table 3 compares the efficiency and key features between the EC and EGI configurations designed for a 450 000 t/y propane dehydrogenation unit. The EC design generates a higher pressure for the net gas product that feeds to the net gas product compressor, reducing the horsepower required for the effluent boost compressor or the product gas compressor. In addition, the EC configuration also benefits from an oil-free system, which prevents process contamination, reduced unit footprint and capex, as well as increased reliability with minimal maintenance requirements.

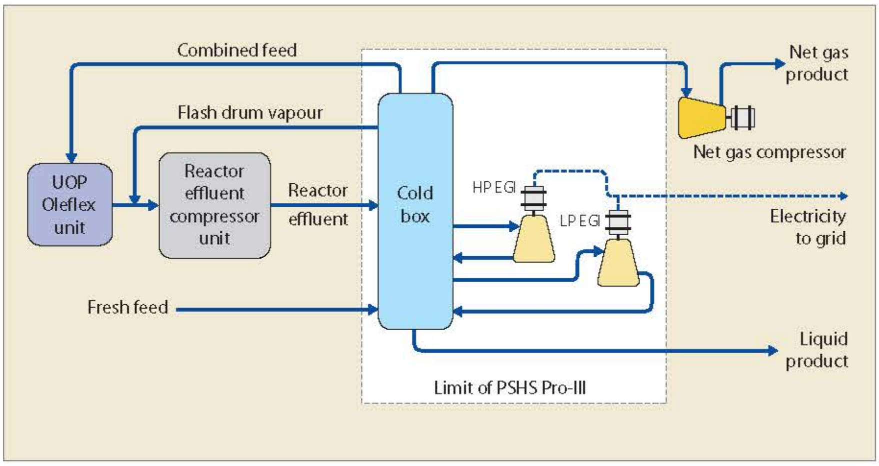

Figure 9 Configuration for a 450 000 t/y propane dehydrogenation unit with an EGI

Efficiency comparison between PSHS Pro-I and PSHS Pro-III designed for a 450 000 t/y PDH unit

Enflex PSHS process	Pro-I	Pro-III
PDH plant capacity, kTPA	450	450
Expander unit type	EC^1	EGI
Expander units cost factor	1.0	1. 25 to 1. 5^2
Pressure at net gas product compressor Suction/discharge, kPa.G	576/3500	707/3500
Total power input including net gas compressor, kW	3105	3005
Power generated by EGIs, kW	0	-478
Net gas compressor, kW	2700	3078
Liquid product pump, kW	450	405
Reliability	++^{4}	+
Operability	++^{5}	+
Expander unit footprint factor	1^3	3

1: EC units are either oil-fed or active magnetic bearings
2: Two EGI units are about 1.25 to 1.45 times more costly than two EC units
3: The footprint of two EGI units with a common lube oil system is about three times the footprint of two ECM units on a common skid package
4: EC solution eliminates gearbox, generator, mechanical seal, and lube oil system
5: EC has a variable shaft speed capability, enabling expander operation at rich start-up gas conditions, simplifying cooldown operation

Table 3

Conclusion

Propylene is manufactured from propane using dehydrogenation in several licensed processes featuring high temperature reactions in the presence of a special catalyst. Cryogenic separation and product recovery follow the reaction, and turboexpanders are frequently used to efficiently produce refrigeration from the expansion of hydrogen-rich reactor effluent. The most common configuration uses EGI directly coupled to induction generators, utilising the recovered power to reduce the electrical demand of the plant. An attractive alternative, however, is to use ECs with active magnetic bearings, thus eliminating the gearbox, mechanical seal, generator, and lube oil system. This simpler and proven alternative increases the reliability, simplifies start-up and cool down, and reduces maintenance costs over the life of the plant.

PSHS Pro-I and PSHS Pro-III are trademarks of the Enflex Group.

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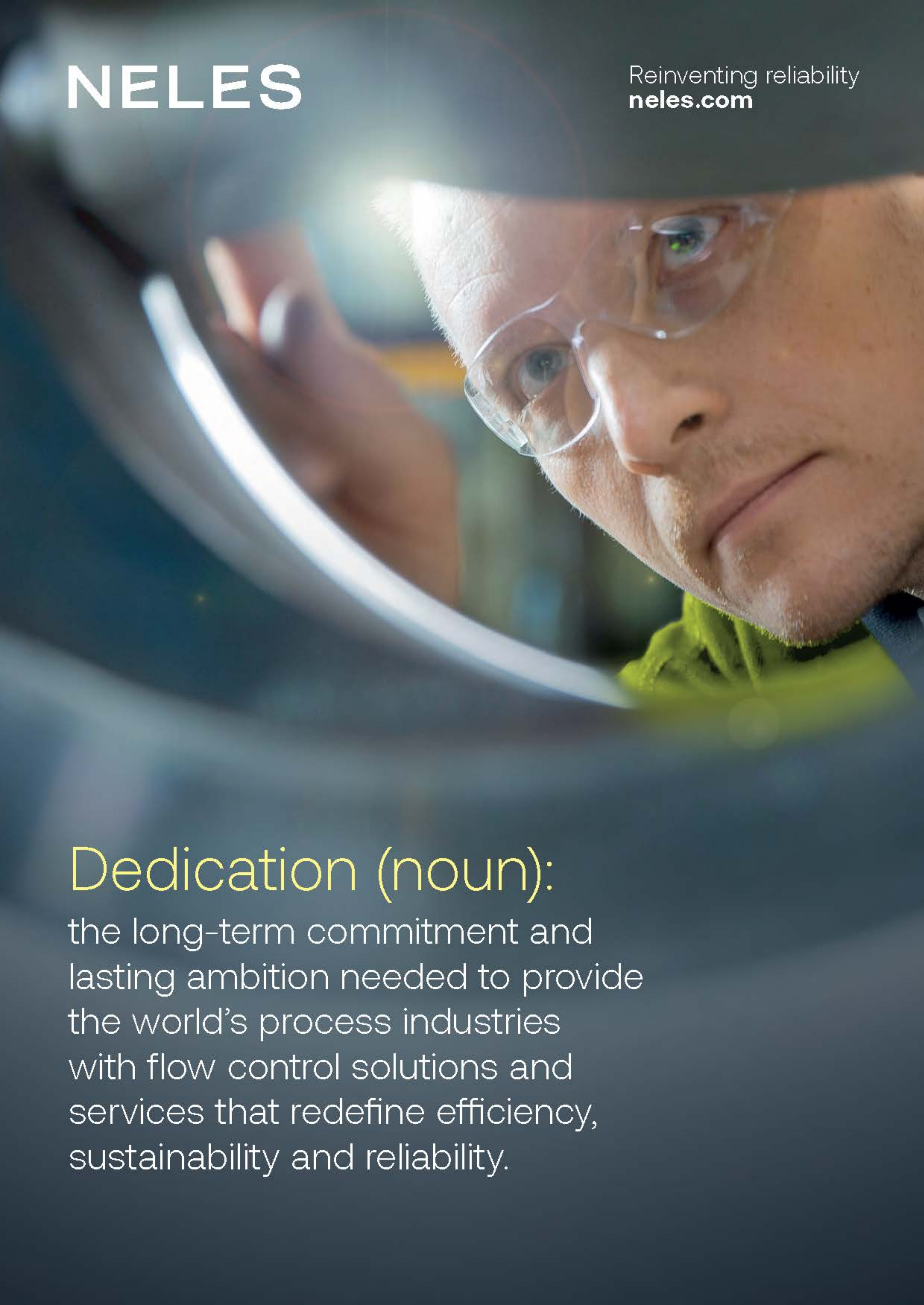

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Digitalisation for improved operations

Increased availability of gas analysis equipment through digital transformation can raise levels of operational excellence

TONY DODD
Servomex

Many industrial production processes depend upon reliable, accurate, and stable gas measurements in order to optimise operations, maintain safety, and meet regulatory requirements. Gas analysis companies continue to innovate in this area. However, they also believe that the solution surrounding the measurement could be improved in the future as technology and digitalisation develop.

In today's Industry 4.0, economic, competitive, and regulatory pressures combine with the challenges arising from cultural and workforce shifts to spur a change in operations. The focus on operational excellence – seeking the optimisation of processes, assets, and people – is increasing and paying dividends.

Top-quartile performers stand out for safety, reliability, efficiency, sustainability, and financial performance when compared to those at the opposite end of the spectrum. They average three times fewer recorded safety incidents, a 4% increase in operational availability, 50% lower maintenance costs, a 30% reduction in emissions and energy use, and 20% lower operating costs – clearly helpful in maximising profits and margins.

With tougher times ahead, a continued focus on operational excellence could be critical for competitiveness or survival. Gains in operational excellence often result from incremental, thoughtful, and focused digitalisation initiatives. These include finding ways to automate or streamline manual, error-prone, or slow activities, and to improve situational awareness.

Low cost sensing, connectivity, data storage, and processing can be harnessed to enable more informed and responsive operations and maintenance, enabling new levels of optimisation and asset management.

Offline gas analysis and operational excellence

Many industrial processes depend on gas concentration measurements to support their operational excellence objectives. If those measurements become unavailable, the result is increased operational costs, decreased operational revenue, and increased operational risks.

> Low cost sensing, connectivity, data storage, and processing can be harnessed to enable more informed and responsive operations and maintenance

When a gas analyser is offline, operational costs can increase because the process control system has less information on which to base adjustments, leading to the degradation of control. In many cases, a process can continue operating and avoid a shutdown, but it cannot run optimally. This may result in higher energy consumption, increased use of fuel or other resources, potential to impact other assets, and, of course, additional overheads to remedy the offline analyser.

A typical application example is the process for the reduction of NOx emissions in combustion power plants (DeNOx) using selective catalytic reduction (SCR). In this process, ammonia (NH_3) is injected into the gas flow from the combustion process; this reacts with NOx in the flue gas in the presence of a catalyst to form H_2O and N_2. A surplus of unreacted NH_3, commonly referred to as ammonia slip, is wasteful and costly, and may also lead to harmful deposition effects which impact the catalyst and potentially cause corrosion of air preheaters located further downstream.

Operational revenue can also decrease when a gas analyser is offline. The degradation in control capability can result in off-spec product quality, lower product yield, or product scrappage. As an example, during semiconductor wafer manufacture – where ultra-pure gases are required – the smallest impurities can result in major defects, leading to product scrappage.

An offline gas analyser also increases operational risks. Using the ammonia slip example above, harmful emissions increase and can have regulatory consequences.

In addition, some processes depend on accurate gas analysis to maintain safe operation. One example is combustion in control fired heaters, integral to many hydrocarbon processes. These heaters are highly dependent on reliable, continuous measurement of excess air. Efficient operation of larger, fuel-hungry units, such as those on ethylene crackers, involves a delicate balancing act to remain on the safe side of a tipping point from efficient, low emission operating conditions to potentially explosive low oxygen and fuel rich conditions.

Factors that reduce availability

It is clearly important to achieve high availability for gas analysis while balancing cost and risk. However, reduced availability can occur due to a number of factors. Firstly, installation and commissioning issues can impact upon tightly planned and coordinated construction, upgrades, and shutdowns, and may lead to delayed start-up of production. The cost of such a delay can amount to hundreds of thousands of dollars each day, due to lost revenue and the need to reschedule dependent works. Factors contributing to these delays include late delivery, defective materials, poor installation, and limited field access to information.

Exposure to unforeseen process and operating conditions is often detectable by analyser diagnostics, but not in all cases. Depending on the exact nature of the conditions, gas measurements may discontinue while the analyser reports faults or out-of-specification indications to the plant control system. Examples of conditions in this category include ambient or sample gas temperature/pressure/flow levels or rate of change beyond specification, poor power supply, excessive vibration, and electromagnetic interference.

Additional conditions may also be detectable by specific gas concentration measurement technologies. For example, unexpected background gases and high dust or particulate loading in the process gas stream can compromise spectral shape quality required to obtain measurements using tunable diode laser spectroscopy (TDLS) measurements. Some conditions can result in damage and require replacement parts.

Another factor which can lead to degraded performance, and ultimately to an unavailable measurement, is inadequate maintenance. For example, sampling systems and analysers themselves often include filters to protect the gas sensors from foreseen contaminants such as particulates and moisture. These may need to be cleaned or replaced periodically. Even under expected operating conditions, obscuration can build up over time on the optics within analysers, which requires cleaning.

Maintenance activities, such as cleaning or replacing filters, cleaning optics or performing periodic validation of measurement accuracy (and, if necessary, calibration), typically require analysers to be taken offline.

If the analyser is incorrectly operated – for example, through the inadvertent adjustment of critical configuration – it can create effects that effectively render the analyser offline or untrustworthy. Examples of this include disabling or changing the temperature or pressure compensation configuration, modifying assigned behaviour of outputs, or even modifying essential measurement details, such as optical path length of an in-situ installation.

Availability issues and activities could look very different if future products and services enabled timely access to the right data, for the right people, in the right place

Finally, unexpected component failures typically result in diagnostics identifying the faulty part. The impact this has on the gas measurement and its availability to the control system depends on the nature of the faulty part.

Resolving availability issues

There is a common theme to many of the activities currently used to resolve the different types of 'unavailability event'; these are manual, inefficient, error-prone, and not always sufficiently data-driven.

Often, they involve writing notes, taking photographs, or capturing limited digital logs at the site, travelling from the site to an office, then referring to various documents (orders, delivery notes, contracts, manuals, drawing, technical bulletins, and the like) to determine next steps, before either returning to the site or contacting the distributor/supplier for support.

Emails and phone calls are a limited and imprecise way to convey all the necessary information about an issue. Multiple emails and trips to site can be necessary to incrementally find and add details before remote support workers gain enough contextual awareness to offer insight. In the meantime, offline duration increases.

Visits by service teams do not happen instantly, so the impact on revenue is potentially extended further. Travel and subsistence add costs and introduce new workers onto the site, increasing risk. Their expertise and direct access to a team of experts will help resolve the problem, but one visit may not be sufficient. Was a diagnosis based on notes, pictures and limited data logs enough to ensure the right tools and parts were brought along to provide a fast and accurate first response?

While gas analysers have been intelligent devices for many years, and integrated into control systems, they have been focused on providing the gas measurement and health indications necessary to provide situational awareness to process control systems and operators.

They have not continuously recorded or exposed all events and data streams to allow a retrospective and contextualised analysis of analyser and process behaviour since there has not been sufficient processing and storage capacity or connectivity bandwidth.

A further consequence of not recording all events and data streams is that maintenance activities remain scheduled events, regardless of system conditions, and so contribute to waste and unnecessary risk.

Finally, some issues are resolved through a process of elimination or experience. Inbuilt diagnostics may not explicitly detect a condition, but experts may infer or postulate that a condition exists from other data. Examples include excess vibration, poor power supply, and some spectral quality issues.

Digital transformation and improved work processes

Digital transformation offers a significant opportunity to improve these work processes. However, this depends on a combination of increased amounts of real-time and static digital data, along with increased access to it.

These availability issues and activities could look very different if future products and services enabled timely access to the right data, for the right people, in the right place.

Increased data collection and tracking from order to delivery, throughout our internal processes, could improve transparency and communication of supply issues. While the elimination of supply issues is the goal, problems do sometimes occur, and early situational awareness enables sites to take early action to minimise disruption.

Industrial facilities increasingly build digital twins of their facilities and assets, using asset management systems. These enable connected workers – carrying out installation, commissioning, or maintenance work – to access 2D drawings, 3D models, manuals, technical bulletins, and other information at the site via appropriate mobile or wearable devices. Some systems provide an annotated augmented reality capability, enhancing the worker's view with a digital overlay which provides visual guidance for the task.

Access to data on this 'right time, right place' basis removes many of the delays in resolving issues. Equipment suppliers like Servomex need to provide product data in appropriate ways or formats in order to extend these services to gas analysis systems.

Not every facility has advanced asset management in place, but site-wide wi-fi access is increasingly available. This could support an always up-to-date, always-on E-Ink based QR code on every gas analysis system, encoding its unique identity, current physical build, firmware details, and other vital data. Scanning the QR code with an app installed on a smartphone or tablet would provide immediate access to correct and searchable versions of 2D and 3D data, manuals, and technical bulletins that may help fast local resolution.

The app could also provide direct access to technical or application support and ensure that maximum context about the asset is available to the support operative, minimising the need for emails and phone calls to collect more information.

Annotated augmented reality technology may be possible here too, enabling experts to provide the visual guidance and over-the-shoulder support a workforce may need to guide their actions more efficiently.

Misoperation of the analyser is avoidable through additional security controls. For example, well-established methods such as two-factor authentication could be employed by analysers to protect against ill-considered or inadvertent changes to critical configurations.

Objectives of operational excellence may be enhanced through the application of digitally transformed capabilities

Service plans provide increased confidence that unplanned downtime can be avoided. However, preventative maintenance, while nowhere near as costly as reactive maintenance, is still not optimal. Operational costs could be reduced, revenue less affected, and risks lowered if maintenance was carried out only when conditions require it. This can be accomplished through predictive condition based monitoring.

Condition based monitoring needs significantly more data than is required for process control. Instead of using the Namur NE 107 type diagnostic health indicators that gas analysers currently provide for process control, the data behind those indicators is exposed. Patterns, trends, and correlation analysis can then deliver greater insight into how things are changing over time, and at what moment those changes may impair performance.

Increasingly, capable plant operational intelligence systems, built on top of, or integrated into, plant historians, are optimised to ingest and cleanse this type of data, contextualise it, analyse it, and provide dashboards or notifications of critical events to the workforce.

It is possible to integrate equipment into these systems using traditional Fieldbus protocols such as Modbus. However, because Modbus maps for all types of device are unique and do not conform to any standard profile, ingestion would need to be configured, introducing another cost and productivity overhead. Support by gas analysers for newer connectivity methods, such as Wireless HART or OPC-UA, would enable a more plug-and-play approach.

Given the provision of appropriate device, system, and service level security, additional operational intelligence services could enable suppliers to monitor gas analyser assets for operators under service level agreements, providing new levels of optimised service response.

Conclusion

Operational excellence is key to the competitiveness and even survival of many industrial operators, and can pay huge dividends in safety, reliability, efficiency, and financial performance.

These objectives of operational excellence may be enhanced through the application of digitally transformed capabilities. Innovative gas analysis suppliers can take advantage of developing technologies to support these capabilities, ensuring maximum availability of their equipment.

Tony Dodd is Head of Digital Architecture with Servomex. He writes a regular blog for Servomex, Beyond the Measurement, which looks at the key issues surrounding gas analysis and digital transformation.

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Furnace cleaning by robots

Remotely cleaning furnace tubes slashed the cost of hydrogen production for a refiner

YAHYA AKTAŞ, SONER OZAYLAK, SAMET ŞANLI, METIN BECER, SULTAN ORMAN and ASLI REYHAN DINÇER
Tüpraş

The adsorbents in a pressure swing adsorption unit, part of Tüpraş Izmir refinery's hydrogen manufacturing unit (HMU), were changed during a turnaround. After start-up, some of the adsorbents were carried by the tail gas stream from misplaced screens in one of the beds and accumulated over the steam methane reformer furnace's convection bank tubes. This resulted in lower heat transfer, more fuel gas consumption, and increased flue gas temperatures. Within the scope of a turnaround three years later, a cleaning procedure by Tüpraş's Combustion & HC Loss Control Engineering group was applied in order to mechanically clean the tubes and therefore restore the design performance of the furnace. The aim of the study is to evaluate the performance of the cleaning operation on hydrogen production costs and on overall unit operation.

The HMU was designed to produce pure hydrogen using naphtha as feedstock, but natural gas and net gas from continuous catalytic reforming can also be used. The hearth of the unit is the steam methane reformer furnace in which there are 188 radiant tubes, each filled with catalysts promoting the endothermic reforming reactions. In the convection section of the furnace, there are six coils transferring energy to the feed and the steam streams.

To increase heat transfer and therefore to save energy in the convection section of the furnace, the decision was taken to apply mechanical cleaning. In addition and as further motivation for the project, since 1993 and the first start-up of the unit, no mechanical cleaning had been carried out in the convection tubes due to their inaccessible locations.

In order to compare the furnace's performance before and after the cleaning procedure, a valid simulation was used for the furnace and the unit. The results can be found later in this article.

Figure 1 Tube cleaning robot

Figure 2 Robot during tube cleaning

Tubetech was assigned for robotic cleaning activities in the furnace's convection section and the work was led by the refinery's Combustion & HC Loss Control Engineering group.

Before installation of the robots (see **Figure 1**), some preparations were carried out. A pool of nylon covers was established at the bottom part of the convection zone to prevent wetting of the radiant zone side refractories. Wastewater that accumulated as a pool was discharged from the furnace by means of a channel.

In addition, four new 60x45 cm² windows were cut into the metal surface so the robots could access the convection tubes. Cleaning of the tubes in the convection zone was carried out by the robots. These can deliver water pressurised to 1000 bar from their nozzles (see **Figure 2**). The robots' motion over the tubes was managed via a control panel connected via cables. Two robots were installed in two different locations and the cleaning was completed in approximately 60 hours.

Diagnostics

Within the study, operational parameters before the shutdown for cleaning were regarded as the base case. According to the model's results, the average cost of hydrogen production before and after cleaning was calculated at $943.9-919.3 $/t. The production cost of hydrogen decreased by $24.6/t after cleaning and the payback period for the project was 68 days.

After cleaning, the heat duty of the convection section increased. At the same time, the steam production rate and the steam temperature also increased. As a result, the flue gas temperature leaving the furnace decreased by about 60°C.

Evaluation after cleaning

Izmir hydrogen plant's SMR furnace was evaluated with respect to operational and economic effects following cleaning in the convection zone. A simulation model was built using Aspen Hysys. After cleaning, the existing model of the unit was updated according to field data. In the model, the convection/radiant duty ratio and the fouling coefficients in the convection banks were revised to match the measured field data to the model. The effects of each of these parameters are examined in this section. Since there was a 4% difference between the inputs and outputs in the original operational data, routine unit laboratory analysis and mass balance reliability were checked and unreliable laboratory analyses were not used in the model. The simulation model is based on the following assumptions:

- In the model, the reformer outlet temperature is set according to the

Figure 4 SMR furnace convection bank tubes before and after cleaning

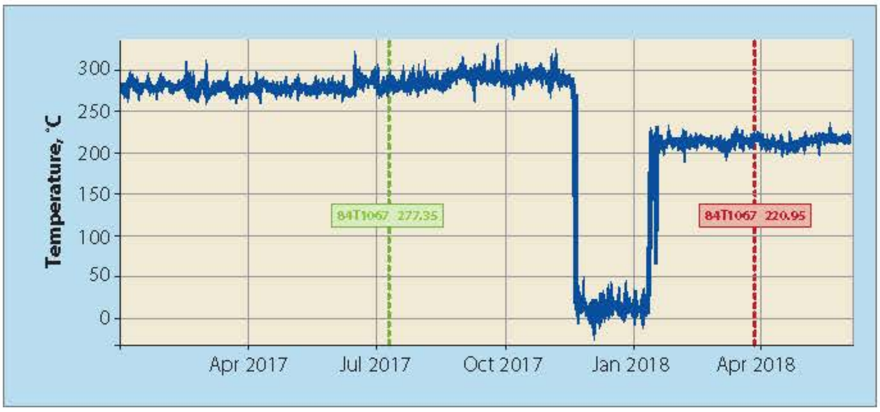

Figure 3 SMR furnace flue gas temperature leaving the stack, before and after cleaning

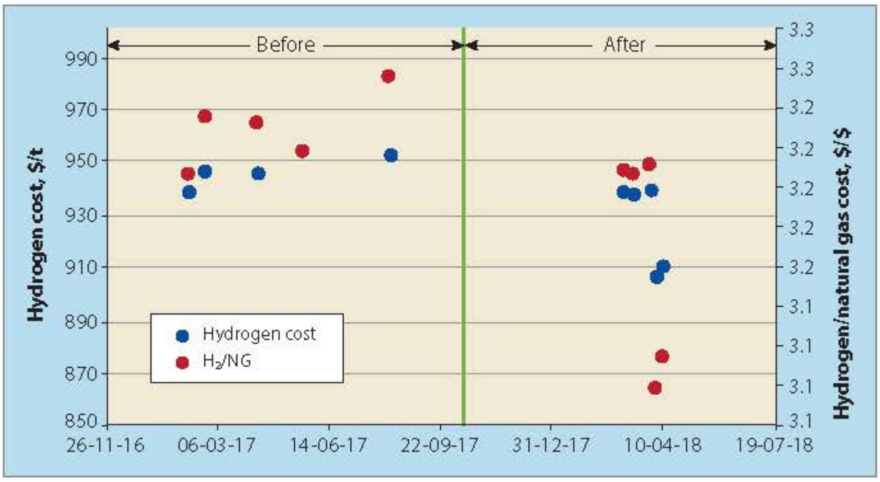

Figure 5 Hydrogen production cost analysis

exit methane content. There are also thermal losses between the temperature at which the reaction takes place and the location of temperature measurement. Therefore, the exit temperature is set 25°C above the measured value to match the exit methane slip

- In the cost analysis before and after cleaning, natural gas/CCR net gas and utility prices were considered as constant and only fuel costs were changed according to their thermal content
- To compare the economic effects of cleaning on the same basis, the analysis days were selected such that unit operation is similar in terms of several operating parameters since the hydrogen production cost is very much affected by these parameters
- Feed quality and unit capacity: as the net gas feed, thus feed hydrogen content, increases, the cost of hydrogen production decreases
- SMR exit temperature: as the temperature increases, the cost of hydrogen production decreases
- Steam/carbon ratio: as this ratio decreases, hydrogen production cost decreases

Operational improvements after cleaning

The most significant improvement after cleaning was in the flue gas temperature. The average flue gas temperature was 278°C before cleaning (see **Figure 3**), and reduced to 220°C after cleaning. Thus, the furnace's thermal efficiency increased by about 3%.

Conclusions

Within the scope of a planned shutdown of the SMR plant at Tüpraş Izmir refinery, the aim was to increase the thermal efficiency of the convection zone of the reformer furnace by robotic cleaning performed by Tubetech. The furnace's performance following cleaning was evaluated by a validated SMR unit simulation model using Hysys. After the convection banks were cleaned, the ratio of convection duty to total duty increased to the design level.

The flue gas temperature leaving the stack decreased by 60°C and the steam production rate rose by 20%.

Changes in utility rates (increased steam generation) resulted in a decrease in the unit cost of hydrogen production. In this study, in order to calculate the difference in the unit cost of hydrogen production independently of changing operating conditions, analysis days were selected such that the operational parameters were similar. In addition, a simulation study was performed for different steam/carbon ratio cases. The effect of changing SMR outlet temperature on cost was not evaluated. The improvement in the unit cost of hydrogen production is 24.6 $/t (see **Figure 5**) and the payback time for robotic cleaning costs is approximately 68 days.

In summary:

- Steam production increased by approximately 20%
- The generated steam temperature increased by 10°C-15°C
- The flue gas temperature leaving the stack decreased by 60°C
- The desulphuriser reactor furnace feed temperature increased by 40°C and the SMR furnace's thermal efficiency increased by about 3%

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Mid-cycle skim doubles run time and throughput

Not long after a recent summer turnaround, a major Gulf Coast refinery had a problem. The engineering team noticed a pressure drop (dP) increase in bed 1 of their hydrocracker pretreat reactor shortly after start-up, all but guaranteeing they would not meet their cycle length goal without performing a mid-cycle skim. The site's challenges did not end there. A year later, they experienced an unexpected two hour equipment shutdown. Upon restart, the team observed a dP increase in bed 2 while the state of bed 1 continued to worsen.

The engineers had little time to dream about extending the cycle length – they needed just to keep the reactor online and to run at required rates. As in most refineries, the hydrocracker needed to deliver consistently high throughput for stable operations and to meet demand.

The refinery's engineers knew that the increased pressure drop could limit the hydrocracker's performance. With their standard configuration, which utilised traditional grading, the run times were short. Downtime from mid-cycle skims reportedly ranged from 20 to 60 days. At high-complexity facilities, disruptions like these can seriously impact availability, profitability, and risk associated with turnaround and maintenance operations.

Having worked with Crystaphase to solve tough challenges at other locations, the engineers turned to the company's filtration technologies to deliver results with a novel, empirically based solution to a common reactor problem – pressure drop due to crust layer formation.

Working with the site's process engineer, Crystaphase collected samples from two previous cycles to analyse and better understand the reactor's foulant profile. After lab analysis of these samples, the Crystaphase team identified the foulants that appeared most likely to be contributing to pressure drop.

From this detailed analysis, Crystaphase's process and development engineer, Umakant Joshi, and director of technology, Austin Schneider, developed a tailored solution that could optimise the reactor's configuration. Following the next mid-cycle skim of the hydrocracker pretreat reactor, Crystaphase installed an ActiPhase TRANS solution designed with enough capacity to reach the next scheduled changeout, about one year later, without dP limitations.

With the system installed, the customer met that goal, and when the reactor was shut down for a scheduled full catalyst changeout, the customer installed an optimised ActiPhase system designed, together with Crystaphase, to extend the cycle length even further. Over the duration of that cycle, the reactor suffered several unrelated setbacks, including equipment failures. Despite all of these events, the pressure drop remained virtually flat after each restart.

Through the mid-point of the hydrocracker's first complete cycle with the Crystaphase solution, the pressure drop appeared to remain effectively flat. Given the impressive results, the customer approached Crystaphase to see if the system could continue past its next scheduled shutdown. Because of Crystaphase's work with the customer and understanding of the reactor's foulant profile, the Crystaphase team could turn to its data modelling capabilities for a projection of the pressure drop over the next several months. The customer received some good news – the system would likely continue to perform without dP limitations over an extended cycle.

At the time of its most recent shutdown, the hydrocracker's run time and throughput were each roughly twice what the reactor had been able to achieve before.

With help from Crystaphase to tackle pressure drop and extend run time, the site's mid-cycle skims became a thing of the past, helping the reactors stay online longer and reduce related costs and risks. Ultimately, it was a day-and-night change for the customer's hydrocracker.

Crystaphase
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Lessons for ethane cracking

As automation technology becomes more and more essential, plant operators need to glean everything they can as legacy systems are modernised. That is exactly why, when a Texas facility experienced a strange process upset in the steam cracking furnace, a team of experts applied knowledge gained from a different facility's upgrade to solve the mystery. The lessons learned from the experience enabled the development of best practices for safer and more efficient operations across all natural gas processing plants.

The breakdown

At the heart of an olefins plant is the ethane cracking furnace. To get from natural gas to the products we use every day, you need to break it down into smaller, usable hydrocarbons. To accomplish this task, steam cracking begins the process. Here ethane is fed into a cracking (or pyrolysis) furnace to produce ethylene (80%), propylene (3%), butylene (2%), and other high-value chemicals (remaining 15%).

Coke residue is an unavoidable by-product of this process. Coke formation clogs the furnace and transfer lines, hurting product yields and impairing heat transfer. If the build-up is left to continue, the tubes can burst, causing catastrophic failure resulting in expensive repairs and significant down time. These shutdowns cost the industry millions of dollars in unrealised revenue every year.

To prevent these failures, steam is used to flush out the system in decoking cycles. Unfortunately, decoking itself causes wear and tear on the process equipment. The ethane feedstock remains stable in temperature during standard procedures, but the steam injection for decoking quickly increases both the velocity and heat within the system. If steam is added too rapidly and there is condensate in the line, vapour can explode in the lines, causing damage to the pipes and the water hammer effect on sensitive equipment. It is easy to see how ethylene production is a delicate balancing act between these cycles.

Leading the way in Austria

Innovations in automation technology allow for more process control during steam cracking. Coriolis flow meters can measure mass directly in the line, providing data intelligence to maximise yield efficiencies. This specialised equipment is less impacted by the changing fluid compositions in these hydrocarbon feedstocks. They are very accurate, have high turndown ratios, and straightforward designs that make for easy installation.

Modern equipment can also be used to automate the decoking process. Traditional plant designs still rely on manual decoking, requiring an operator to slowly and carefully open the steam valve over the course of 30-45 minutes to minimise the impact of condensate flashing in the line. Automating these challenging procedures increases the safety, reliability, and longevity of the equipment.

A plant in Austria spared no expense in making these upgrades to their systems. With the help of some of the best in automation technology, their operator had an optimised cracker with more throughput and higher yields while maintaining the highest levels of safety for personnel.

Pipes to blame

A plant in Texas implemented a smaller system upgrade, focusing on adding Coriolis meters, but without keeping the best practices of a fully automated system in mind. It did not take long for things to go wrong with the ethane cracking furnace.

At first, the operator assumed the newly installed meters were to blame, but advanced diagnostic capabilities on their Coriolis meters told a different story. Software checks the health of the meter itself, assuring operators that the flow meter is performing within normal parameters, and its measurement output is reliable. In this case, the meters were fully functional.

Learning lessons from the recent installation at the Austrian plant, the team could trace the Texas plant's steam lines and discover the issue. To reduce the flow rate and keep the steam at a higher pressure, the facility had added a restriction orifice to the steam lines, yet neglected to drill a small hole in the bottom of the line to drain condensate, resulting in loud knocking and shaking in the pipes due to the exploding steam. This was also causing water hammer damage to equipment.

The incident provided the opportunity to develop best practices to implement these newer automation capabilities in ethane cracking furnaces across the industry. Now, no matter the type of technology upgrade, operators can follow the appropriate steps to ensure good piping practices and monitor any potential process upsets with advanced flow meter technology.

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Analysis solves vibration problems

This story starts with a familiar scenario for a fluidised catalytic cracking (FCC) unit; a 30 year old waste heat boiler (WHB) had become a maintenance headache. For the first 20 years, the boiler combusted CO and operated largely reliably. Then when the burners were pulled (and it changed from a CO boiler to the current WHB), there was some vibration – enough to cause eventual cracking at the boiler front wall corners, both in the end connections of the horizontal stiffening members ('buckstays') and in the furnace enclosure itself. While the flue gas leaks were an increasing nuisance, all-in-all the operating experience was not a bad one, and in 2015 replacement-in-kind with improved buckstays was the path forward.

During the first start-up, the new boiler vibrated so violently that only a fraction of the normal gas flow could be achieved. The lower front wall was still the trouble spot, though the vibration magnitudes were way beyond the nuisance vibration seen previously. Even operating at partial load, the internal refractory around the inlet duct was quickly compromised and gas leaks made the lower front wall inaccessible. End connections were again found to be fractured.

So what went wrong? As far as anyone could tell, the boiler really was an in-kind replacement, and there were no gross design or fabrication errors found. The only external change was lowering of the restriction orifice chamber (ROC) upstream to give it more distance from the slide valve above it. Could that be enough of a difference to cause the new vibration? A model of the inlet piping and WHB is shown for reference in **Figure 1**.

Becht was brought in to do to a root cause investigation and fix the vibration issues – starting with field

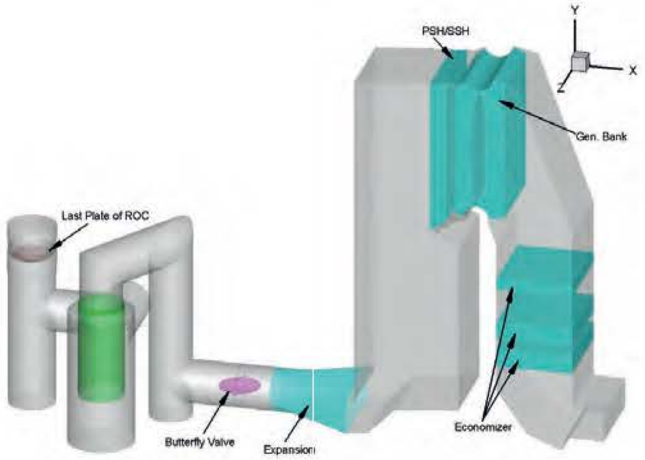

Figure 1 FCC unit waste heat boiler and inlet piping layout

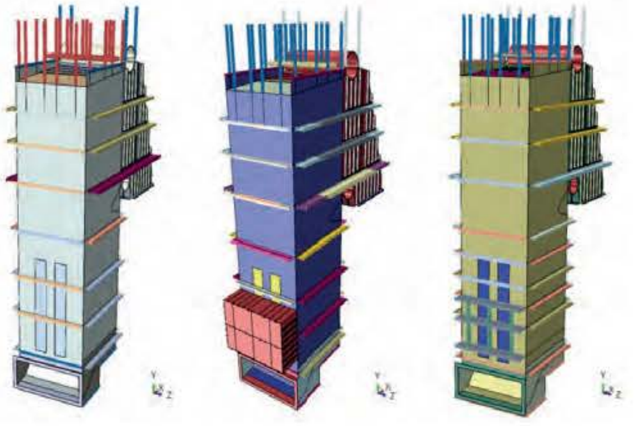

Figure 2 (l to r) Existing configuration, previous windbox configuration (including buckstay stiffeners), and new design modification

vibration measurements more than two years ago, and culminating a few months ago in the successful start-up of the boiler with operation at full capacity. The vibration is not just improved, but in the words of a site manager, it has "gone" altogether. Like most things, the answer did not turn out to be exotic or mysterious – it was hidden in plain view.

Becht assembled a team of vibration, fluid flow, simulation, and boiler structural experts for this project. While simulation played a key role in ruling out the ROC position change, and in helping to prove out the eventual fix, knowing what to look for was the turning point. Becht's boiler structural specialist realised that there was actually a major difference between this in-kind replacement and its predecessor.

A major structure, called a 'windbox', was missing from the lower front wall of the new boiler. It was missing because there was no reason for it to be there, since the windbox housed the previous burners, supported their weight, and reinforced the burner openings in the front wall. After the burners were removed from the previous boiler, the wall openings were patched solid and, with no burners to support or openings to reinforce, the windbox structure became essentially a giant stiffener on what turned out to be a very flexible front wall.

While stiffening up the front wall would be considered a small capital expense, replacing a structure the size of the previous windbox is not trivial either. To help prove out the theory, and to design an effective replacement stiffening scheme, fluid-structure interaction simulation was used to complement the experience based findings. This advanced simulation leveraged computational fluid dynamics (CFD) and coupled dynamic acoustic-structural finite element analysis (FEA).

The CFD was used to provide inlet pressure-time profiles across the WHB inlet for the structural-acoustic analysis and to redesign targeted features in the inlet line. The WHB showed both shedding instabilities across the valve and unstable recirculation zones that collapse and reform along the expansion side walls. The results of the redesign were a 10x drop in predicted pressure pulsation energy.

The structural-acoustic FEA leveraged a high fidelity model of the WHB boiler itself; **Figure 2** shows the three cases evaluated: existing, previous, and proposed modification. The simulation predicts the new stiffening to be as effective as the previous windbox. Specialist knowledge, advanced analysis, and a well-executed implementation earlier this year all came together to give the same result.

Becht Engineering
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New boiler cuts NOx, boosts efficiency

A Texas based producer of products derived from petrochemical raw materials such as C_4 needed to replace ageing boilers. Drivers included a desire for higher efficiency and reliability, reduced operating costs, and gains in environmental performance.

Changes in the plant's processes meant that steam requirements dropped from 1.5 million lb/h to between 850 000 and 1.2 million lb/h. This enabled the facility to eliminate its original nine boilers, replacing them with two Rentech boilers using Coen ultra low NOx burners. Due to their size, boiler components were prefabricated at the manufacturer's site in Abilene, Texas, transported, and assembled on site.

The two D-style field-erected water tube boilers had a heat input of 664 mmBtu/h and produced around 474 000 lb/h steam flow at 725 psig and 710°F superheat. Each boiler included dual burners, a superheater, an economiser, a fan, ladders, platforms, a stack, and trim.

To avoid the firebrick and refractory problems common in traditional package boilers, the furnace section features membrane wall construction, built with 2.0" OD x .135" MW tubes on 4" centres. These tubes are connected by ¼" x 1" membranes made of carbon steel to form a water-cooled enclosure. The furnace size is 13.0 ft x 44.0 ft, with a volumetric heat release rate less than 60 000 btu/h-ft^3. This is an important element in achieving ultra low NOx conditions. Continuous, high frequency resistance welded finned tubes raise convection section efficiency. To combat acoustic vibration, longitudinal, vertical baffles are included throughout the convection section.

Boiler changeout had to be done rapidly during a scheduled outage. To avoid poor combustion issues that may lead to coking of burner elements, the fresh air and core air inlets were modified. This involved changing the usual 45-degree turn to a 180-degree turn to eliminate potential wind gust problems due to it being in the vicinity of the Gulf of Mexico. Further work and tuning done on the burners and the control logic eliminated any possible flame failure issues.

Operators reported easier operation. They no longer have to adjust bias on air dampers or O_2 bias two to three times per hour to control NOx emissions. Upgrading the gas pressure regulator from a control valve configuration to a Fisher 1098 pressure reducing regulator improved response time. This addressed an earlier problem of boiler trips due to pressure swings.

Overall, operators note a 5-7% boost in efficiency compared to the previous boilers. In addition, the facility reports a significant improvement in environmental performance and a reduction in NOx emissions. This has enabled it to meet far more stringent regulatory standards.

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Figure 1 SRU and tail gas treating unit

Figure 2 Wireless UT sensor

Real-time wireless corrosion monitoring

One of the most critical areas for many refineries to be able to manage and maintain from an asset integrity perspective is the sulphur recovery unit (SRU) and tail gas treating unit (see **Figure 1**). The tail gas treating unit is designed to convert the minimal remaining sulphur compounds, not converted originally in the SRU, into hydrogen sulphide (H_2S), which is then reprocessed by the SRU. The SRU tail gas is heated and sent to a catalytic reactor where it is cooled and sent to the absorber column, and here amine removes the H_2S and some CO_2. It is during this and succeeding processes that many find corrosion/erosion events which can cause setbacks in asset integrity planning.

During these processes, amine corrosion with high heat stable amine salts (HSAS) act as a common culprit to failure/damage mechanisms for tail gas units. As per industry standard API 571, HSAS above 2 wt% will cause corrosion rates to significantly increase and limit the existing life of associated equipment/piping. HSAS are corrosive because they lower the pH, increase solution conductivity, and can dissolve the protective oxide layer (film) in equipment/piping. HSAS coupled with areas of high turbulence or changes in flow also cause tremendous increases in corrosion through erosion-corrosion. In this case, it was determined that the design of a nozzle in the horizontal position of the exchanger is a bad industry design and causes turbulence (eddys) that increases the corrosion rate in specific areas.

The solution

Due to the sporadic nature of this erosion-corrosion damage mechanism, achieving a reliable corrosion rate and zeroing in on the most likely affected locations can be challenging. After years of repeated manual ultrasonic thickness inspection at different intervals with limited success which ultimately resulted in unplanned leaks and downtime, the asset owner decided it was time to go in a different direction. Instead of a periodic manual inspection approach, they decided to monitor. The owner, using the help of the inspection, corrosion, and operations teams, mapped out the most likely areas of concern and performed some baseline screening/inspection to identify where to monitor. Then, using automated, wireless, battery-operated ultrasonic (UT) sensors, which were temporarily installed at strategic locations on the asset, the asset owner was able to program reading intervals for the sensors to take wall thickness measurements which were then plotted over time.

The outcome

Using the monitoring approach via wireless UT sensors (see **Figure 2**), the owner was able to quickly (one month) and accurately (to within 0.001") trend the corrosion rate at each point where the sensor was located. Further, with the help of the operations and corrosion teams, the owner was able to tweak process parameters to remediate or reduce the corrosion at this location of the unit.

Financial impact

Since the unit was built, there have been more than 10 unplanned outages over a 15 year period which have been traced back to this issue at an estimated $12 million in maintenance cost and $200 million in downtime. The ability to trend and, in this case, remediate the corrosion rate for the tail gas unit allowed the asset owner to safely operate the unit for an estimated 4.62 additional years, saving an estimated $4.8 million maintenance activities for this unit. A $40 000 investment in a microPIMS starter kit yielded an ROI of 98% and payback period of less than nine months. The rest of the site can also now benefit from the long range wireless infrastructure investment and place sensors across the entire facility to monitor other critical assets.

Sensor Networks, Inc.
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Level measurement for improved process control

A diversified refinery on the US Gulf Coast with a crude oil refining capacity of more than 550 000 b/d operates delayed coker units around the clock. The coke drums are large diameter vessels with thick walls. The vessel design and the aggressive, hot process conditions within make it difficult to reliably control the process with level measurement instrumentation.

Many refineries, including this one, use radiometric technology for point level and continuous level measurements. This refinery had been using neutron backscatter sensors (NBS) for point level density measurements. They were also using VEGA radiometric detectors for a continuous level measurement. Radiometric sensors of all kinds provide non-contact measurements operators can use to control the process efficiently.

Unfortunately, the reliability of their measurement control system began to drop when the neutron backscatter sensors approached the end of their service life. These types of sensors last an average of about 15 years depending on how and where the sensor is installed. When they are installed, they are directly mounted to the vessel, and they need regular recalibrations to provide an accurate output. Plus, this technology is no longer supported by the original manufacturer, making it obsolete. Fortunately, there are more reliable measurement options available from experienced radiometric instrumentation manufacturers.

Replacing an ageing system

The refinery was already using a different radiometric solution for continuous level measurements in their coke drum – VEGA's FiberTrac 31. When the site needed to replace the NBS sensors, they turned to a radiometric technology partner they could count on for support.

VEGA suggested replacing the neutron backscatter sensors with newer, more reliable PoinTrac 31 detectors. These radiometric point level sensors convert incoming gamma radiation into a point level measurement. The highly sensitive scintillation material used in these sensors can detect the smallest amount of radiation activity through the coke drum's thick vessel walls.

Installing three PoinTrac 31 sensors at the same elevations as the neutron backscatter sensors was relatively simple. Each sensor is installed on the outside of the coke drum and mounted to the rigid conduit of the existing FiberTrac31 using U-bolts and the factory supplied mounting bracket – no welding necessary. The entire setup is external to the vessel, which means the sensor does not interfere with the process, and the process does not cause any wear and tear to the sensor. Additionally, no new source material was required because it was using the same existing sources as the FiberTrac 31 continuous level sensor.

The continuous level sensor, in conjunction with the newly installed point level sensors, track the leading edge of the level, providing insight as the coke drum fills with heavy residuum crude oil residual. The PoinTrac 31 sensors inform operators when to inject antifoam, when they have reached their target switch out point, and when they have reached maximum quench water or act as a high-level process alarm. This combination of point level sensors paired with a continuous level sensor offers a complete level measurement solution which coke drum operators can rely on and refinery managers can use to monitor efficiency and throughput.

The delayed coker units are arguably the most important application at any refinery, which is why they require fine process control. That can only be accomplished with reliable, repeatable measurements operators can depend on.

VEGA's PoinTrac 31 point level sensors are easily installed, and they only need to be calibrated once. Calibration can be accomplished using existing sources, which presents an economical, as well as reliable, point level measurement solution.

The measurement output provided by these radiometric detectors does not interfere with the process, and conversely, the process does not have any adverse effects on the sensor. Once installed, a refinery can expect consistent measurements on their delayed coker units for decades into the future.

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Level measurement in coke drums

If heavy components of crude oil are to be converted into lighter ones, cracking processes come into play. The desired conversion effect is achieved by overheating the distillation residues under pressure. Such thermal cracking can be done in a coker. Therefore, a mixture of preheated fresh feed (residual oil) is passed from the fractionator via a heater to one of the large coker drums. Here the cracking and expansion of the fluids is allowed. The lighter cracked hydrocarbons are taken off at the top of the drums to the fractionation tower, while cracking heavy hydrocarbons results in their conversion into a vapour due to the high temperature.

As the vapours escape the viscous liquid, they tend to create a foam layer and solid coke remains in the drum which slowly fills up. The foam layer can vary depending on many parameters such as operating temperature, pressure of the drum, type of crude, or charging rate. In a worst case scenario, this leads to a foam over, which can be a costly event (up to $2 million), not only causing loss of production with downtimes of 2-6 weeks but also requiring a lot of manual labour to clean coke out of the overhead lines and fractionation tower. To prevent such foam overs and reduce carryover, but also to improve the utilisation of drum capacity, a level measurement in a coke drum is necessary. Also, to increase throughput of the unit, one of the most important objectives is to fill the drum higher, safely, and reliably. However, to achieve this, one must have a reliable measurement method for the foam front in the drums.

But level measurements in coker units are quite different when compared to typical level measurements. Common measurements are installed on continuous processes with no changes in process conditions, which means that the lower fluid density as well as vapour density is relatively constant, and one calibration is enough. But due to the continuous switched feed between two drums in a time based cycle, delayed coking is the only semi-continuous batch process in a refinery with different process conditions during a cycle and possible build-ups.

A simple calibration is not sufficient for this measurement task, calibration changes depending on the cycle. Due to the conditions in the coke drum, a level measurement is a very challenging task. Where other measuring technologies tend to fail or end up being extremely unreliable, radiometric level technology is ideal for monitoring the coke level due to its non-intrusive nature. Thereby, use of gamma continuous level measurement has many advantages. Measuring a continuous level instead of single point information with neutron backscatter measurements helps to determine the rate of change and thus to increase the throughput of the unit. By using gamma radiation instead of neutron radiation, a radiation area is not necessary. The typical dose rate of a gamma continuous measurement 1 m from the drum at the detector side is 0.1-0.2 µSv/h (0.01-0.02 mrem/h) or at the source side 0.5-1.5 µSv/h (0.05-0.15 mrem/h) compared to 85 µSv/h (8.5 mrem/h) from a neutron backscatter measurement. A point measurement only in proximity to the probe does not detect any foam, which rises faster outside the reach of the point neutron backscatter probe, but with a gamma level it is possible to reliably detect non-uniform rising of foam front as the measurement covers the entire drum diameter. This not only reduces the foam overs, but also the use of anti-foam chemicals. Minimising the use of anti-foam saves a considerable amount of money and increases hydrotreater catalyst life.

Berthold's measurement systems for coker units consist typically of two or three fan beam point sources, a continuous level measurement (up to 32 m) by use of cascaded TowerSENS detectors, a top density measurement with gas property compensation, and a detector for auto calibration. With this system, it is possible to measure the level during the normal filling of a drum as well as the outage measurement, which has completely different conditions. This measurement is unaffected by vapour channels inside the drum, product falling from the trays, different product densities, or scaling/coking. Since large temperature variations through the whole operational cycle of a coke drum are a known issue to the operators, Berthold's automatic stabilisation technology has proven to be the most important feature to guarantee a stable and reliable level measurement without the need for recalibration. Separate level alarms ensure additional process safety. Other benefits of this solution are significantly lower source activities due to the use of solid scintillators with high sensitivity and minimised influences of interference radiation during weld inspections with the aid of internal algorithms such as X-ray interference protection.

With Berthold's solution for delayed coker units, operators have a high-repeatable and long-term stable measurement, not only increasing the throughput but also the reliability of the drum. In the long term, this can increase profits while maintaining plant safety at the same time.

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